

# Hydrochemistry of the Mocorito river coastal aquifer, Sinaloa, Mexico: water quality assessment for human consumption and agriculture suitability

## Hidroquímica del acuífero costero del Río Mocorito, Sinaloa, México: evaluación de la calidad del agua para consumo humano y agricultura

José R. Rivera-Hernández<sup>1</sup>, Carlos Green-Ruiz<sup>2</sup>, Lawren Pelling-Salazar<sup>1</sup> and Alejandra Trejo-Alduenda<sup>1</sup>

<sup>1</sup>Posgrado en Ciencias del Mar y Limnología, Universidad Nacional Autónoma de México. Av. Joel Montes Camarena s/n, Col. Playa Sur, Mazatlán, Sin., 82040. México

<sup>2</sup>Unidad Académica Mazatlán, Instituto de Ciencias del Mar y Limnología, Universidad Nacional Autónoma de México. Av. Joel Montes Camarena s/n, Col. Playa Sur, Mazatlán, Sin., 82040. México  
e-mail: cgreen@ola.icmly.unam.mx

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### ABSTRACT

**Background.** Groundwater is a vital source of water for domestic and agricultural activities and the water of the Mocorito River Coastal Aquifer (MORCA), located in the agricultural valley of Culiacan, Sinaloa, Mexico, is not an exception. **Goals.** To assess MORCA's groundwater quality for drinking and irrigation purposes and the geochemical processes affecting its composition. **Methods.** Twenty-two well samples were collected during the dry and rainy seasons. Physical and chemical parameters, major ions, drinking quality (WQI and PHASECH water quality index), and irrigation suitability Richards (1954) and Wilcox diagrams) were studied. **Results.** Total Dissolved Solid (TDS) ranged from 1688 - 8762 mg L<sup>-1</sup> for the dry season and 89-10016 mg L<sup>-1</sup> for the rainy season. From inland to the coastal zone, MORCA's groundwater was considered hard and very hard, with non-dominant hydrochemical facies in the dry season and calcium, magnesium and sodium (cationic), and bicarbonate and chloride (anionic) types, in the rainy season. US Salinity Staff and Wilcox diagrams revealed that MORCA's groundwater is not suitable for use in irrigation. Further, the geochemical processes controlling the chemical composition of MORCA were evaporation and weathering. **Conclusions.** According to the TDS and water quality index (WQI and PHASECH) classifying just 4.5 % and over 50 % of the samples, respectively, MORCA water can be considered suitable for human consumption; only the groundwater from site EE-1, in the rainy season, was considered suitable for human consumption. US Salinity staff and Wilcox diagrams indicate that almost 50% of MORCA's groundwater is not suitable for irrigation use. MORCA's groundwater composition is dominated by evaporation and weathering of minerals such as anorthite, illite, and kaolinite.

**Key words:** Geochemical processes, hydrochemical facies, major ions, Piper diagram.

### RESUMEN

**Antecedentes.** El agua subterránea es una fuente vital de agua tanto para actividades domésticas como agrícolas; y el agua del acuífero costero del río Mocorito (MORCA), localizado dentro del valle agrícola de Culiacán, Sinaloa, México, no ha sido la excepción. **Objetivos.** Evaluar la calidad del agua subterránea del MORCA para propósitos de consumo humano e irrigación, así como conocer los procesos geoquímicos que gobiernan su composición. **Métodos.** Veintidós muestras de agua de pozo fueron colectadas en épocas de sequía y de lluvias. Parámetros fisicoquímicos, iones mayoritarios, calidad del agua para consumo humano e irrigación fueron estudiados. **Resultados.** Los valores de TDS variaron de 1688-8762 mg L<sup>-1</sup> para época de secas y 89-10016 mg L<sup>-1</sup> para lluvias. Desde tierra adentro hacia la zona costera, el agua subterránea del MORCA se consideró de dura a muy dura, observando que las facies hidroquímicas son principalmente de tipo no-dominante, en época de secas; mientras que en lluvias son clasificadas como de tipo cálcio-magnesio-sódica (cationico) y bicarbonato y cloruro (aniónico). Los diagramas US Salinity Staff y Wilcox revelaron que el agua subterránea del MORCA no es apta para usos en irrigación. Por otro lado, los procesos geoquímicos que controlan la composición química de MORCA fueron la evaporación y meteorización. **Conclusiones.** De acuerdo con la clasificación del contenido de TDS e índices de calidad del agua (WQI y PHASECH) solo el 4.5 % y más del 50 % de las muestras, respectivamente, pueden ser consideradas apropiadas para el consumo humano. En el caso de aptitud agrícola, los diagramas US Salinity Staff and Wilcox, indicaron que casi 50% del agua subterránea del MORCA no es apta para ese propósito. La composición del agua subterránea del MORCA es dominada por evaporación y meteorización de minerales como anortita, illita y caolinita.

**Palabras clave:** Diagrama de Piper, facies hidroquímicas, iones mayoritarios, procesos geoquímicos.

## INTRODUCTION

Groundwater is the major source of water supply around the world and is mainly employed for domestic, agricultural, and industrial activities. Groundwater chemistry determines its quality and therefore its proper use. It is influenced by natural factors such as climatic conditions, rain and surficial water percolation, recharge water quality, regional geology, sub-surficial geochemical processes, as well as discharges, leaching and organic matter addition from anthropogenic activities carried out over the aquifer, extraction, and irrigation practices (Brindha & Elango, 2011; Davraz & Özdemir, 2013).

In some places, groundwater is vital for human consumption and biota, thus continuous quality monitoring is crucial since irrigation with poor quality groundwater could threaten the health of all consumers and inhibit the growth and quality of crops. The hydrogeochemical study of groundwater is essential to understand the origin and evolution of its chemical composition and hence its quality. There is an extensive literature on groundwater quality assessment for human consumption and agricultural uses (Onwuka *et al.*, 2013; Murkute, 2014; Dar *et al.*, 2014; Krishna-Kumar *et al.*, 2014), based on conventional techniques such as the Piper (1953) and Gibbs (1970) diagrams in order to identify hydrochemical facies and geochemical processes. There are also quality indices like WQI (Vasanthavigar *et al.*, 2010; Krishna-Kumar *et al.*, 2014) and PHASECH (Peinado-Guevara *et al.*, 2011); Richards (1954) and Wilcox (1948) diagrams for assessment of agricultural suitability.

All of them take into account groundwater chemical composition (e.g., major ions, total dissolved solids, pH and conductivity). There are no studies on groundwater quality assessment in the MORCA area. However, Peinado-Guevara *et al.* (2011) studied the Sinaloa River coastal aquifer (SIRCA), the northern neighbor basin (between  $25^{\circ} 16' 38''$  and  $25^{\circ} 41' 13''$  N and from  $108^{\circ} 25' 02''$  to  $108^{\circ} 41' 22''$  Wt), and concluded that the SIRCA is highly sensitive to salinization due to its coastal condition, with a latent threat of saltwater intrusion during droughts, as well as the occurrence of evaporitic rocks away from the coast line.

