

## **Geochemistry of the hydrogeological reserve of Mérida, Yucatán, Mexico**

O. Escolero<sup>1</sup>, L. E. Marín<sup>2</sup>, B. Steinich<sup>3</sup>, J. A. Pacheco<sup>4</sup>, A. Molina-Maldonado<sup>2</sup> and J. M. Anzaldo<sup>2</sup>

<sup>1</sup> *Instituto de Geología-UNAM, México, D. F., México*

<sup>2</sup> *Instituto de Geofísica-UNAM, México, D. F., México*

<sup>3</sup> *Centro de Geociencias, UNAM, Campus Juriquilla, Querétaro.*

<sup>4</sup> *Facultad de Ingeniería, Universidad Autónoma de Yucatán, México*

Received: April 12, 2003; accepted: August 19, 2003

### **RESUMEN**

Se utilizaron datos hidrogeoquímicos para describir los procesos que modifican la calidad del agua subterránea en el noroeste de Yucatán. Se encontró que los procesos de disolución de rocas carbonatadas de gran pureza, la mezcla con agua salada y el intercambio iónico en calizas arcillosas están presentes en la zona en estudio. Las nuevas observaciones confirman los resultados de estudios previos sobre las medidas recomendadas para la conservación del agua subterránea en la zona. Se encontró agua salobre varios kilómetros tierra adentro, cuya presencia se debe a la intrusión de fondo de agua salada en pozos relativamente profundos o por la concentración del bombeo.

**PALABRAS CLAVE:** Calizas, calidad del agua subterránea, intrusión de agua salobre, karst, Yucatán, México.

### **ABSTRACT**

Hydrochemical data are presented to describe the process that modifies the groundwater quality in northwest Yucatán. Solution of almost pure carbonate rocks, conservative mixing with seawater and ionic interchange in clayey limestone of middle Eocene are found. Groundwater flow is from the central zone of the study area outward. New observations confirm earlier studies on proposed conservation measures in the area. Brackish water is found several kilometers inland. Salinity increase is due to saltwater upconing in relatively deep wells or by the concentration of pumping.

**KEY WORDS:** Karst, groundwater quality, saltwater intrusion, limestone, Yucatán, Mexico.

### **INTRODUCTION**

The main geochemical process in karst aquifers is the dissolution of carbonate rocks. Stringfield and LeGrand (1973) conclude that solution features such as cavities and channels are found chiefly in the upper part of the water table. After carbonates have been transformed into rocks, many additional chemical changes occur both in groundwater and in aquifer mineralogy (Hanshaw and Back, 1973). In recharge areas, groundwater is typically of the CaHCO<sub>3</sub> type. During the groundwater movement towards the coast, Mg increases owing to dissolution of dolomite and high-Mg calcite while Ca remains relatively constant.

Melloul and Goldenberg (1998) define three stages to characterize the exchange process of freshwater by saline water in wells located along the coastal aquifer of Israel and the Gaza Strip. The first stages of salt water intrusion entail initial Cl concentrations less than 60 mg/l, characterized by imperceptible fluctuations in chloride. The second stage is characterized by Cl concentration between 60 – 130 mg/l,

and the third stage begins when Cl values increase rapidly above 130 mg/l.

### **SETTING OF THE STUDY AREA**

The northern half of the Yucatán peninsula, Mexico (Figure 1), has a surface elevation with an average of 15 meters above mean sea level (a.m.s.l.), bounded on the south by the Sierrita de Ticul, a range of low hills with an elevation of about 150 a.m.s.l. The annual rainfall ranges between 500 and 1500 millimeters, increasing from the coastal area inland. The rainy period is from May through September (SARH, 1988). The temperature ranges from 23° C in January to 28° C in May. The region features a tropical savannah climate that is constantly swept by warm, moisture laden breezes (Ward *et al.*, 1985).

The geology consists of almost pure carbonate rocks and evaporites, forming a mature karstic system. The dissolution process leaves little residue. The soil cover is thin to non-existent. There are no rivers in northwest Yucatán. Due

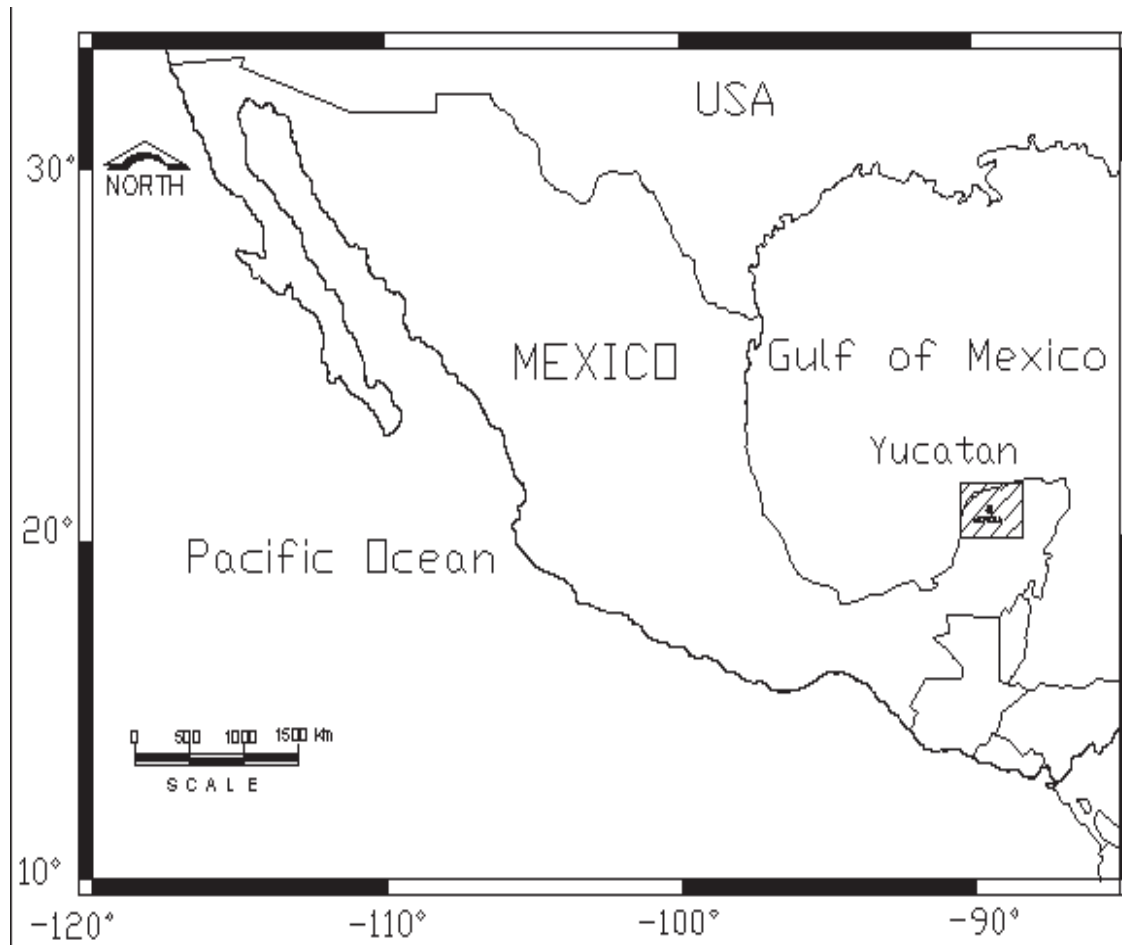


Fig. 1. Location of the study area.

to the karstic terrain, rainfall infiltrates rapidly down to the water table, so that the aquifer is highly vulnerable to contamination (Marín and Perry, 1994). The aquifer is unconfined except for a narrow band parallel to the coast (Perry *et al.*, 1989). The hydraulic gradient is very low, on the order of 7-10 mm/km (Marín *et al.*, 1987; Marín, 1990). The hydraulic conductivity is very high (Back and Hanshaw, 1970; Marín, 1990).

Sinkholes locally known as “cenotes” are a common feature throughout the Yucatán peninsula. The Ring of Cenotes (RC) (Pope and Duller, 1989) is approximately 5 km wide, with a radius of approximately 90 km centered on Chicxulub (Marín *et al.*, 1990). Cenote density varies from several per kilometer to several kilometers between cenotes (Figure 2). The RC has been shown to be a zone of high permeability. It exhibits spatially variable hydraulic characteristics (Steinich and Marín, 1997), including a ground water divide (Steinich *et al.*, 1996).

Regional ground water flow is from southeast to northwest (Marín, 1990; Steinich and Marín, 1996). Marín (1990)

proposed the inversion of ground water flows at the north of the RC due to its high permeability. Steinich *et al.* (1996) showed that in the central region of the ring, east of the ground water divide, the aquifer does not behave as a porous medium as proposed by Marín (1990), and that reversals in the hydraulic gradient occur regularly.

