

## **Geochemical groundwater analysis for the establishment of an hydrogeological reserve in a karstic aquifer.**

### **Hydrogeochemistry of the Cenotes Ring, Yucatán, México**

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#### **Abstract**

The Yucatan Peninsula groundwater is the only source of water to the population. The geology of this place is a carbonated and evaporite rock platform, a karstic system with rainfall infiltration, vulnerable to pollution, with flow recharge and seawater intrusion, a problem for its use.

Hydrogeochemical analyses are a valuable to obtain information: quality and type of groundwater, recharge flows, in situ processes and to infer the relationship among geographic location and anthropogenic activities. The interpretation of the data is useful to propose or decree the areas that can be considered as hydrogeological reserves for water supply.

Representative samples from the 14 cenotes considered for this project were analyzed. This investigation reports: physical-chemical parameters (pH, T, EC) and the chemical composition of cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Sr}^{2+}$ ) and anions ( $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ).

The results from this investigation were evaluated with different hydrogeochemical tools for classification (Piper and Stiff Diagrams, ionic relations). Data interpretation indicates that the analyzed groundwater samples are classified in three water types: Mg-Cl type, Ca-Cl type, and Mg-HCO<sub>3</sub> type. The lack of homogeneity at the groundwater classifications may be related to the geographic features of the sampled caves (cenotes).

**Keywords:** Yucatán, hydrogeochemistry, karstic

#### **Introduction**

The Yucatan Peninsula aquifer, located at the southeast of Mexico, is mainly composed by caves, caverns, and sinkholes (cenotes) which are aligned in a circular shape called "Cenotes Ring". This geological structure acts like an "underground river" and is connected to the sea. The karstic, coastal and high permeability characteristics of this system, besides the importance of its hydrological contribution to the region, are the basis of numerous investigations at the zone.

The geology of this area is constituted by a carbonate and evaporitic rock platform forming a mature karstic system; with special characteristics as a high rainfall recharge, becoming a vulnerable area to pollution. The aquifer is also described as a fresh water lens that lays over sea water; it has been determined that saline intrusion is present 100Km from the shore to the continent hindering overtime the groundwater use.

The Merida city, capital of Yucatan, is the most important at the Mexican southeast with a total population of 781,146 inhabitants. The water supply is limited to three groundwater sites of 60m thickness; in this area does not exist surface water bodies. (Escolero et al, 2002)

Because of this problem, and with the main objective of helping to maintain and assure a water supply (in quantity and quality) for the area, covering since the human until the consumption needs (industry and agriculture), the FOMIX-YUC-2008-C6 project's main objective is to propose the establishment of an hydrogeological reserve; what leads to appropriate an correct previous researches for the evaluation of different areas.

Groundwater in karstic system, as the Yucatan Peninsula, has natural processes associated (carbonated and evaporitic rock dissolution, precipitation and evapotranspiration); and an important saline intrusion. As a consequence, the groundwater chemical composition at the Yucatan

Peninsula is described, in general terms, as rich in cations like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  y  $\text{Sr}^{2+}$ , and in anions like  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$

The project is focused in the groundwater geochemical analysis of selected sinkholes located at the Yucatan Peninsula in order to select a specific area to be declared as a reserve for freshwater supply for human needs. The results of hydrogeochemical analyses, quality and type of groundwater in selected sites are presented.

### Methodology

#### Sampling area

The sampling area is located in the Cenotes Ring, located at the northeast of Yucatan. 13 cenotes or caves at the south of Merida with different characteristics were selected. In this area there are not important agricultural activities. The sampling was made at May 2010. The table 1 presents the information of the name of the samples, and its geographic coordinates.