## MATERIALS AND METHODS

**Study area.** The Mocorito River Coastal Aquifer (MORCA), with an area of  $1180 \text{ km}^2$ , lies between  $24^{\circ} 56' 17''$  N and  $25^{\circ} 47' 26''$  N, and  $107^{\circ} 38' 07''$  and  $108^{\circ} 23' 35''$  W (Fig. 1), in the central portion of the state of Sinaloa, Mexico, adjacent to important cities. It is an unconfined aquifer with fluvial and alluvial sediments (Cretaceous to Tertiary) lying on a consolidated conglomerate of low permeability, which in turn overlies volcanogenic materials (acid igneous rocks with the presence of Au, Ag, Cu, Pb and Fe) (Anonymous, 1978). MORCA's recharge is approximately  $208 \times 10^6 \text{ m}^3/\text{year}$  (Comisión Nacional del Agua, 2009a). The Mocorito River basin (180 km in length) has its origin in the town of Terrero (Cerro San Pedro-Sierra Madre Occidental), at 1950 m AMSL, and its river mouth is on the Santa María La Reforma coastal lagoon, Playa Colorada bay (INEGI, 1995).

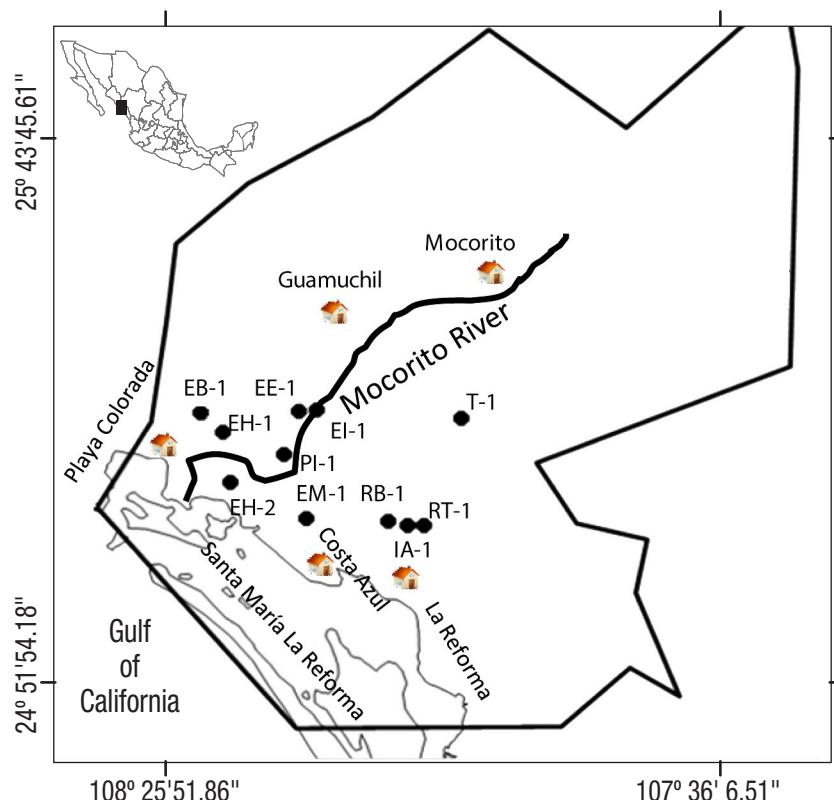


Figure 1. Location of the Mocorito River coastal aquifer area (Sinaloa, Mexico) and sampling stations.

The Culiacan Valley, where the MORCA is located, is the most important agricultural region in Sinaloa, with intensive agriculture activity (193,481 ha irrigated and 184,547 ha rain-fed) (Páez-Osuna *et al.*, 2007), growing vegetables such as corn, tomatoes, chili, and sorghum. Thus the main use for MORCA's groundwater, mainly in the dry season, is for irrigation; however, during drastic climatic events like drought or hurricanes, some communities employ groundwater for their drinking water consumption.

According to the Köppen Climate Classification System, modified by García (1964), the MORCA area has a warm, very dry climate, with an average annual temperature of 22 °C, and the rainy season occurs during summer (BW (h') W (e')). The precipitation on the MORCA region was 846.7 mm in 2013; however, significant variations were observed between both dry (0.1 and 0.2 mm in March and April, respectively) and rainy (169.4, 197.2 and 298.6 mm in July, August, and September) seasons (CONAGUA, 2014).

The main objective of this study was to evaluate the groundwater quality for both human consumption and agricultural suitability of the Mocorito River Coastal Aquifer in two different climatic seasons, using hydro-geochemical tools. Groundwater in this region is employed for irrigation and drinking water.

**Sampling.** Using a Bailer sampler, groundwater samples were collected from a network of 22 coastal wells (on average, the water table was 7 m below ground level) in two different climatic seasons, i.e., April (dry) and July (rainy) 2013 (Fig. 1). All the groundwater samples were collected 1 m below the water table. Sampling wells were selected based on the National Water Commission (CONAGUA, for its acronym in Spanish) (CONAGUA) well network. In addition, depending on their accessibility, we also took samples on private property, in houses and agriculture fields. Samples were collected in 60 mL high-density polyethylene (HDPE) bottles for chemical elements (cations and anions) and stored at 4 °C until they could be chemically analyzed in the laboratory. Auxiliary environmental parameters (pH, temperature, total dissolved solids (TDS), and Electrical conductivity (CE)) were measured *in situ* with previously calibrated potentiometers (HANNA models HI98127 and HI98130). Cation and anion concentrations were volumetrically ( $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ), gravimetrically ( $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ) with drying of residue, and flamometrically ( $\text{Na}^+$  y  $\text{K}^+$ ) defined in the Water, Soil and Plant Analysis Laboratory of the Irrigation District 010 Culiacán-Humaya of CONAGUA, a federal agency. Procedures were based on the soil and water analysis manual from the Agriculture and Hydric Resources Ministry of Mexico (Secretaría de Agricultura y Recursos Hidráulicos, 1974). Quality assessment for cations and anions concentrations was carried out according to the following ionic balance error expression proposed by Cabrera-Sansores *et al.* (2002):

$$\% \text{ Error} = (\sum \text{cations} - \sum \text{anions}) / (\sum \text{cations} + \sum \text{anions}) * 100 \quad (1)$$

where % Error must be less than 10 %.

Total dissolved solids (TDS) content, soluble sodium percentage (%  $\text{Na}^+$ ), the sodium-adsorption-ratio (SAR), and total hardness (TH) were determined following the equations:

$$\text{TDS} = \text{EC} / 1.65 \text{ in mhos/cm} \quad (2)$$

$$\text{TH} = 2.497 \text{ } \text{Ca}^{2+} + 4.115 \text{ } \text{Mg}^{2+} \quad (3)$$

$$\% \text{ } \text{Na}^+ = \text{Na}^+ + \text{K}^+ \times 100 / \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+ \quad (4)$$

$$\text{SAR} = \text{Na}^+ / \sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+}) / 2} \quad (5)$$

where all ionic concentrations are expressed in meq/L for eqs. (3), (4), and (5).