The fresh water lens is 45 to 50 meters thick under the city of Mérida. The unsaturated zone in Mérida ranges between 8-12 meters. There is practically no sewage treatment for Mérida. As the aquifer is highly permeable, untreated sewage reaches the aquifer quickly. This is also true for industrial effluents as well as leachates from landfills. As a result, water from the upper 20 meters of the aquifer is not considered fit for human consumption. High nitrate values have been reported just north of Mérida (Pacheco and Cabrera, 1997). Pacheco *et al.* (2000) have reported very high counts of fecal coliforms in communities north of Mérida. Graniel *et al.* (1999); Pacheco *et al.* (2001) have reported organic contaminants, as well as heavy metals, in the aquifer that supplies drinking water to the population of Mérida (Pacheco *et al.*, 2001; Marín *et al.*, 2002).

A thin freshwater lens is the only source of water in the peninsula of Yucatán. An area of 900 km<sup>2</sup> located southwest of Mérida has been proposed as a hydrogeological reserve zone (HRZ) to ensure an adequate source of drinking water for the city of Mérida (Escolero *et al.*, 2000). The proposed HRZ is bounded to the south by the RC, to the west by the road from Hunucma to Celestun, to the north by the road from Sisal to Uman, and to the east by the highway between Uman and Kapoma (Figure 2). The distance between the midpoint of the HRZ and Mérida is 35 km. A detailed ground water management scheme has been proposed by Escolero *et al.* (2002) for the implementation of the HRZ for Mérida.

The main purpose of this study is to apply a combination of interpretation techniques of hydrochemical data in order to (1) establish the different processes that modified groundwater quality, (2) analyze the hydraulic control imposed to the groundwater flow, supported by hydrochemical analysis, and (3) study the origin of salinity in wells located inland.

**DESCRIPTION OF STUDY**

Twenty-four sites were selected to collect groundwater samples, covering the region in a representative way. Ground-

water samples were collected in March 2000. This date corresponds to the dry season. It is representative of groundwater quality conditions with no rainfall influence (Figure 2). The 24 sampled sites include wells, springs and sinkholes. The sites were located using a handheld GPS, model Garmin II (Table 1).

Groundwater samples were taken directly from the wells. They were filtered with a 0.2 micron filter and collected in polyethylene-sterilized bottles that were previously washed in 5% nitric acid. The bottles were rinsed with sample water before filling. Care was taken to avoid contaminating the sample by surface scum. Each sample was sealed, labelled, and kept at a temperature of 4° C until analysed.

Groundwater samples were measured in the field for temperature, ph and electric conductivity, and analysed in laboratory for bicarbonate, calcium, chloride, magnesium, potassium, sodium and sulfate; according to the procedures outlined in Standard Methods (APHA, AWWA, WEF, 1996). Alkalinity was normally determinated within 24 hours. All samples as described in Table 2 have ion balance equal to or better than 10%, except samples 5 and 19. We didn't use the data corresponding to these two samples in the analysis.

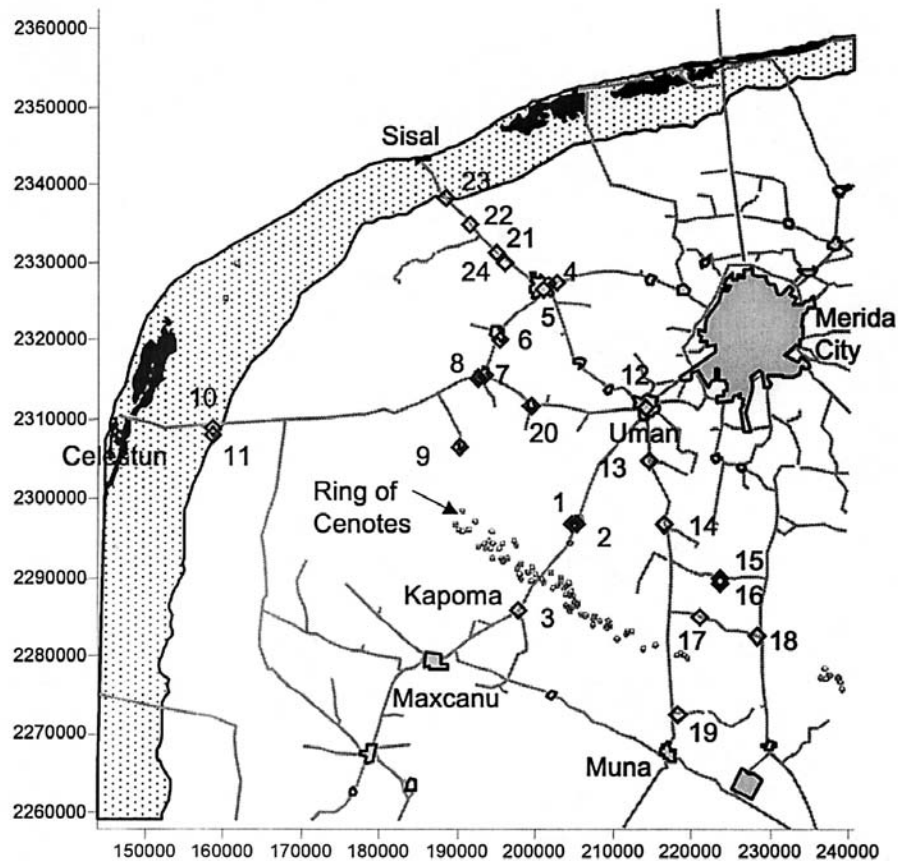


Fig. 2. Location of groundwater sampling sites and the main cities in the region. Dots are sinkholes along the Ring of Cenotes.

**Table 1**

Sampling Sites for groundwater

Nº	Site	x	y	Type
1	CHOCOLA1	204,678	2,296,876	Dug well
2	CHOCOLA2	205,331	2,296,793	Dug well
3	KOPOMA	197,837	2,285,743	Well
4	ASPTE1HUNUCMA	202,752	2,327,297	Dug well
5	ASPTE2HUNUCMA	201,106	2,326,510	Dug well
6	TETIZ AP	195,516	2,320,055	Well
7	ASPTE7 KINCHIL	193,420	2,315,555	Dug well
8	KINCHIL AP-1	192,583	2,315,181	Well
9	ASPTE-8BIS TETIZ	190,325	2,306,411	Dug well
10	ASPTE9 CENOTE	158,614	2,308,895	Sinkhole
11	CELESTUN AP	158,633	2,308,063	Spring
12	UMAN	214,161	2,311,372	Dug well
13	TEPEN1	214,611	2,304,786	Dug well
14	YAXCOPOIL	216,607	2,296,710	Dug well
15	TEMOZON	223,558	2,289,885	Dug well
16	CENOTE TEMOZON	223,535	2,289,214	Sinkhole
17	ABALA AP-1	221,099	2,284,958	Well
18	MUCUICHE CENOTE	228,345	2,282,498	Sinkhole
19	CHOYOB	218,345	2,272,484	Dug well
20	ASPTE23 SAMAHIL	199,434	2,311,672	Dug well
21	RANCHO S. PEDRO	194,987	2,331,235	Dug well
22	ASPTE 3 CENOTE	191,655	2,334,944	Sinkhole
23	SISAL AP	188,468	2,338,259	Spring
24	ASPTE 5	196,030	2,329,911	Dug well

**RESULTS**

The results of the chemical analysis, as well as typical seawater from Appelo and Postma (1996) were plotted on a Durov diagram (Figure 3). Mixing is shown by samples located in the upper left corner such as samples 9 and 20, to those at the lower right, like samples 12 and 22. Several samples are located along the mixing path between fresh water and seawater.

Melloul and Goldenberg, (1998) define fresh water as having a chloride content between 30 and 150 mg/l, brackish (300–1000 mg/l), salt (10 000–20 000 mg/l), and hyperhaline (> 20 000 mg/l). We classify samples 9, 16 and 20 as fresh water, and samples 12, 22 and 24 as brackish water. In order to classify the water types, several circular diagram types were constructed (Figure 4). Here sample 20 is defined as calcium-bicarbonate type: it represents fresh water from recent rain infiltration, modified by dissolution of carbonate rocks. Sample 22 is of sodium-chloride type and represents brackish water. Samples 2 and 17 correspond to typical mixing phases.