**Table 1.** Name and location of the sample points

Name of the cenote	UTM Coordinates	
	W	N
Yaxputol	242655	2278139
Telchaquillo	243234	2285077
Chich	242519	2276517
Aguil Chinkila	250308	2292088
Calcuch	254023	2286617
Tanimax	252810	2285088
Chonkila	255919	2285010
Aktun Ha	258458	2293143
Teabo	253756	2258828
Chelentun	255421	2278171
Xaquiniché	253341	2278893
Bolonchol	251663	2278253
Chichí de los Lagos	275144	2278487



**Figure 1.** Cenotes in the Yucatan Peninsula (blue dots). The black square indicates the sampling area.

#### Sample Collection

Were collected samples for the physical chemical analysis (alcalinity,  $\text{CO}_2$ , sulphates, chlorides) and for the cation measurement. Basic parameters (pH, T, EC, SDT) were determined *in situ*. For the ICP-OES analysis and nutrients, were taken 30 and 250mL of water, filtered previously with a  $0.2\mu\text{m}$  Whatman® and Nalgene® pore. For the physical chemical analysis were taken water samples of 25mL without previous filtered. The samples collection were done with a Van Dorn sampling bottle. In field; pH, temperature (T) and electric conductivity (EC) were measured with a Hydrolab® DS5

The cations measurement was carried out with a Thermo Dual ICP-OES previously verified with a certified reference material (Trace Metals in Drinking Water from High Purity Standards). The samples were treated by the 3030D and 3030K methods of the Standard Methods for Examination of Water and Wastewater del APHA

The physical chemical parameters were measured according to the methods showed in the table 2 (APHA, 1998).

**Table 2.** Standard methods for the measurement of anions in groundwater samples of the Cenotes Ring, Yucatán, México.

Parameter	Method	Equipment
Chloride	Método Argentométrico por titulación 4500-Cl <sup>-</sup> B	APHA
Sulphates	Método Turbidimétrico 4500-SO <sub>4</sub> <sup>2-</sup> -E.	Barnstead SP-830Plus Spectrophotometer
Alcalinity	Método por titulación 2320 B.	APHA

#### Discussion

All the shown samples results accomplished with a ionic balance under 10% and with consequent EC measurements. The concentrations for cations are presented in table 3 and for anions in table 4.

**Table 3.** Cation concentrations (mg/L) for groundwater samples of the Cenotes Ring, Yucatán México.

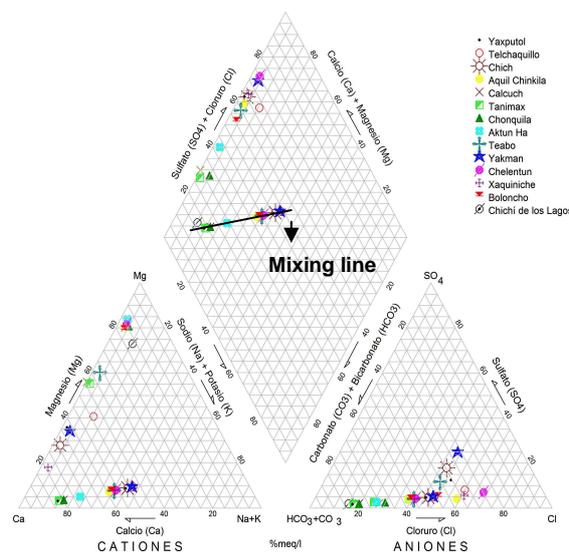
Cenote	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Si <sup>2+</sup>
Yaxputol	127.90	44.65	3.56	2.56	8.03
Telchaquillo	73.31	37.04	2.98	2.75	10.11
Chich	168.56	41.31	5.56	5.50	11.51
Aquil Chinkila	19.49	59.53	3.86	2.57	16.12
Calcuch	35.96	27.78	0.42	0.80	7.58
Tanimax	34.55	26.90	1.43	0.60	14.51
Chonquila	13.05	44.90	0.93	4.64	11.76
Aktun Há	13.61	51.93	2.73	1.77	11.78
Teabo	65.63	65.65	4.21	4.37	14.43
Yakman	143.18	47.66	5.72	7.45	18.33
Chelentun	19.30	64.06	4.67	2.71	20.51
Xaquiniche	114.90	16.10	4.61	2.23	21.49
Bolonchohol	21.71	62.68	5.21	2.88	18.27
Chichí de los Lagos	19.52	52.07	13.35	6.20	3.21