Equation (2) was described by Peinado-Guevara *et al.* (2011) from a database compiled during more than 20 years, which takes into account the electrical conductivity (EC) of each sample. Equations 3, 4, and 5 were used by Vasanthavigar *et al.* (2010).

Once all the values were obtained, hydrochemical facies and the geochemical processes involved were identified using the Piper (1953) and Gibbs (1970) diagrams. Quality of drinking water was evaluated using two indices, WQI (Vasanthavigar *et al.*, 2010; Krishna-kumar *et al.*, 2014) and PHASECH (Peinado-Guevara *et al.*, 2011). Agriculture suitability was evaluated with the diagrams proposed by Richards (1954) and Wilcox (1948).

## RESULTS

Results of laboratory and *in situ* measurements, data of environmental and hydrochemical parameters, TDS, and secondary parameters (%  $\text{Na}^+$ , SAR and TH) are reported in Table 1. Overall, pH values were within an acceptable range that is suitable for human consumption (Secretaría de Salud, 2000), i.e., 6.8 and 8.4, averaging 7.6, during the dry season and 7.3 to 8.5, averaging 7.9 during the rainy season. The temperature of MORCA's groundwater averaged 26.6 and 28.3 °C in dry and rainy seasons, respectively. Likewise, EC high values were measured in both climatic seasons; they oscillated between 1,023 and 5,310  $\mu\text{S cm}^{-1}$ , averaging 2,223  $\mu\text{S cm}^{-1}$  in the dry season; and from 54 to 6,070  $\mu\text{S cm}^{-1}$ , with an average of 2,343  $\mu\text{S cm}^{-1}$  in the rainy season. TDS values (Table 1) during the dry season (1,688-8,761.5 mg  $\text{L}^{-1}$ ) were higher than those in the rainy season (89-10,015.5 mg  $\text{L}^{-1}$ ). Total hardness (TH) values were found between 180 to 2,001 mg  $\text{L}^{-1}$  in the dry season and 25 to 1,750 mg  $\text{L}^{-1}$  in the rainy season.

The concentrations of  $\text{Ca}^{2+}$  ranged between 2.3-20.8 meq  $\text{L}^{-1}$  in the dry season and 0.3-7.3 meq  $\text{L}^{-1}$  in the rainy season.  $\text{Mg}^{2+}$  fell below 19.2 meq  $\text{L}^{-1}$ , with a minimum of 0.5 meq  $\text{L}^{-1}$  in the dry season and 31.9 and 0.2 meq  $\text{L}^{-1}$  in rainy season.  $\text{Na}^+$  varied from 2.7 to 14.7 meq  $\text{L}^{-1}$  in the dry season and from not detectable to 34.4 meq  $\text{L}^{-1}$  in the rainy season. Anions had a lower content, except the case of  $\text{Cl}^-$ , which had a minimum of 0.8 meq  $\text{L}^{-1}$ , with a maximum of 34 meq  $\text{L}^{-1}$  in the dry season, and a minimum of 0.1 meq  $\text{L}^{-1}$  and a maximum of 35 meq  $\text{L}^{-1}$  in the rainy season.

## DISCUSSION

**Groundwater chemistry.** A wider variation of EC was found in the rainy season, which can be related with dilution and/or differential rock-water interactions during water infiltration from the surface to the aquifer. According to Sánchez-Pérez and Trémolières (2003), Choi *et al.* (2005), and Murkute (2014), groundwater with high EC and large variations of this parameter are attributed to an ion exchange and solubilization processes within the aquifers (geochemical processes through water-rock interaction), as well as anthropogenic activities in aquifers. Peinado *et al.* (2011) have registered the occurrence of salt domes or lenses in the region. This kind of geological bodies can also produce the high EC values, especially in sites far from the coastline. In accordance with the irrigation water EC classification proposed by Richards (1954),

Table 1. Environmental and physicochemical parameters of groundwater samples from the Mocorito River coastal aquifer (MORCA), Sinaloa, Mexico. Units: Major ions (meq/L), T = temperature (°C), S = salinity (‰), EC (µS/cm), TDS (mg/L), TH (mg/L), SAR (Sodium-Adsorption-Ratio, no units), and %Na (%).

ID	pH	T	S	EC	TDS	TH	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	SAR	%Na	%Error
<b>Dry season</b>																
EH-1	8.3	27.7	1	1104	1821.6	200.1	7.04	2.3	1.7	2.4	4.2	3.6	0.8	5	63.8	0
EH-2	7	23.8	2	2460	4059	700.3	10.6	6.7	7.3	13.8	5.6	4.8	0.4	4	43.1	0
EB-1	8.4	24.3	1	2250	3712.5	390.2	14.7	4	3.8	12.8	5.5	3.8	0.4	7.4	65.3	0
PI-1	7.5	27.4	1	1023	1688	290.1	4.4	3.1	2.7	3.8	1.6	4	0.8	2.6	43.3	0
EE-1	6.9	26.6	0	1132	1867.8	430.2	2.7	3.3	5.3	2.6	3.3	4.6	0.8	1.3	24	0
EI-1	7.6	27.6	5	5310	8761.5	2000.9	13.1	20.8	19.2	34	14.1	5	0	2.9	24.7	0
EM-1	8.4	24.8	2	1657	2734.1	250.2	11.6	4.2	0.8	4.4	3	7.2	2	7.3	69.8	0
IA-1	6.8	29.6	0	1476	2435.4	450.1	5.8	2.3	6.7	7.2	2.6	4.6	0.4	2.7	39	0
RB-1	7.6	28.4	0	1042	1719.3	180.1	6.8	3.1	0.5	3	3.8	2.8	0.8	5.1	65.5	0
RT-1	8	26.2	2	3210	5296.5	980.4	12.5	7.3	12.3	12.6	13.7	5	0.8	4	38.9	0
T-1	7.4	26.1	5	3790	6253.5	1520.7	7.5	15	15.4	20.6	13.5	3.4	0.4	1.9	19.8	0
<b>Rainy season</b>																
EH-1	8.5	27	1	1084	1788.6	170.1	7.4	2.1	1.3	3	2.4	3.8	2.6	5.7	68.6	0
EH-2	7.3	27	0	2030	3349.5	520.2	9.9	3.1	7.3	10	5.1	4.8	0.4	4.3	48.8	0
EB-1	7.5	27	1	731	1206.2	150.1	4.3	1	2	2.8	1.9	2.2	0.4	3.5	59	0
PI-1	8.3	28	0	1112	1834.8	300.1	5.1	2.1	3.9	3.8	2.3	3	2	3	46	0
EE-1	7.8	27	0	54.2	89.4	25	0.0	0.3	0.2	0.1	0	0.2	0.2	0.1	7.8	0
EI-1	7.7	34	4	6070	10015.5	1750.4	25.7	3.1	31.9	35	22.7	1	2	6.1	42.3	0
EM-1	7.8	27	1	1576	2600.4	140.1	13	1.3	1.6	4	2	5.8	4	11	82.2	0
IA-1	8.5	33	1	1715	2829.8	450.1	8.2	2.3	6.7	8.8	2.2	4.2	2	3.8	47.5	0
RB-1	8.2	27	2	4140	6831	350.7	34.4	5.2	1.8	15	20.4	4	2	18.4	83.1	0
RT-1	8.1	27.5	3	3500	5775	1000.4	15	7.3	12.7	13.2	15.8	2.8	3.2	4.7	42.9	0
T-1	7.7	27	2	3760	6204	1400.3	9.6	3.1	24.9	21	14.2	1.6	0.8	2.6	25.5	0