Generally, water anions change systematically from bicarbonate to chloride as groundwater flows from the recharge zone to the discharge areas (Appelo and Potsma, 1996). After Chadha (1999), we present the chemical compositions in Table 2, plus seawater contents from Appelo and Postma

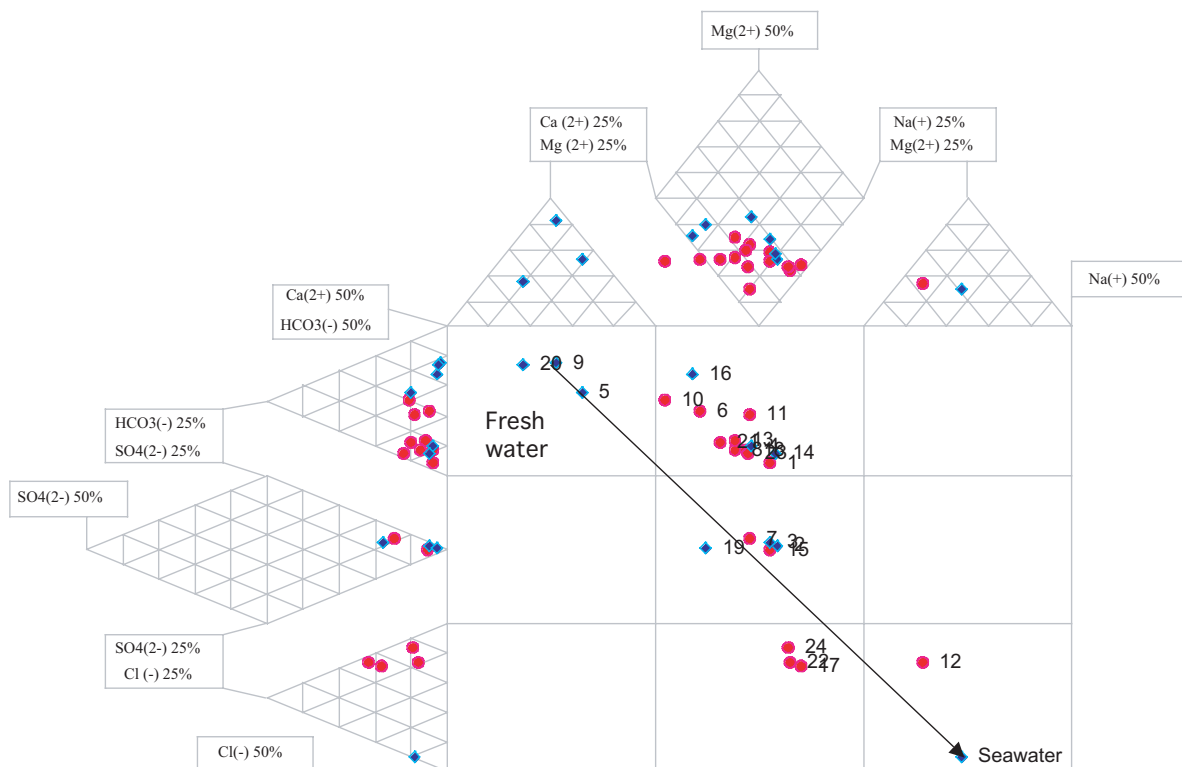


Fig. 3. Durov diagram showing the relative cation and anion composition of the groundwater in sample sites.

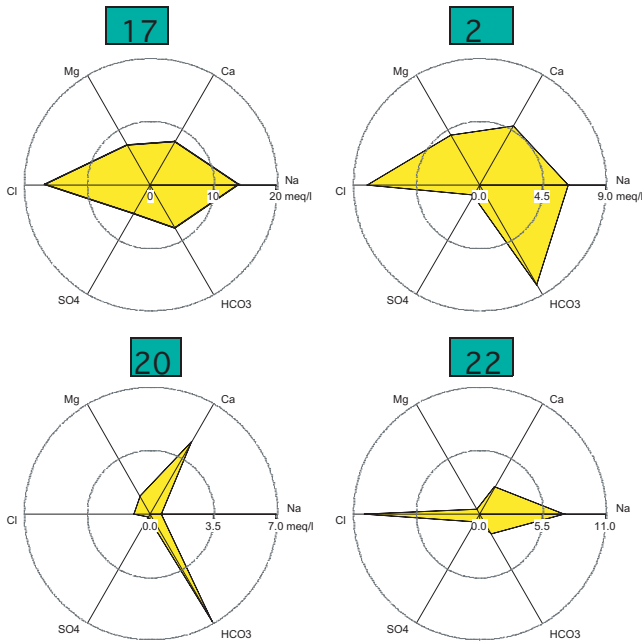


Fig. 4. Circular diagrams that represent different water types. Sample 20 corresponds to freshwater, and sample 22 corresponds to brackish water. Samples 2 and 17 are typical mixing phases.

Table 2

Hydrogeochemical data (mg/l)

Sample N	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
1	134.5	8.4	55.1	96.8	260.6	527.5	30.5
2	146.7	9.0	49.5	96.0	283.6	505.1	41.9
3	136.4	6.8	70.5	99.8	260.6	499.5	160.2
4	85.3	5.4	71.9	81.4	159.5	409.7	23.5
5	35.7	11.6	25.2	81.4	67.4	491.1	55.1
6	38.5	8.8	23.3	72.2	70.9	328.3	19.1
7	124.0	7.0	66.3	119.8	239.3	491.1	120.3
8	71.1	27.0	49.5	76.8	159.5	392.8	42.7
9	9.8	1.6	39.2	81.4	26.6	359.2	6.4
10	43.1	96.0	40.6	106.0	95.7	592.1	70.0
11	126.6	31.5	23.8	107.5	130.3	578.0	61.8
12	340.0	3.6	53.7	145.9	605.3	578.0	110.9
13	86.6	11.8	40.1	99.8	161.3	454.6	35.5
14	112.2	6.2	42.9	76.0	214.5	499.5	35.4
15	154.1	7.8	51.8	113.7	305.8	527.5	50.2
16	24.1	3.8	28.0	61.4	37.2	364.8	9.8
17	326.8	15.2	86.8	157.4	591.1	488.2	260.8
18	107.8	6.0	54.1	110.6	216.3	533.1	31.3
19	37.5	11.6	46.7	76.8	257.9	449.0	22.5
20	13.9	2.0	13.5	92.9	31.9	420.9	10.3
21	75.5	24.0	38.7	98.3	141.8	404.1	58.8
22	308.8	15.6	78.4	175.1	569.9	488.2	326.0
23	100.8	7.6	35.5	98.3	177.3	420.9	77.9
24	223.4	12.4	61.6	130.6	436.0	516.3	104.8

(1996). The difference in milliequivalent between alkaline earths (Calcium+Magnesium) and alkali metals (sodium+potassium) is plotted on the x-axis and the difference in milliequivalent between weak acids (bicarbonate) and strong acids (chloride+sulfate) is plotted on the y axis (Figure 5). The figure shows that most of the samples lie along a conservative mixing path.

The chemical reactions in the area where fresh water is displaced by saltwater can be deduced from a calculation of conservative mixing, considering chloride as a conservative ion. In order to find the seawater contribution, the chloride concentration of seawater is assumed as 566 mmol/l (Appelo and Postma, 1996). No other source of chloride is assumed. We calculate that samples 12, 17 and 22 contain about 3% of seawater, while the samples 9 and 20 contain less than 0.15%. The samples 10, 11, 19, 4, 7, 3, 22 17 lie outside the conservative mixing path (Figure 5). We conclude that the mixing of fresh water and saltwater is not the only process that modifies the groundwater quality in the study area.

Figure 6 shows the relationship between potassium and chloride. Several samples are in the fresh water - seawater mixing pathway, and others, such as sample 5, 8, 10, 11, 13, 16 and 21 present an increase of potassium in relation to the mixing path. Graniel *et al.* (1999) and Pacheco *et al.* (2001) observed the same behavior in northwestern Yucatán. Sample 12 shows lower potassium values than for the mixing pathway. One possible explanation is that potassium is exchanged for calcium in seawater. The behavior of the sulfate anion in relation to SO<sub>4</sub>/Cl is presented in Figure 7, we observe an excess of SO<sub>4</sub> in relation to the mixing of fresh water - seawater pathway for samples 3, 7, 10,11, 17, 21, 22 and 24 This may be due to dissolution of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) or anhydrite (CaSO<sub>4</sub>), or from highly sulfate bearing waters reported by Velázquez (1986) and Perry *et al.* (2002).

The saturation index (SI) of a mineral in solution is obtained from (Appelo and Postma, 1996):

$$SI = \log (IAP/Kt) ,$$

where IAP is the ion activity product of the dissociated chemical species in the solution, and Kt is the equilibrium solubility product for the chemical involved at the sample temperature. Saturation indices (SI) of minerals are useful for evaluating the extent to which water chemistry is controlled by equilibrium with solid phases (Appelo and Postma, 1996). The computer code PHREEQC (Appelo and Postma, 1996) was used to calculate the saturation index (SI) for common evaporite minerals and the distribution of major aqueous species.