**Table 4.** Anion concentrations (mg/L) for groundwater samples of the Cenotes Ring, Yucatán México.

Cenote	Alcalinity	HCO <sub>3</sub> <sup>-</sup> **	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	TDS
Yaxputol	184	224.48	191.25	62.10	664.6
Telchaquillo	166	202.52	220.30	40.40	612.4
Chich	204	248.88	198.52	101.20	781.1
Aquil Chinkila	126	153.72	140.41	13.40	409.1
Calcuch	184	224.48	51.32	5.60	351.8
Tanimax	180	219.6	44.54	6.60	348.7
Chonquila	164	200.08	51.32	5.90	332.6
Aktun Há	160	195.2	77.47	10.70	365.2
Teabo	184	224.48	154.94	51.60	585.3
Yakman	166	202.52	215.46	148	788.3
Chelentun	82	100.04	159.78	22.30	393.4
Xaquiniche	122	148.84	157.36	19.90	485.5
Bolonchohol	184	224.48	147.67	20.80	503.7
Chichí de los Lagos	336	409.92	43.00	7.63	554.9

The best lineal correlations were for the TDS with Ca<sup>2+</sup>+Mg<sup>2+</sup> (0.92); and EC with chloride (0.92), meaning those are the predominant ions in the groundwater samples, the processes that take place are highly controlled by them.

With the concentrations of all the measured ions, Piper diagrams were done (Figure 2) for the establishment of water type for the samples. The mixing line for groundwater with seawater was also calculated; in the diagram, it is located in the Ca-Mg-HCO<sub>3</sub> area, the most common chemical composition for carstic groundwater. The trend of the line goes to the Cl-SO<sub>4</sub>-Na composition.



**Figure 2.** Piper Diagram for geochemical classification of groundwater samples

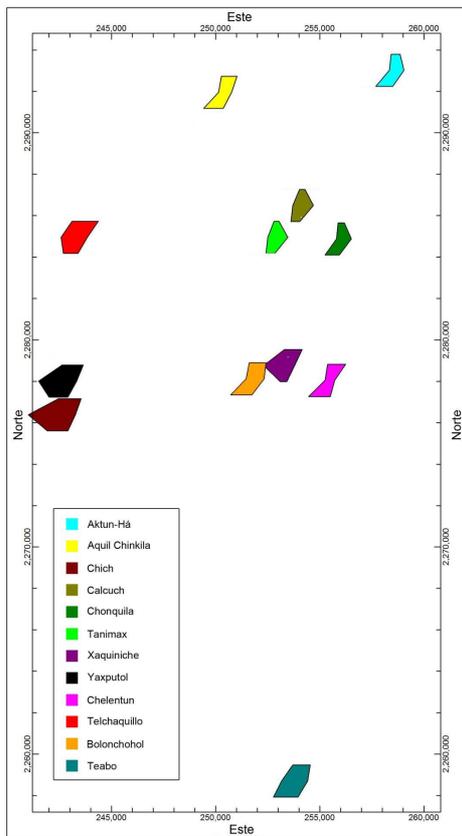
The groundwater samples can be classified in two main families by the Piper diagram,

- Mg-HCO<sub>3</sub> type: *Aktun Há, Calcuch, Tanimax, Chonquila, Chichí de los Lagos*
- Cl/SO<sub>4</sub>-Ca type: *Telchaquillo, Yakmam, Yaxputol, Chich, Xaquinicé*
- Cl/SO<sub>4</sub>-Mg type: *Aquil Chinkilá, Teabo, Chelentun, Bolonchohol*

In comparison with the resulting mixing line, is clear that the groundwater samples do not have an ideal chemical composition of mixed water. The chemical composition is displaced because of a major concentration of species like calcium and magnesium.

Eventhough the lineal trend for the samples indicates an increase on the chloride concentration in samples (saline intrusion) this is not the main process affecting the composition of water, because of the main predominance of calcium and magnesium above all the other cations.