on average, MORCA groundwater was classified as having very high salinity (2,250–5,000 µS cm<sup>-1</sup>).

Krishna-Kumar *et al.* (2014) suggested that waters with low TDS (373–895 mg L<sup>-1</sup>) are influenced by rock-water interaction related to recharge, while waters with high TDS (959–4,669 mg L<sup>-1</sup>) are influenced by anthropogenic sources. A classification of the type of groundwater based on TDS content (Heath, 1983) is shown in Table 2. Most of the samples from both seasons can be classified as slightly to moderately saline, except for one sample (EI-1) took during the rainy season, which was classified as highly saline, and another (EE-1) from the same period that was classified as freshwater. According to the desirable maximal value of TDS suggested by the World Health Organization (WHO 2006; 500 mg L<sup>-1</sup>) and NOM-127-SSAI-1994 (Secretaría de Salud, 2000; 1,000 mg L<sup>-1</sup>), only 4.5 % of the samples (site EE-1) during both seasons are considered suitable for human consumption.

Following Sawyer & McCarty's classification (1967), all samples collected in the dry season are hard to very hard, while of those collected in the rainy season, 9 % are soft, 9 % are moderately hard, 18 % are hard, and 64 % are very hard (Table 3). Significant differences were not found for any of the aforementioned parameters in either climatic season. The World Health Organization (WHO 2006) and NOM-127-

SSAI-1994 (Secretaría de Salud, 2000) indicate that the maximal value of TH tolerated by human beings is 500 mg L<sup>-1</sup>. In this regard, most of the MORCA samples showed a good degree of hardness (< 500 mg L<sup>-1</sup>), except for the EH-2, EI-1, RT-1, and T-1 sites (> 500 mg L<sup>-1</sup>) in both seasons.

On average, the ionic order observed was Cl<sup>-</sup> > Na<sup>+</sup> > Mg<sup>2+</sup> > Ca<sup>2+</sup> > SO<sub>4</sub><sup>2-</sup> > HCO<sub>3</sub><sup>-</sup> > CO<sub>3</sub><sup>2-</sup> and Na<sup>+</sup> > Cl<sup>-</sup> > Mg<sup>2+</sup> > SO<sub>4</sub><sup>2-</sup> > HCO<sub>3</sub><sup>-</sup> > Ca<sup>2+</sup> > CO<sub>3</sub><sup>2-</sup> for dry and rainy seasons, respectively. A special concern involved the low observed SO<sub>4</sub><sup>2-</sup> concentrations (Table 1) in all samples (max= 22.7 mg/L, in well EI-1), which may indicate reduction processes occurring in the system that produce sulfide minerals precipitates. Unfortunately, tests for NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and oxidation-reduction potential, some trace elements, and microbiological composition, which might serve as proxies for specifying the oxidation-reduction condition of water, were not carried out.

**Hydrochemical facies and geochemical processes involved.** The triangular Piper's diagram is commonly used in water chemistry studies to show the percentage of ionic composition and to identify water types. The study area showed significant variations in the concentrations of cationic and anionic composition (Figure 2). Na<sup>+</sup> and Mg<sup>2+</sup> dominated over Ca<sup>2+</sup>; while prevalence of HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> was evident in the anionic

Table 2. Mocorito River coastal aquifer groundwater classification based on TDS content (Classification suggested by Heath, 1983).

	EH-1	EH-2	EB-1	PI-1	EE-1	EI-1	EM-1	IA-1	RB-1	RT-1	T-1
Dry season											
TDS (mg L <sup>-1</sup> )	1821.6	4059	3712.5	1688	1867.8	8761.5	2734.1	2435.4	1719.3	5296.5	6253.5
Classification	■	▲	▲	■	▲	▲	■	■	■	▲	▲
Rainy season											
TDS (mg L <sup>-1</sup> )	1788.6	3349.5	1206.2	1834.8	89.4	10015.5	2600.4	2829.8	6831	5775	6204
Classification	■	▲	■	■	●	★	■	■	▲	▲	▲

● Fresh= (0-1000), ■ Slightly saline=(1000-3000), ▲ Moderately saline = (3000-10000), ★ Highly saline= (10000-35000), ★ Briny= (>35000 (mg L<sup>-1</sup>)).

group. Most of MORCA's groundwater in the dry season fell within the area of non-dominant type B; however, a few samples can be classified as sodium (cation triangle) and bicarbonate and chloride (anion triangle) types. During the rainy season, groundwater can be classified as calcium, magnesium, and sodium cationic types, and as bicarbonate and chloride anionic types (Fig. 2). Similar results were recorded by CONAGUA (2009a y b), which noted that groundwater from the MORCA belongs to the sodium, calcium, and bicarbonate types (Na-Ca-HCO<sub>3</sub>).

A dominance of Na was found in the EH-2, EB-1, EE-1, EI-1, RT-1, and T-1 wells, attributable to the occurrence of salt domes or lenses in the region (Peinado-Guevara *et al.*, 2011), as well as the coastal condition of the study area, with a possible saline intrusion from the shore.