Table 3 presents the results of geochemical modeling. We observe saturation for calcite in all samples, and in most

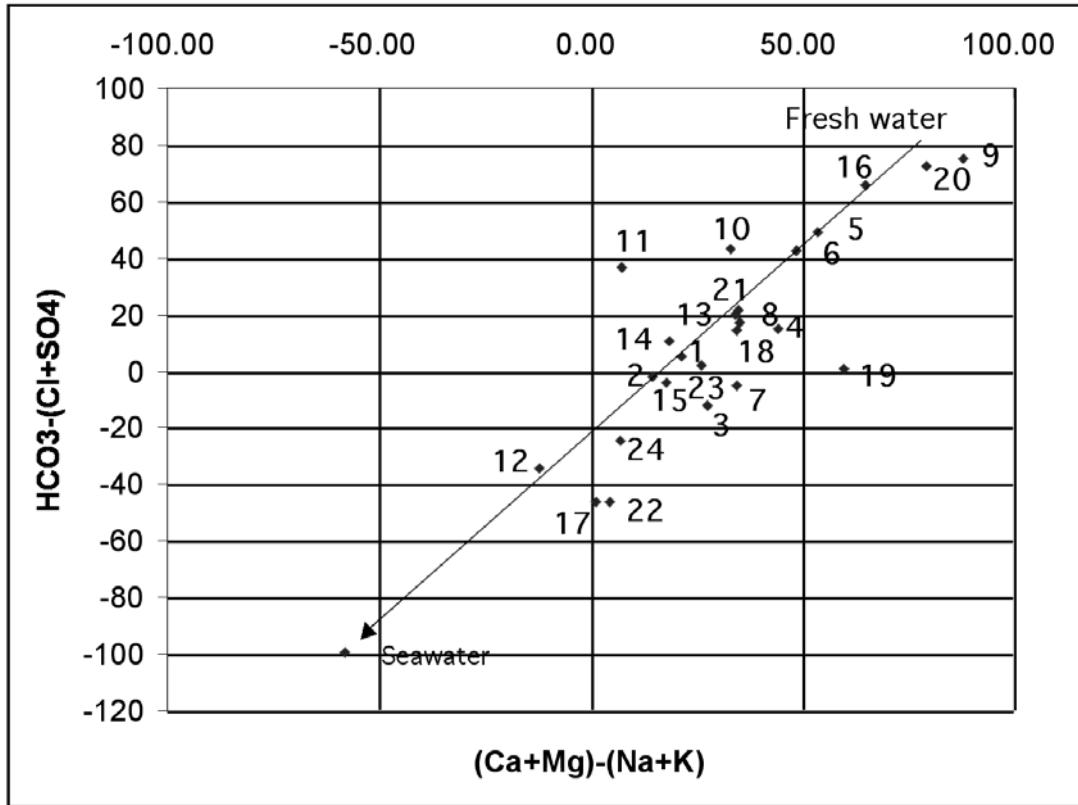


Fig. 5. Groundwater analysis plotted on Chadha diagram. The mixing pathway for freshwater – seawater is indicated.

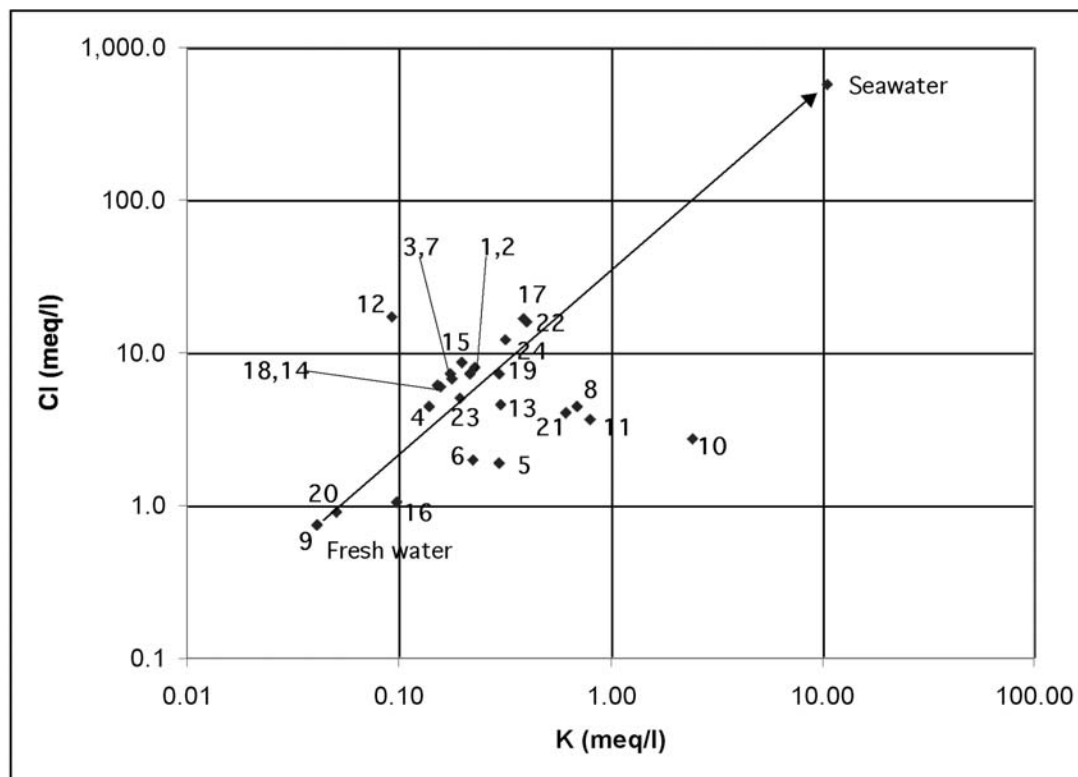


Fig. 6. Relationship between potassium and chloride concentrations in the groundwater samples, the arrow indicates the mixing of fresh water with seawater.

samples also for dolomite and aragonite. Under saturation for anhydrite, gypsum and halite is present in all samples. Samples 6 and 20 are under saturated for dolomite, and samples 1, 4, 10, 12, 15, 17, 22 and 24 are over saturated for dolomite.

The relationship between calcite precipitation and aragonite dissolution, is studied after Perry *et al.* (2002). We find a good correlation between calcite SI and aragonite SI, (Figure 8), according to the following equation:

$$SI(\text{calcite}) = 0.9958 SI(\text{aragonite}) + 0.1435; R^2 = 0.9997$$

Figure 9 presents the relationship between chloride (meq/l) and calcite SI. There is no correlation of calcite SI with chloride. Samples 3, 6, 7, 8, 14, 18 and 21 are under saturated for calcite SI in relation to the fresh water – seawater mixing pathway, and samples 1, 4, 5, 10, 12, 13, 15, 22, 23 and 24 are over saturated in relation to the same pathway. The same behavior is found for dolomite SI and aragonite SI in relation to chloride.

Maps showing the concentration of major ions were constructed. Figure 10 for chloride concentration in mg/l shows an unexpected behavior, as chloride concentrations increase from less than one meq/l in the central part of the study zone, to more than 17 meq/l inland to the east, and to 3

meq/l in the coastal zone. Samples 12 and 17 located 40 km and 80 km inland, respectively, and present the highest chloride concentrations.

Velázquez (1986), Steinich (1996) and Perry *et al.* (2002) propose the  $SO_4/Cl$  ratio as a natural tracer to indicate the mixing of fresh water and sea water, Steinich *et al.* (1996) used the ratio  $(SO_4/Cl) \times 1000$ . Assuming a value of 103.4 for sea water, they propose that fresh water samples can be grouped as follows: (1) samples with a sulphate – to – chloride ratio similar to that of seawater, and (2) samples with a ratio of  $SO_4/Cl \times 1000$  greater than 300.0, mainly influenced by the contact with and dissolution of evaporites. Figure 11 shows the  $SO_4/Cl$  ratio in the study zone. The samples corresponding to the first group are located east of the study zone, several kilometers inland; while the values corresponding to the second group are located to the west and south of the study zone. Ratios higher than 0.3 are located outside of the central part of the Ring of Cenotes, except for the west portion of the study zone.

Figure 12 shows the distribution of the Calcite saturation index (SI). Observe that the lower SI, between 0.1 and 0.2, are located in the central and southern part of the study zone and the SI between 0.3 and 0.8 are located east and north of the central part of the study zone. Interestingly, calcite SI lower than 0.3 is located outside of the inner part of