In fact, Mtoni *et al.* (2012) indicated that water Cl<sup>-</sup> and Na<sup>+</sup>-Cl<sup>-</sup> chemical types are due to a saline intrusion process caused by stronger interaction between fresh water and seawater in many coastal aquifers, such as MORCA. Since chloride is a dominant anion in seawater and bicarbonate in groundwater, they can be used as end-members of these two water types and can indicate salt-water intrusion (Jamshidzadeh & Mirbagheri, 2011). Figure 3 shows the Cl<sup>-</sup> versus HCO<sub>3</sub><sup>-</sup> plots for both climatic seasons. A line with a slope of 2.8 was drawn on the plots to represent the threshold for this process (Raghunath, 1990). For both seasons, Cl<sup>-</sup> concentration in samples EI-1 and T-1 were markedly more than 2.8 times higher than HCO<sub>3</sub><sup>-</sup> concentration, probably due to Cl<sup>-</sup> external sources. The sites where these samples were collected are the farthest wells from the seacoast and no evidence of salt-water intrusion

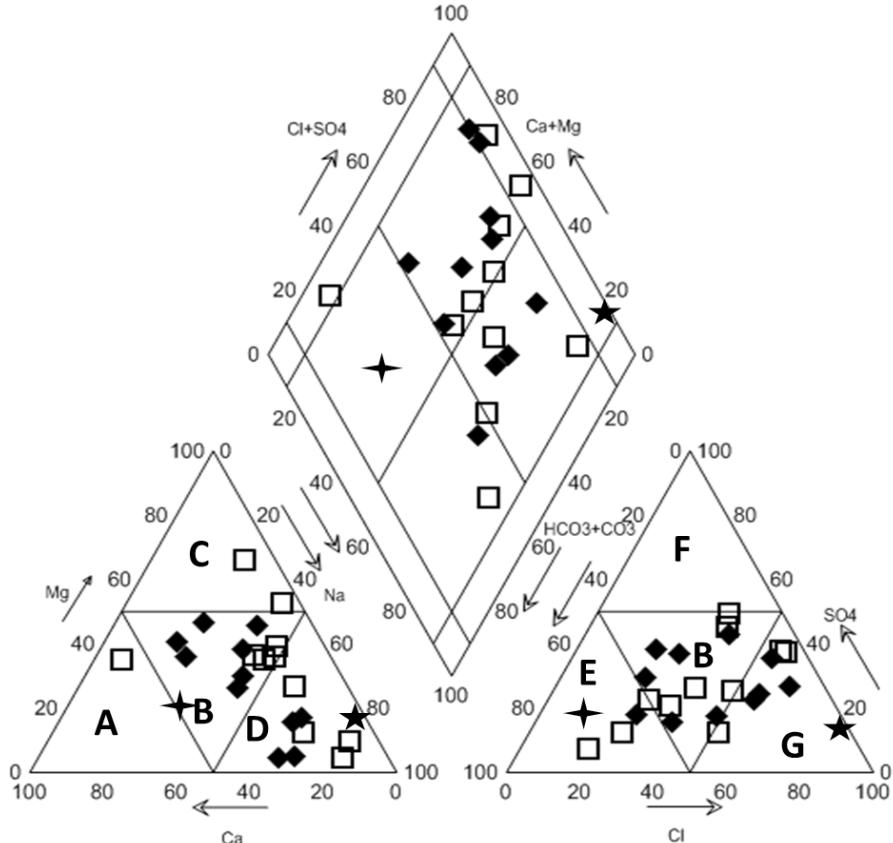
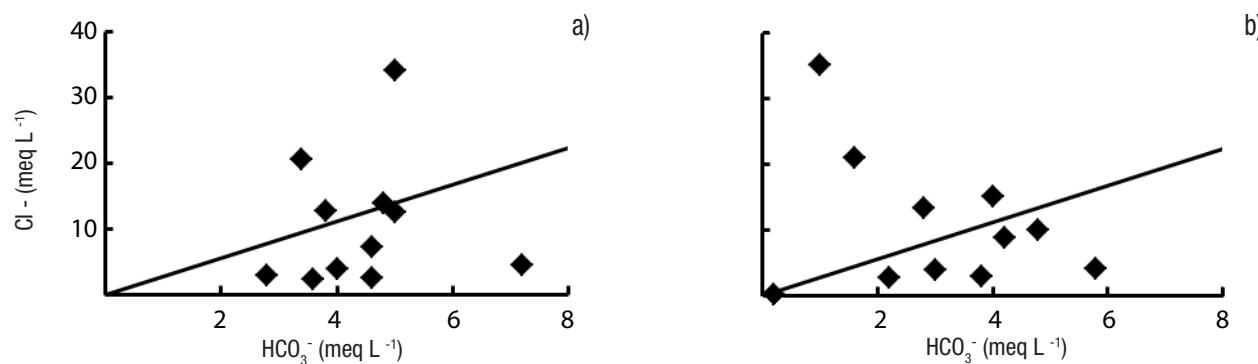


Figure 2. Piper-Hill-Langelier diagram for groundwater samples from the Mocorito River coastal aquifer (Sinaloa Mexico) taken in dry (◆) and rainy season (□). A = Calcium Type, B = no dominant type, C = Magnesium type, D = Sodium and potassium type, E = Bicarbonate type, F = Sulfate type and G = Chloride type. Typical seawater (★) and groundwater (▲). Data were also plotted as references (Millero & Sohn, 1992).



Figures 3a-b. Chlorine versus bicarbonate content in groundwater samples from the Mocorito River coastal aquifer (Sinaloa, Mexico). a) Dry season. b) Rainy season.

was observed in the coastal wells. According to Peinado-Guevara *et al.* (2011), low-quality water in terms of its salt content was observed in the Sinaloa River coastal aquifer (SIRCA), sufficiently away from the coastline due to occurrence of Pleistocene saline lenses.

We used a Gibbs diagram (1970) in order to understand the geochemical processes (precipitation, rock-interaction, and evaporation dominance) that affect the chemical composition (source of dissolved chemicals) of the MORCA's groundwater. According to this diagram (Fig. 4), the chemical composition of MORCA's groundwater is controlled by processes of evaporation and weathering in both climatic seasons. Similar results have been observed in different studies (Drago & Quiros, 1996; Subba-Rao, 2006; Peinado-Guevara *et al.*, 2011; Murkute, 2014; Krishna-Kumar *et al.*, 2014), that state that the prevalence of evaporation processes is related to the climate conditions of the region. In semi-dry regions, such as the one where MORCA is located, these climate conditions increase the evaporation rate, raising Na<sup>+</sup>, Cl<sup>-</sup> and TDS contents and, therefore, salinity, such as the waters we studied herein. Likewise, these authors indicate that the dominance of a weathering process is due to water percolating into the subsoil, as well as the lack of good drainage conditions and long residence time of the groundwater that increase rock-water interaction, releasing different ions into the water. Moulia *et al.* (2013) studied the hydro-geochemistry of the Wadi Nadir alluvial aquifer in the Western Algiers Coastal Area. They plotted the Na<sup>+</sup>/Cl<sup>-</sup> ratio vs Cl<sup>-</sup> concentration and observed two trends; one was related to matrix dissolution, where the ratio variability seems to be independent of chlorinity, and the other, where the ratio increased with chlorine, suggesting marine intrusion. Data from our study were also plotted (Fig. 5) and a matrix dissolution trend was observed, with Na<sup>+</sup>/Cl<sup>-</sup> ratio independent of Cl<sup>-</sup> concentration.

**Water quality for human consumption.** Groundwater chemistry has been used as a tool to evaluate water quality for human consumption and agriculture suitability (Subba-Rao, 2006; Vasanthavigar *et al.*, 2010; Krishna-Kumar *et al.*, 2014). For human consumption, two water quality indices were used in this study: (1) WQI proposed by Krishna-Kumar *et al.* (2014) and, (2) PHASECH, developed by Peinado-Guevara *et al.* (2011). Both indices take into account the standard values of several key parameters of groundwater chemistry established by the WHO (2006).