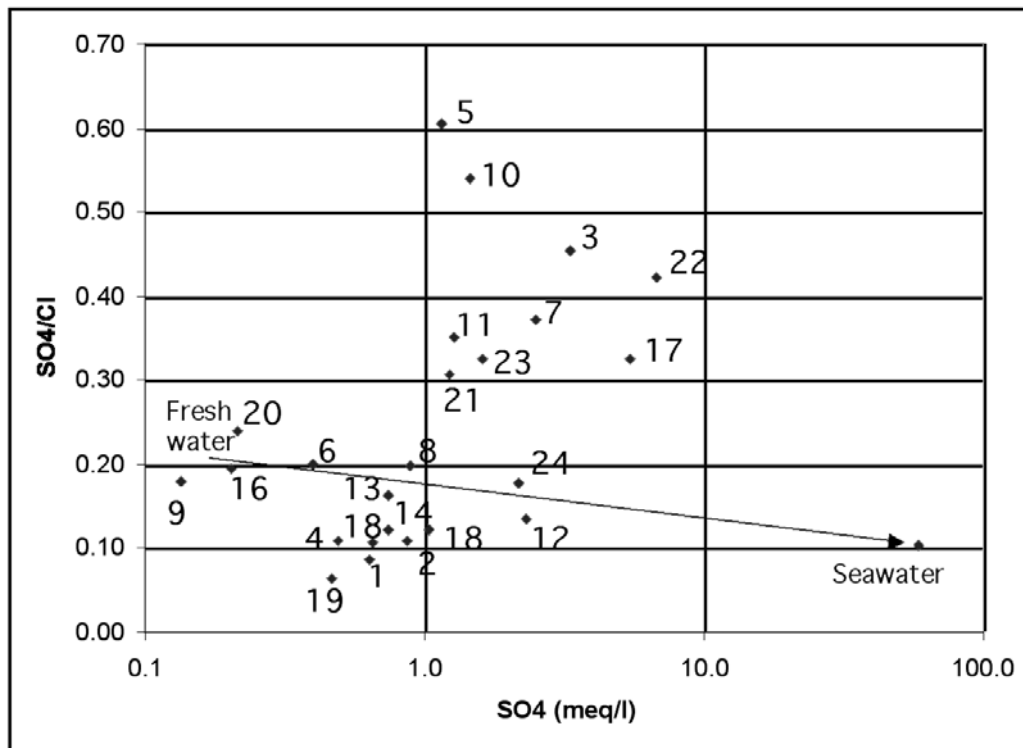


Fig. 7. Relationship between sulfate and chloride concentrations in the groundwater samples. The arrow indicate the mixing of fresh water with seawater.

**Table 3**

Saturation Index of groundwater

Sample N°	Anhydrite	Aragonite	Calcite	Dolomite	Gypsum	Halite
1	-2.38	0.52	0.66	1.48	-2.17	-6.08
2	-2.24	0.27	0.41	0.92	-2.03	-6.00
3	-1.69	0.01	0.15	0.53	-1.48	-6.08
4	-2.55	0.31	0.45	1.24	-2.34	-6.48
5	-2.09	0.35	0.50	0.88	-1.89	-7.22
6	-2.56	-0.10	0.05	-0.02	-2.35	-7.16
7	-1.73	0.06	0.20	0.53	-1.53	-6.16
8	-2.28	-0.10	0.05	0.29	-2.07	-6.56
9	-2.99	0.09	0.23	0.57	-2.80	-8.19
10	-1.95	0.39	0.53	1.05	-1.75	-7.00
11	-1.98	0.21	0.35	0.45	-1.78	-6.40
12	-1.75	0.58	0.72	1.40	-1.54	-5.34
13	-2.25	0.46	0.60	1.19	-2.04	-6.47
14	-2.37	0.15	0.29	0.72	-2.16	-6.23
15	-2.11	0.38	0.53	1.11	-1.91	-5.96
16	-2.90	0.13	0.27	0.61	-2.70	-7.64
17	-1.40	0.53	0.67	1.46	-1.20	-5.37
18	-2.31	0.14	0.28	0.64	-2.10	-6.25
19	-2.55	-0.11	0.04	0.25	-2.34	-6.63
20	-2.70	0.06	0.20	-0.05	-2.50	-7.95
21	-2.04	0.13	0.27	0.54	-1.83	-6.58
22	-1.27	0.45	0.59	1.20	-1.06	-5.41
23	-1.92	0.38	0.52	0.99	-1.71	-6.36
24	-1.79	0.68	0.82	1.71	-1.58	-5.65

the Ring of Cenotes, except west of the study zone, as in the case of the SO<sub>4</sub>/Cl ratio. This may be due to the Ring of Cenotes, which hydrogeologically isolates the east portion of the study zone, as suggested by Marín (1990).

Combining maps with the spatial distribution of contents for major ions (chloride, sulfate, calcium, bicarbonate, sodium and magnesium), we may define a zone with the lowest concentrations for all ions in the study zone. This zone is shown in Figure 13. It corresponds to the central portion of the study area, where the groundwater is the best inorganic quality water. It is important to note that this area crosses the Ring of Cenotes. This suggests that the Ring of Cenote is not isolated, as originally proposed by Marín (1990).

**DISCUSSION**

Sample 20 (Figure 4), corresponds to fresh water type. This suggests that the limestone consists of almost pure carbonate rocks and evaporates. Dissolution leaves no residue, except for an increase of K detected in samples 8, 10, 11, and 21.

Some authors consider that a K increment may be produced by the use of agrochemicals (Pacheco *et al*, 2001) or dissolution of clayey limestone (Graniel *et al*, 1999). However, if the agrochemicals are the origin of K as observed in Figure 6, this may be due to an excess of SO<sub>4</sub>, as observed in samples 10, 11 and 21 in Figure 7. Sample 8 may be asso-

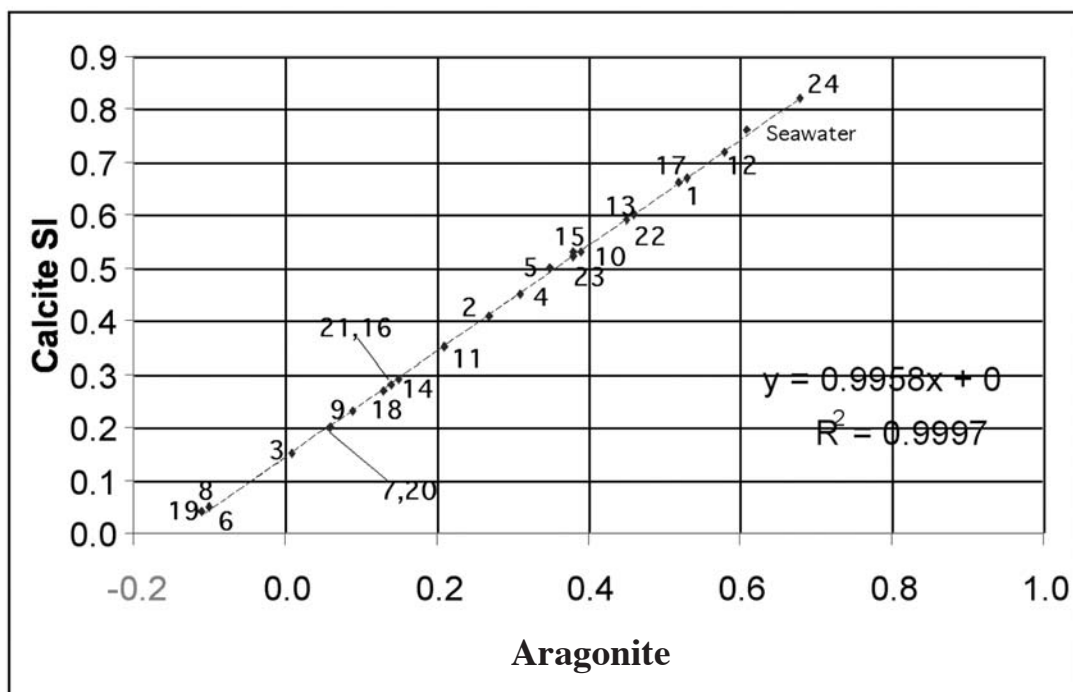


Fig. 8. Relationship between calcite SI and aragonite SI in the groundwater samples.



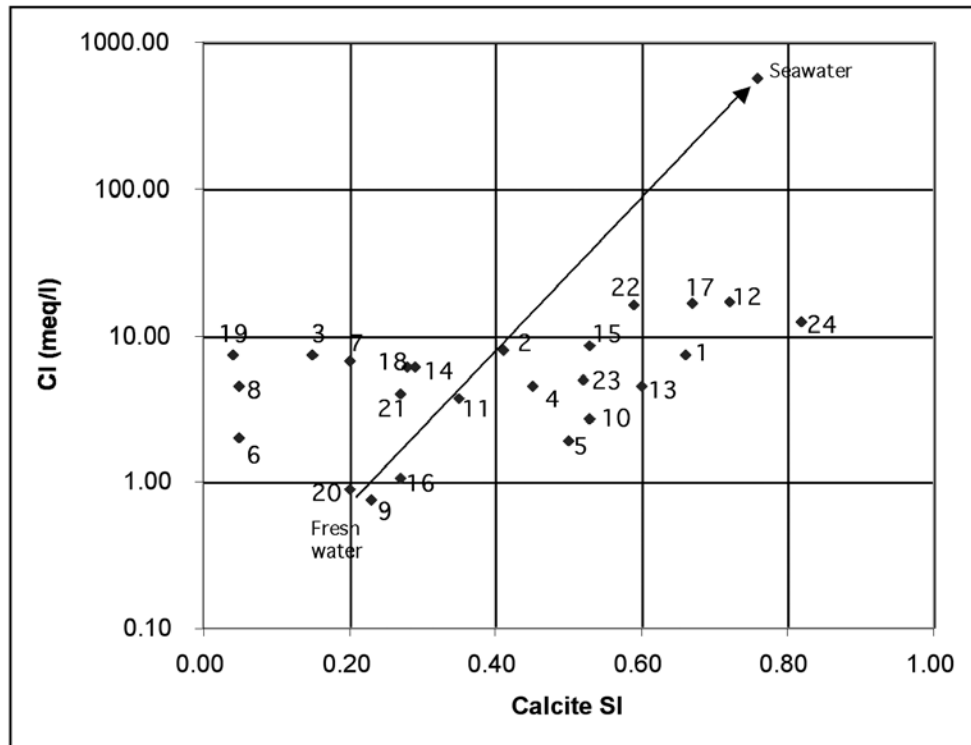


Fig. 9. Relationship between calcite SI and chloride (meq/l).

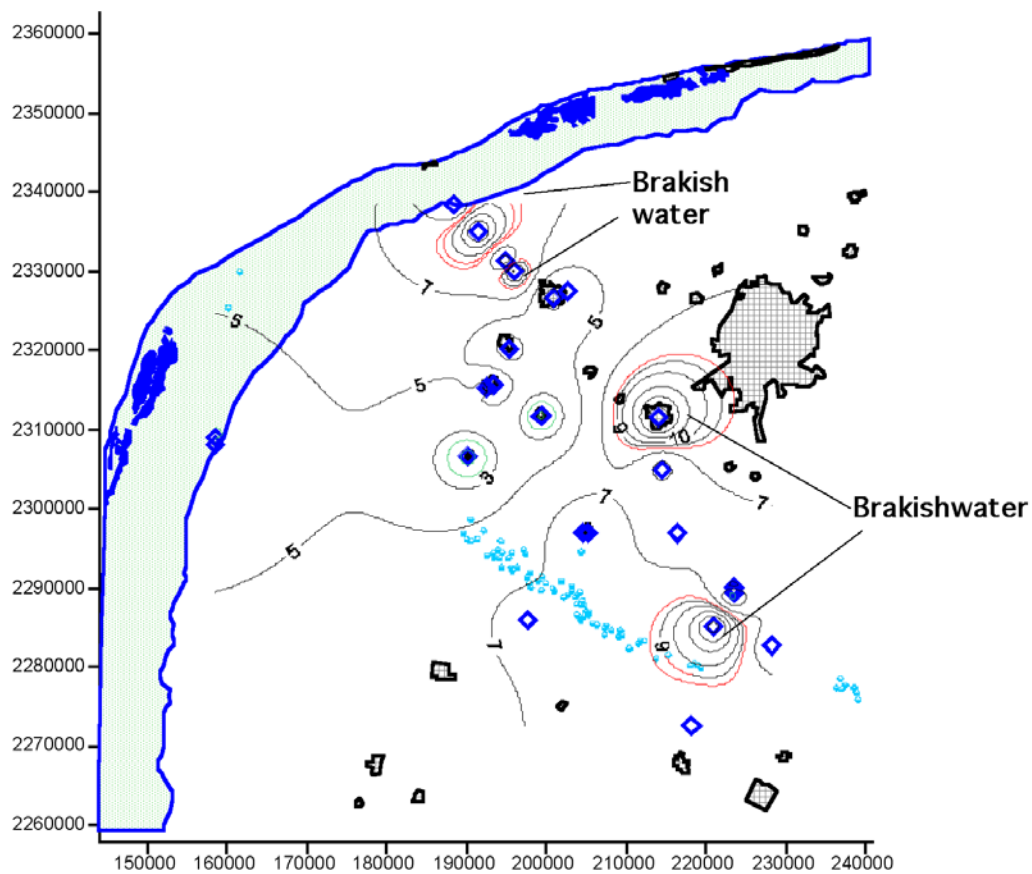


Fig. 10. Spatial distribution of chloride (meq/l) concentrations. The values above 8.5 meq/l maybe considered as brackish water.

ciated with dissolution of clayey limestone, probably from the Carrillo Puerto formation of middle Eocene that outcrops in the central region of the study zone. Thus the K excess may be associated with different factors, depending on the geology and/or the human activities in the area.

Calcite SI is lowest outside of the Ring of Cenotes, while in the inner zone of the Ring of Cenotes SI increases gradually from the central portion of the study zone outward.

The  $SO_4/Cl$  ratio (Figure 11) is above 0.3 (compare  $(SO_4/Cl) \times 1000 = 300$ , proposed by Steinich, 1996). This confirms the ideas of Marín (1990), Steinich (1996) Perry et al. (1995) and Perry et al. (2002) that the Ring of Cenotes isolates hydrogeologically the Chicxulub sedimentary basin, also known as the Mérida block, due to the high permeability in the Ring of Cenotes. This ring carries groundwater from the southern interior northward to the Gulf of Mexico, while the sulfate-rich groundwater located west and south of the study zone is discharged through the Ring of Cenotes to the Gulf of Mexico. However, the results in this paper sug-

gest that the effect of the Ring of Cenotes disappears in the western portion of the study zone. One possible explanation is a reduction of the permeability. There are no sinkholes in the Ring of Cenotes in this part of the study zone.

Perry et al. (1995) propose using the Chloride/sulfate chemical equivalent ratio “for the best discriminant between seawater and seawater-freshwater mixtures, because this ratio is dramatically different from that for seawater (9.6)”. The  $Cl/SO_4$  ratios for the samples in this study vary from less than two in samples 5 and 10, to more than nine in samples 1, 2, 4, 18 and 19. The  $Cl/SO_4$  ratio for sample 20, the freshwater end member, is about 4.2 and for sample 22, the brackish water end member, is 2.37. The results are in disagreement with the suggestion by Perry et al. (1995). We should take care in the use of this ratio in the study zone, because an excess of sulfate may be due to the presence of agrochemicals or the dissolution of gypsum.

Perry et al. (1998); Marín, (1990), Pacheco et al. (2000) and Steinich et al. (1996) state that the regional groundwater

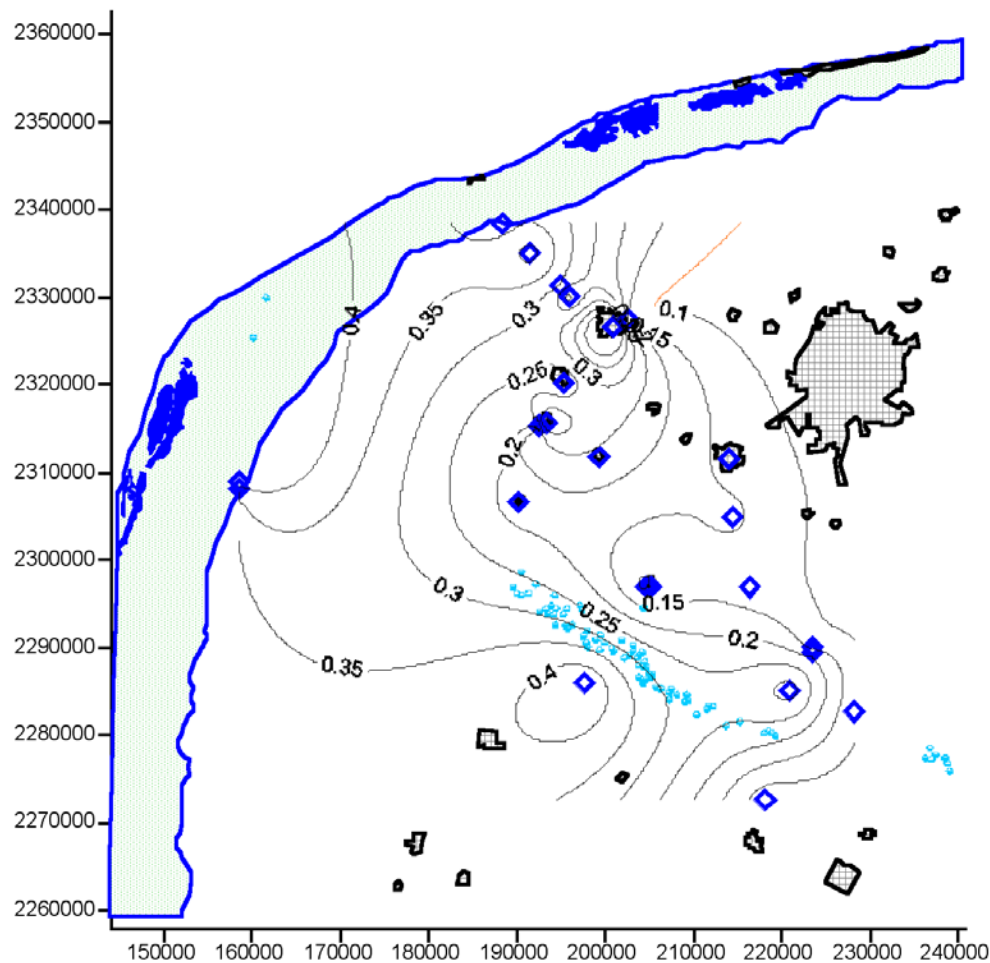


Fig. 11. Spatial distribution of  $SO_4/Cl$  ratios. Concentrations expressed in meq/l, where the values lower than 0.1 may be considered as seawater.

flow is from southeast to northwest, and that the high permeability reported by Marín (1990) and Steinich (1996) generates a high groundwater flow toward the coast that minimizes the mixing with seawater. Hence, we expected to find a gradual mixing of freshwater with seawater, using the chloride concentrations as a conservative tracer. However, our results show (Figure 10) that two samples (12 and 17) located more than 40 km inland present the highest contents of seawater (> 3%), while samples 10 or 11 located near the coast present low contents of seawater (< 0.65%). Apparently the brackish water is not produced by mixing with sea water at the coast. The hypothesis of high groundwater flow to the coast may explain the low contents of seawater in samples located near the coast, but it does not explain 3% of seawater contents in samples 12, 17. The type of water and the ratios found in these samples show that they are clearly affected by seawater mixing. Thus, salt water in samples 12 and 17 must be due to upconing of salt water underlying the fresh water lens, owing to the drilling and pumping of relatively deep wells or pumping for drinking water uses.