To calculate the WQI, weights (from 1 to 5) were assigned according to the relative importance of each physicochemical parameter in water quality as suggested by Vasanthavigar *et al.* (2010) and Krishna-Kumar *et al.* (2014): TDS = 5; pH, EC, and SO<sub>4</sub><sup>2-</sup> = 4; HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> = 3; Ca<sup>2+</sup> and Na<sup>+</sup> = 2; Mg<sup>2+</sup> = 1. The relative weights were calculated with the following equation:

$$W_i = w_i / \sum_{i=1}^n w_i \quad (6)$$

where  $W_i$  is the relative weight and  $w_i$  is the weight of each parameter. The quality rating of each parameter ( $q$ ) was calculated by dividing its concentration in a groundwater sample ( $C$ ) by its respective standard value ( $S$ ) and multiplying by 100:

$$q_i = (C_i / S_i) \times 100 \quad (7)$$

After that, the quality sub-index ( $SL_i$ ) was computed for each  $i$ th parameter:

$$SL_i = W_i \times q_i \quad (8)$$

Finally, WQI is determined for each groundwater sample:

$$WQI = \sum SL_i \quad (9)$$

Table 3. Mocorito River coastal aquifer groundwater classification based on total hardness (TH). (Classification suggested by Sawyer and McCarty, 1967).

TH (mg/L)	Water type	Number of Samples		Percentage of samples (%)	
		Dry	Rainy	Dry	Rainy
<75	Soft	-	1	-	9
75 – 150	Moderately hard	-	1	-	9
150 – 300	Hard	4	2	36	18
>300	Very hard	7	7	64	64

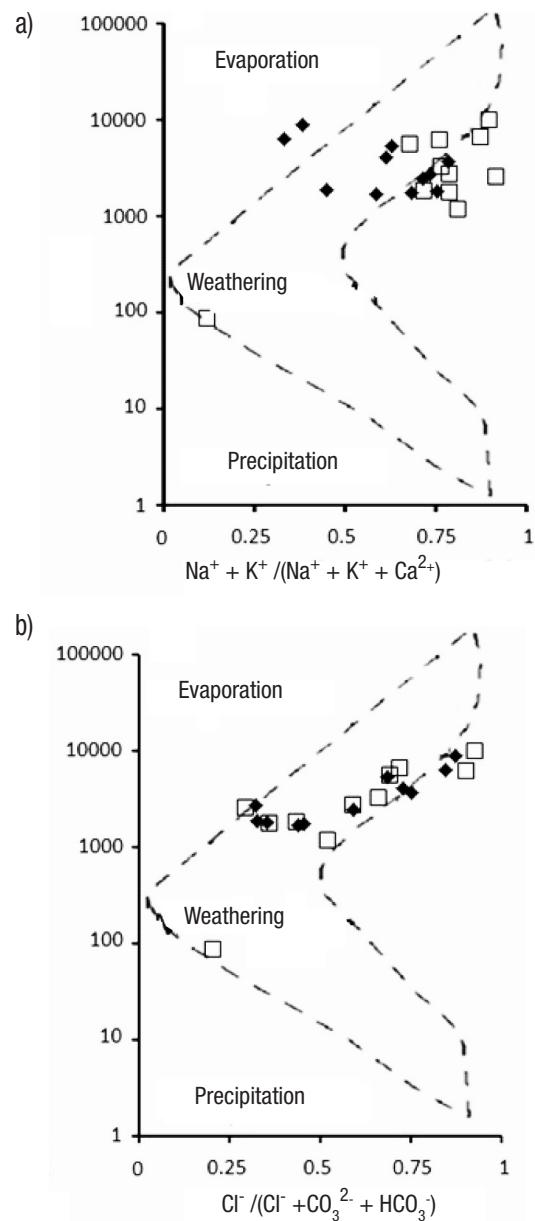
Water quality classification ranges and types of water based on WQI values suggested by Vasanthavigar *et al.* (2010) and Krishna-Kumar *et al.* (2014) are shown in Table 4. According to this classification, most of the MORCA's groundwater is of poor quality, with samples from both climatic seasons falling in the range of poor quality to water unsuitable for drinking purposes; except for samples EB-1 and EE-1 in the rainy season, which were classified as good and excellent water, respectively (Table 5). Onwuka *et al.* (2013) attributed the contamination of groundwater during the dry season to ion leaching and lower groundwater flow; in the rainy season, water table on the aquifers become shallower, allowing infiltration and percolation of surficial runoff loaded with municipal and agricultural wastewater, which can alter the quality of the receiving water body.

Moreover, the PHASECH index suggested by Peinado-Guevara *et al.* (2010) considers only five parameters (pH, TH,  $\text{Na}^+$ ,  $\text{Cl}^-$  and TDS), assigning a value of 1 to those parameters that fulfill the World Health Organization quality guideline. The higher the PHASECH value, the better the water quality in terms of the evaluated parameters. The PHASECH values obtained after comparing the values of each parameter measured against the WHO guideline are shown in Table 6. Like the WQI, in terms of the PHASECH index, over 50% of MORCA groundwater samples can be classified as low to intermediate quality water; while only a few samples had high quality (fulfilled with more than 4 parameters).

According to Paez-Osuna *et al.* (2007), there are 169,232 inhabitants in the study area, with only 40,945 living in Angostura county, where most of the water samples for this study were collected (Instituto Nacional de Estadística y Geografía, 2010). Some of the sampled wells were located inside private houses, where, because of hurricanes and droughts, their owners, as well as the Angostura County Union for Potable Water and Sewage Pipeline System (JUMAPAANG), use groundwater to supply the entire community and cover almost all of human needs for domestic and drinking consumption. Given this use of groundwater, assessing water quality is very important.

For drinking water, several researches have studied groundwater quality (Vasanthavigar, 2010; Nagarajan, 2010; Murkute, 2014; Varol & Davraz, 2015). In their investigation of water quality in the Tefenni aquifer plain, Turkey, Varol and Davraz (2015) employed WQI and multivariate analysis and showed that close to 90% of the 52 sampled wells had excellent quality, suitable for human drinking water in both climatic seasons (dry and wet). These authors concluded that the groundwater chemistry of the Tefenni aquifer is affected by two factors: 1) water-rock interaction; and 2) agricultural activities in the area. On the other hand, in Mexico, Peinado-Guevara *et al.* (2011) studied the quality and suitability of SIRCA water for agricultural and domestic use found that the sites with better quality, in terms of the PHASECH index, were located close to the banks of the Sinaloa River, but tended to decrease in quality the closer to the coastline they were. They explained this behavior due to the presence of evaporitic bodies and to the potential effect of the saline intrusion from the seawater. Our study was carried out in the more coastal portion of the MORCA, where the effects of saline intrusion or intensive agriculture can be the main factors affecting water quality.

**Water quality for irrigation uses.** The assessment of groundwater quality for irrigation purposes was based on the estimation of two secondary parameters: sodium absorption ratio (SAR) and soluble sodium percentage ( $\% \text{Na}^+$ ), as well as EC values, which are related to the amount of soluble salts in irrigation water. According to Khodapanah *et al.* (2009) and Onwuka *et al.* (2013), reduction in water uptake by plant



Figures 4a-b. Mechanism affecting the chemical composition of the groundwater samples from the Mocorito River coastal aquifer (Sinaloa, Mexico) in Dry season (◆) and Rainy season (□). TDS vs a) cations and b) anions contents (Classification suggested by Gibbs, 1970).

Table 4. Classification of water type suggested by Vasanthavigar *et al.* (2010).

Range	Water type
<50	Excellent water
50 – 100	Good water
100 – 200	Poor water
200 – 300	Very poor water
>300	Water unsuitable for drinking purposes

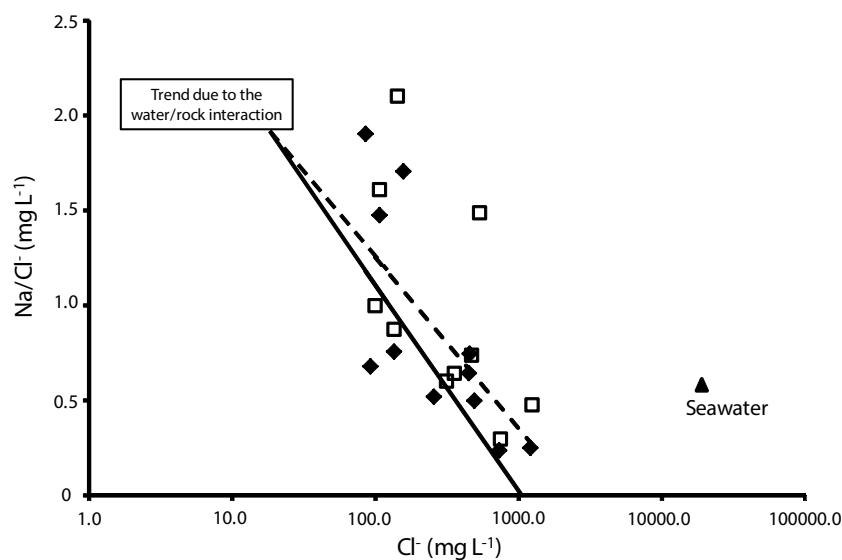


Figure 5.  $\text{Na}^+/\text{Cl}^-$  vs  $\text{Cl}^-$  content plots for dry (◆) and rainy season (□) in samples from the Mocorito River coastal aquifer (Sinaloa, Mexico). Seawater data were taken from Millero & Sohn (1992).

roots may be due to an increase in the osmotic pressure of the soil, which is due to an excess of dissolved solids in the water.

Sodium Absorption Ratio (SAR), %Na and EC values for MORCA's groundwater samples are shown in Table 1. SAR oscillated between 1.3 and 7.4, with an average of 4.0 for the dry season and from 0.1 to 18.4, with an average of 5.7 in the rainy season. Similar results were recorded by Vasanthavigar *et al.* (2010), who indicated that groundwater with  $\text{SAR} > 2$  is unsuitable for irrigation. A higher average of %Na<sup>+</sup> was found in the rainy season (50.3%) than in the dry season (45.2%). The variation in %Na<sup>+</sup> between both periods may be due to the residence time of water in the aquifer and the dissolution of minerals from the lithological composition.

Richards (1954) and Wilcox (1948) diagrams were applied to assess water quality for irrigation (Fig. 6 and 7, respectively). Richards (1954) plots the EC values on the "X" axis, which are classified based

on salinity (alkali) hazards as follows: low (C1), medium (C2), high (C3), and very high (C4); the SAR values are placed on the "Y" axis and are classified as low (S1), medium (S2), high (S3), and very high sodium hazards (S4). On the other hand, the Wilcox diagram is obtained by plotting the EC values on the "X" axis and %Na<sup>+</sup> values on the "Y" axis. This diagram classified water from unsuitable to excellent for irrigation.

In general, groundwater samples from MORCA have combinations of high (C3) to very high salinity risk (C4) and a low (S1) to medium sodium risk (S2) for both climatic seasons; except for two samples from the rainy season that are classified as C3 - S3 and C4 - S4 (Fig. 6). This means that most MORCA's water cannot be used for irrigation in agricultural soils with restricted drainage. For agriculture to be profitable in this region, the soil must have a coarse texture or be organic, with high permeability to allow leachate of irrigation water, with crops and plants appropriately selected for high salinity tolerance (Richards 1954; Wilcox 1955; Ackah *et al.* 2011).

Table 5. Water quality index (WQI) classification for individual water samples from the Mocorito River coastal aquifer (Sinaloa, Mexico).

ID	Dry season		Rainy season	
	WQI	Water type	WQI	Water type
EH-1	121	Poor water	116	Poor water
EH-2	251	Very poor water	207	Very poor water
EB-1	231	Very poor water	82	Good water
PI-1	110	Poor water	118	Poor water
EE-1	121	Poor water	18	Excellent water
EI-1	540	Water unsuitable for drinking purpose	600	Water unsuitable for drinking purpose
EM-1	170	Poor water	154	Poor water
IA-1	151	Poor water	173	Poor water
RB-1	115	Poor water	421	Water unsuitable for drinking purpose
RT-1	331	Water unsuitable for drinking purpose	358	Water unsuitable for drinking purpose
T-1	393	Water unsuitable for drinking purpose	379	Water unsuitable for drinking purpose

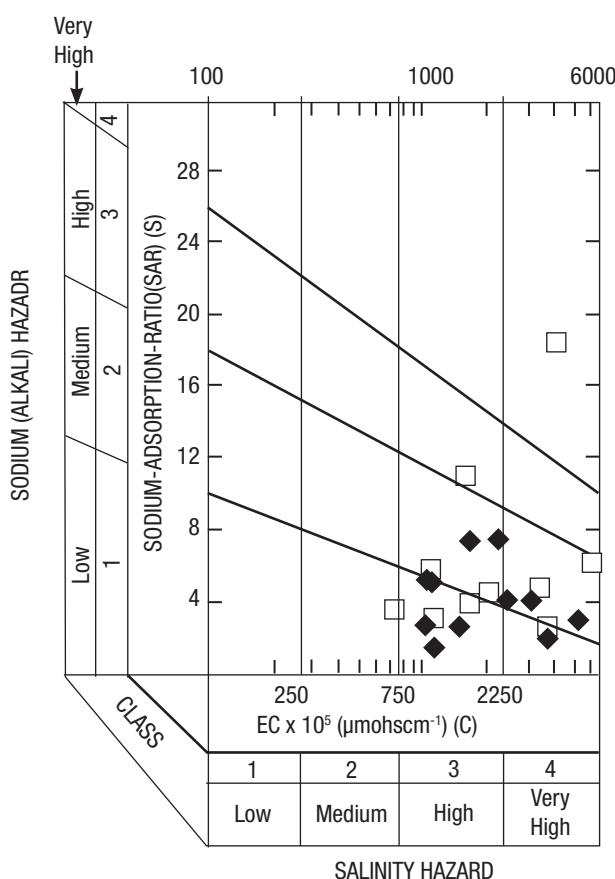


Figure 6. US salinity diagram for classification of the groundwater samples from the Mocorito River coastal aquifer (Sinaloa, Mexico) (◆ = Dry season; □ = Rainy season).