Escolero *et al.*, (2000) proposed that the local groundwater flows radially from the central zone, because of drainage of the Ring of Cenotes into the south, pumping in the east, and the influence of the shoreline in the north and west. The distribution of different SI as Calcite SI (Figure 12) and the clear zone presented in Figure 13, support this suggestion.

### CONCLUSIONS

Hydrochemical data establish the processes that modify groundwater quality in northwest Yucatán. These processes by order of importance are: dissolution of almost pure carbonate rocks, conservative mixing with seawater, ionic interchange in clayey limestone of middle Eocene, upconing of salt water by concentration of pumping, dissolution of gypsum, and the probable presence of agrochemicals. Detailed studies are needed in order to confirm the presence of agrochemicals in the study zone.

Different ratios were used to differentiate between freshwater and seawater samples and to help define the water type.

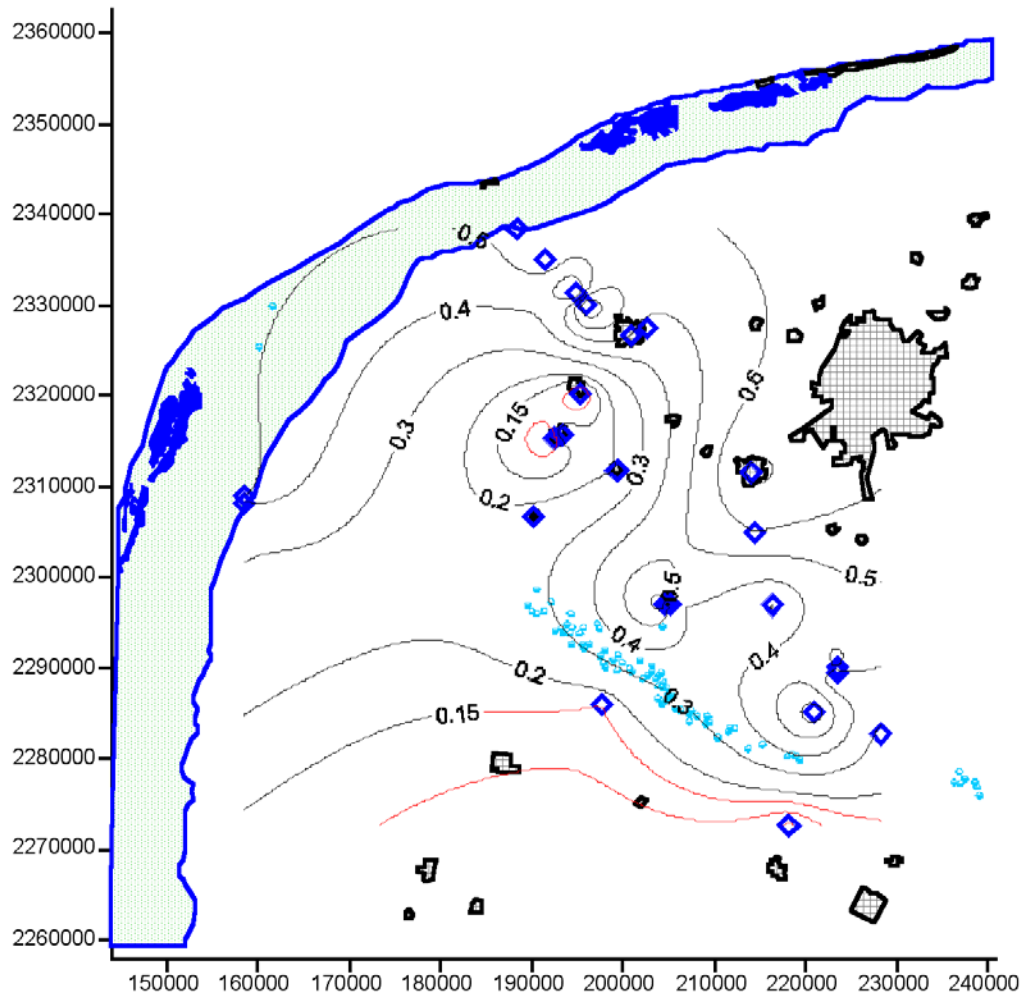


Fig. 12. Spatial distribution of calcite SI, showing the effect of RC and the radial increase of the SI from the central zone.

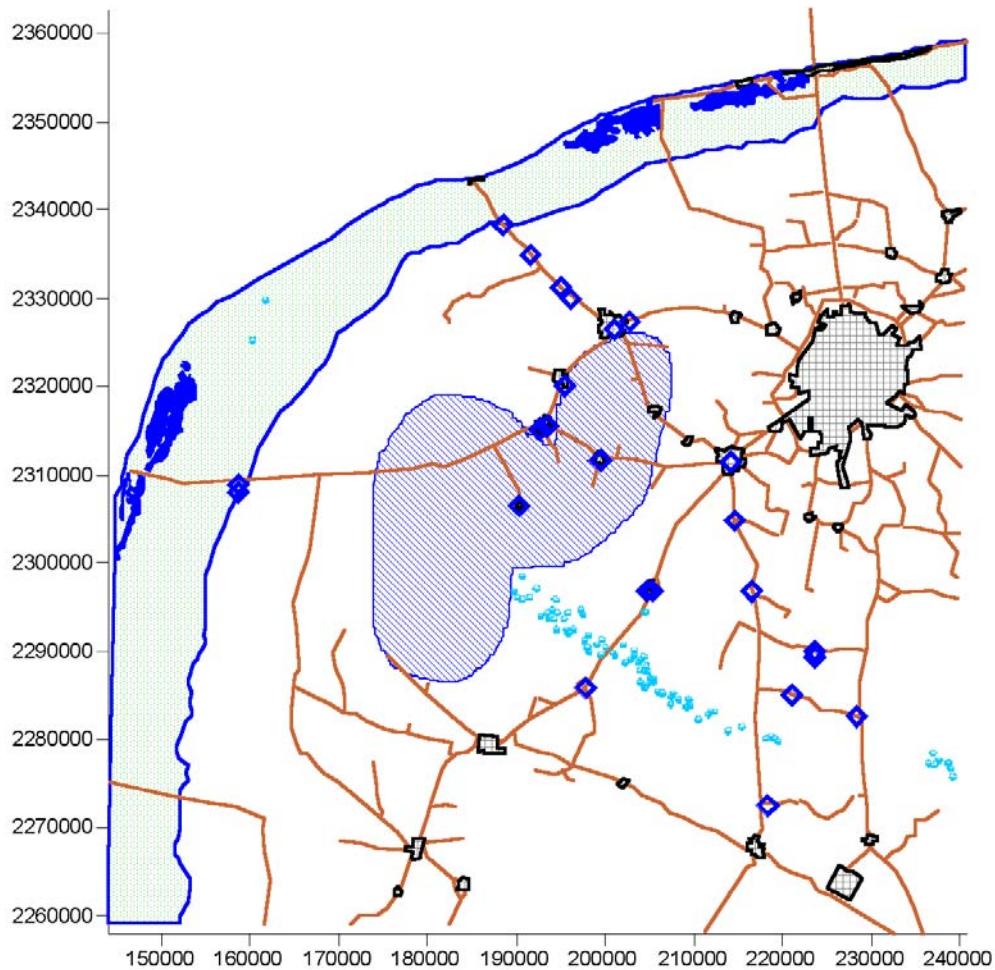


Fig. 13. The shaded area is the clear zone defined using the combination of the lowest concentrations of major ions.

The results show that the use of these ratios alone is not very useful. If combined with mapping we are able to define the hydraulic control imposed by the Ring of Cenotes and the concentration of pumping for drinking water use. Combined with the presence of the coast, these generate a radial groundwater flow from the central portion of the study zone, as supported by hydrochemical distribution of major ions and SI.