To confirm the above, a Wilcox diagram (Fig. 7) revealed that only 5% of the groundwater samples (for both seasons) fell in the excellent to good classification for irrigation, 23% were classified as good to permissible for irrigation, 27% were permissible to doubtful water, and the remaining 45% were classified as doubtful to unsuitable for irrigation.

Paez-Osuna *et al.* (2007) reported that 378,028 ha of agricultural fields lie on the MORCA, a part of the Santa Maria La Reforma Coastal Lagoon sub-basin. About 193,481 ha are used for agricultural irrigation; seasonal agriculture occurs on the remaining 184,547 ha. The extraction of groundwater from the MORCA becomes necessary during severe droughts.

Peinado-Guevara *et al.* (2011) studied the Sinaloa River aquifer, which is adjacent to the northern portion of MORCA, and observed that almost 35% of their groundwater samples fell inside the C3 (high salinity hazard) – S1 (low sodium hazard) zone in the US Salinity diagram, suggesting that they are suitable for irrigation. In addition, these authors observed that 52% of the evaluated water samples were classified as unsuitable for irrigation according to the Wilcox diagram ( $EC > 3000 \mu\text{S cm}^{-1}$ ). Water with low SAR but high EC can be used for irrigation only where fields have efficient drainage.

Nagarajan *et al.* (2010) state that the concentration of sodium in irrigation water is very important, because a high  $\text{Na}^+$  concentration has the ability to increase the exchange of this ion with the soil and affect its permeability. These authors also indicate that a high combination of  $\text{Na}^+$  and  $\text{CO}_3^{2-}$  in the water leads to the formation of alkaline soils, while a high combination of  $\text{Na}^+$  and  $\text{Cl}^-$  leads to the formation of saline soils. These two types of soils prevent normal plant growth.

They conclude that MORCA's groundwater has a neutral-alkaline pH in both dry and rainy seasons, with an average temperature of 26.6 and 28.3 °C, respectively. Most of the MORCA's groundwater can be classified as light to highly saline and moderately to very hard. Ionic concentrations follow the sequence  $\text{Cl}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{CO}_3^{2-}$  and  $\text{Na}^+ > \text{Cl}^- > \text{Mg}^{2+} > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{Ca}^{2+} > \text{CO}_3^{2-}$  for dry and rainy seasons, respectively. The Piper diagram revealed hydrochemical facies such as sodium, bicarbonate, and chloride during the dry season; during the rainy season, the facies were calcium, magnesium, sodium, bicarbonate, and chloride types. Furthermore, the Gibbs diagram indicated that the chemistry of MORCA's groundwater is determined by water evaporation and rock-weathering processes.

In terms of water quality, more than 50% of the groundwater samples were unsuitable for human consumption during both climatic periods; however, two samples had good to excellent quality for consumption. Most of MORCA's groundwater cannot be used for irrigation, since, according to the Richards (1954) diagram samples from most of the sites were classified as C3-S1, C3-S2, C4-S1, and C4-S2. In addition, the Wilcox diagram showed that almost 45% of the groundwater samples are not suitable for irrigation use.

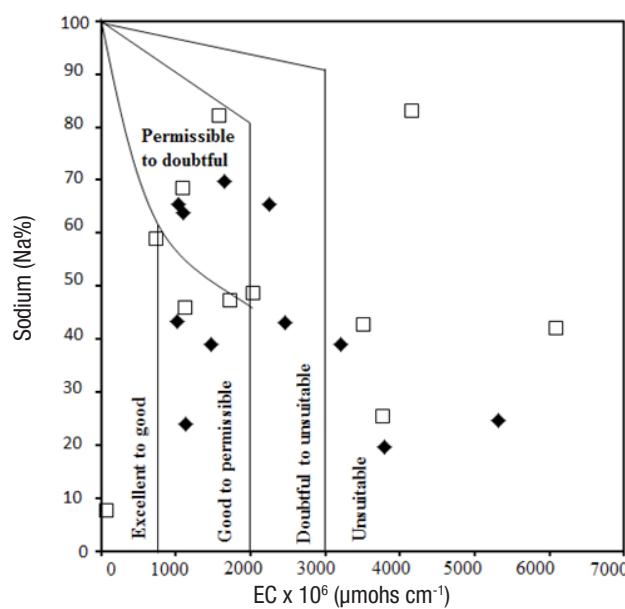


Figure 7. Wilcox diagram for classification of the groundwater samples from the Mocorito River coastal aquifer (Sinaloa, México) for irrigation uses (◆ = Dry season; □ = Rainy season).

Table 6. Mocorito River coastal aquifer (Sinaloa, Mexico) water quality index (PHASECH) classification.

ID	pH		TH (mg L <sup>-1</sup> )		Na <sup>+</sup> (mg L <sup>-1</sup> )		Cl <sup>-</sup> (mg L <sup>-1</sup> )		TDS (mg L <sup>-1</sup> )		PHASECH*	
	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
EH-1	✓	✓	✓	✓	✓	✓	✓	✓	✗	✗	4	4
EH-2	✓	✓	✗	✗	✗	✗	✗	✗	✗	✗	1	1
EB-1	✓	✓	✓	✓	✗	✓	✗	✓	✗	✗	2	4
PI-1	✓	✓	✓	✓	✓	✓	✓	✓	✗	✗	4	4
EE-1	✓	✓	✓	✓	✓	✓	✓	✓	✗	✓	4	5
EI-1	✓	✓	✗	✗	✗	✗	✗	✗	✗	✗	1	1
EM-1	✓	✓	✓	✓	✗	✗	✓	✓	✗	✗	3	3
IA-1	✓	✓	✓	✓	✓	✓	✗	✗	✗	✗	3	3
RB-1	✓	✓	✓	✓	✓	✗	✓	✗	✗	✗	4	2
RT-1	✓	✓	✗	✗	✗	✗	✗	✗	✗	✗	1	1
T-1	✓	✓	✗	✗	✓	✓	✗	✗	✗	✗	2	2

✓ Under the standard; ✗ Over the standard; \*Peinado-Guevara *et al.* (2011).

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