An important issue raised by this study is the unexpected presence of brackish water several kilometers inland, which seems to contradict gradual mixing of fresh water with seawater as one approaches the coast. We propose that this salinity increase is produced by saltwater upconing in relatively deep wells or due the concentration of pumping. We agree with Marín and Perry (1994) that the aquifer is highly vulnerable to contamination from upconing of the underlying saltwater.

The Hydrogeological Reserve Zone proposed by Escolero *et al.* (2002), coincides with the clear zone defined

in this study and with the local groundwater flow scheme proposed. For this reason we urge that the Hydrogeological Reserve Zone be established.

#### ACKNOWLEDGEMENTS

Escolero, Marín, Molina-Maldonado and Anzaldo acknowledge support from the Universidad Nacional Autónoma de México, Dirección General de Asuntos del Personal Académico, Proyecto PAPIIT 2002-IN110602. Pacheco acknowledges support from the Fondo para el Sistema de Investigación Justo Sierra and Consejo Nacional de Ciencia y Tecnología.

#### BIBLIOGRAPHY

APHA, AWWA, WEF, 1996. Standard methods for the examination of water and wastewater (18 th edn). Edited by: Greenberg AE; Clesver LS and Eaton AD Washington, D.C., USA. 1,193 p.

- APPELO, C. A. J. and D. POSTMA, 1996. Geochemistry, groundwater and pollution. Balkema, Rotterdam, 536 p.
- BACK, W. and B. B. HANSHAW, 1970. Comparison of chemical hydrogeology of the carbonate peninsulas of Florida and Yucatán. *J. Hydrology*, 10, 330-368.
- CHADHA, D. K., 1999, A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data. *Hydrogeol. J.*, 7, 5, 431-439.
- ESCOLERO, O. A., L. E. MARÍN, B. STEINICH and A. J. PACHECO, 2000. Delimitation of a hydrogeological reserve for a city within a karstic aquifer: the Mérida, Yucatán, example. *Landscape and Urban Planning*, 51 (1), 53-62.
- ESCOLERO, O. A., L. E. MARÍN, B. STEINICH, A. J. PACHECO, S. A. CABRERA and J. ALCOCER, 2002. Development of a Protection Strategy of karstic Limestone aquifers: The Mérida Yucatán, Mexico Case Study. *Water Resources Management* 16, 351-367.
- GRANIEL, E., L.B. MORRIS and J.J. CARRILLO RIVERA, 1999. Effects of urbanization on groundwater resources of Merida, Yucatan, Mexico. *Environ. Geol.*, 4, 303-312.
- HANSHAW, B. B. and W. BACK, 1973. Major geochemical processes in the evolution of carbonate-aquifer systems. *J. Hydrology*, 43, 287-312.
- LEGRAND, H. E., 1973. Hydrological and ecological problems of karst regions. *Science*, 176, 859-864.
- MARÍN, L. E., E. C. PERRY, C. BOOTH and M. VILLASUSO, 1987. abstract, Hydrogeology of Northwestern Yucatán, Mexico, EOS, (Transactions, American Geophysical Union), v (69), p. 1292.
- MARÍN, L.E., 1990. Field investigations and numerical simulation of the ground water flow in the karstic aquifer of Northwestern Yucatán, Mexico, Ph.D. thesis, Northern Illinois University, DeKalb, Illinois, USA, 183 p.
- MARÍN, L. E., E. C. PERRY, K. O. POPE, C. E. DULLER, C. J. BOOTH and M. VILLASUSO, 1990. Hurricane Gilbert: its effects on the aquifer in northern Yucatán, Mexico. In: E. S. Simpson and J. M. Sharp, (eds.), Selected Papers on Hydrogeology from the 28th International Geologic Congress, Washington, D.C., USA, July 9-19, Hanover, Verlag Heinz Heise, International Association of Hydrogeologists, v (1) 111-128.
- MARÍN, L.E. and E. C. PERRY, 1994. The hydrology and contamination potential of northwestern Yucatán, Mexico. *Geofís. Int.*, 33, 619-623.
- MARÍN, L. E., B. STEINICH, A. J. PACHECO and O. A. ESCOLERO, 2000. Hydrogeology of a contaminated sole - source karst aquifer, Mérida, Yucatán, Mexico. *Geofís. Int.*, 39, 4, 359-365.
- MELLOUL and GOLDENBERG, 1998, Early-indicator signals of groundwater contamination: the case of seawater encroachment. *Environ. Geol.*, 33, 4, 279-288.
- PACHECO, A. J. and S. A. CABRERA, 1997. Ground water contamination by nitrates in the Yucatán peninsula, Mexico. *Hydrogeol. J.*, 2, 47-53.
- PACHECO, A. J., S. A. CABRERA and L. E. MARÍN, 2000. Bacteriological contamination in the karstic aquifer of Yucatán, Mexico. *Geofís. Int.*, 39, 3, 285-291.
- PACHECO, A. J., L. E. MARÍN, S. A. CABRERA, B. STEINICH and O. A. ESCOLERO, 2001. Nitrate temporal and spatial pattern in 12 water-supply wells, Yucatán, Mexico. *Environ. Geol.*, 40, 6, 708-715.
- PERRY, E.C., J. SWIFT, J. GAMBOA, A. REEVE, R. SANBORN, L. E. MARÍN and M. VILLASUSO, 1989. Geologic and environmental aspects of surface cementation, north coast, Yucatán, Mexico. *Geology*, 17, 17-20.
- PERRY, E. C., L. E. MARÍN, J. MCCLAIN and G. VELÁZQUEZ, 1995. The ring of Cenotes (sinkholes) northwest Yucatán, Mexico: Its hydrogeologic characteristics and association with the Chicxulub Impact Crater. *Geology*, 23, 17-20.
- PERRY, E. C., G. VELÁZQUEZ-OLIMAN and L. E. MARÍN, 2002. The Hydrogeochemistry of the Karst Aquifer System of the Northern Yucatán peninsula, Mexico. *International Geology Review*, 44, 191-221.
- POPE, K. and C. DULLER, 1989. Satellite observations of ancient and modern water resources in the Yucatán peninsula. In: Álvarez, R., de., Memoria, Simposio Latinoamericano sobre sensores remotos: Sociedad de Especialistas Latinoamericanos en Percepción Remota

- e Instituto de Geografía, Universidad Nacional Autónoma de México, 91-98.
- PROHIC, E., 1989. Pollution assessment in carbonate terrenos. *In: LaMoreaux, P. (ed.), Hydrology of limestone terrenos: Annotated bibliography of carbonate rocks N° 4*, I.A.H. International Contributions to Hydrogeology 10, 61-82. Heise, Hannover, Germany.
- SARH, 1988. Sinopsis Geohidrológica del Estado de Yucatán, Mexico City, Mexico, 50 p.
- STEINICH, B., 1996. Hydrogeological Investigations in northwestern Yucatán, Mexico, PhD Thesis, Universidad Nacional Autónoma de México, Posgrado en Ciencias de la Tierra, México.
- STEINICH, B., G. VELÁZQUEZ OLIMÁN, L. E. MARÍN and E. C. PERRY, 1996. Determination of the ground water divide in the karst aquifer of Yucatán, Mexico, combining geochemical and hydrogeological data, *Geofís. Int.*, 35, 153-159.
- STEINICH, B. and L. E. MARÍN, 1996. Hydrogeological Investigations in northwestern Yucatán, Mexico, using resistivity surveys. *Ground Water*, 34, 4, 640-646.
- STEINICH, B. and L. E. MARÍN, 1997. Determination of flow characteristics in the aquifer of the north-western peninsula of Yucatán. *J. Hydrology*, 191, 315-331.
- STRINGFIELD and LEGRAND, 1969. Hydrology of carbonate rocks terranes – A review with special reference to the United States. *J. Hydrology*, 8, 349-376.
- VELÁZQUEZ, L., 1986. Aplicación de principios geoquímicos en la hidrología kárstica de la península de Yucatán, Ingeniería Hidráulica en México, mayo-agosto de 1986, 21-29.
- WARD, W. C., A. E. WEIDIE and W. BACK, 1985. Geology and hydrogeology of the Yucatan and Quaternary geology of north-eastern Yucatan Peninsula, New Orleans Geological Society, New Orleans, LA, USA.
- 
- O. Escolero<sup>1</sup>, L. E. Marín<sup>2</sup>, B. Steinich<sup>3</sup>, J. A. Pacheco<sup>4</sup>, A. Molina-Maldonado<sup>2</sup> and J. M. Anzaldo<sup>2</sup>
- <sup>1</sup> Instituto de Geología-UNAM, Cd. Universitaria, México, D. F., CP. 04510. Email: escolero@geologia.unam.mx
- <sup>2</sup> Instituto de Geofísica-UNAM, Cd. Universitaria, Mexico, D.F., CP. 04510. Email: lmarin@geofisica.unam.mx
- <sup>3</sup> Centro de Geociencias, UNAM, Campus Juriquilla, Querétaro.
- <sup>4</sup> Facultad de Ingeniería, Universidad Autónoma de Yucatán, México.