The spatial distribution presented in figure 3 corresponds to the Stiff diagrams for each water sample based on the ion concentration measured, they are located according to the relative position between them. In the external part of the map are located the samples of the cenotes Aquil Chinkila, Yaxputol, Chich y Telchaquillo, with a Cl-Ca water type, excepting Aquil Chinkila with a magnesian composition. The second group is formed by the cenotes Tanimax, Calcuch, Chonquila and Aktun Ha with a Ca/Mg-HCO<sub>3</sub> water type located in the central part.



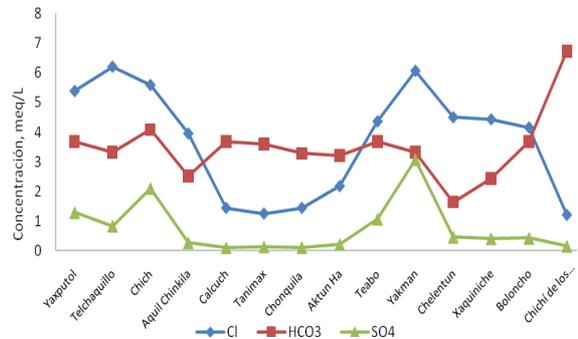
**Figure 3.** Stiff diagrams for geochemical classification of groundwater samples

Between the samples for the cenotes Bolonchohol, Xaquinicé and Chelentun, which are near each other, does not exist any clear relation between their chemical composition.

From the diagrams interpretations is clear that there is no homogeneity between the chemical composition of all the groundwater samples, it is possible to set some isolated groups but the whole area does not accomplish with just one composition or trend.

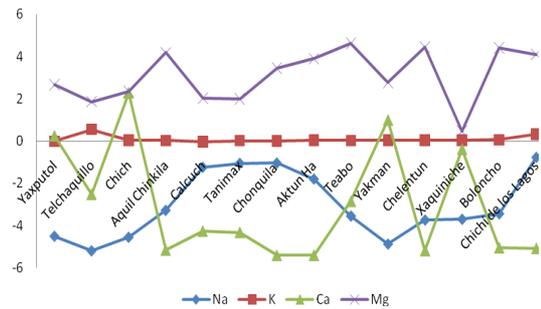
From the graph 4 we can observe an equal trend between chlorides and sulphates, this may indicate

they become from the same source (seawater), it is also clear that sulphate concentrations are low; this may be because a reduction of the specie; process that can be justified by the predominance of HCO<sub>3</sub><sup>-</sup> in front of SO<sub>4</sub><sup>2-</sup>.



**Figure 4.** Anions concentrations for the sampled cenotes (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>)

The calculated ionic deltas for cations show a general decrease of the species Na<sup>+</sup> and Ca<sup>2+</sup>, and an enrichment of Mg<sup>2+</sup>, ( $\Delta\text{Mg}^{2+} > \Delta\text{Ca}^{2+} > \Delta\text{Na}^{+}$ ). The sodium low concentration may reject the possibility of a complete mixing between groundwater and seawater and it can be an indicator of cationic exchange.



**Figure 5.** Ionic deltas (cations) for the sampled cenotes.

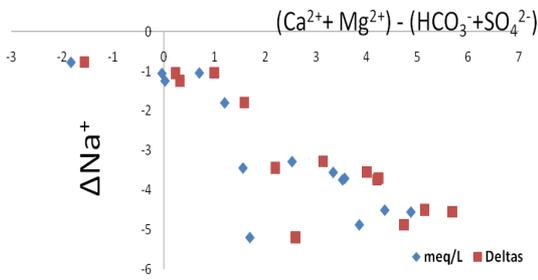
The water in coastal aquifers may have a Ca<sup>2+</sup>-Cl<sup>-</sup> water type, the ratio between Na<sup>+</sup>, and K<sup>+</sup> with Cl<sup>-</sup> is low. This modification is because of a cationic exchange between the host rock and the groundwater.

When seawater goes into a groundwater aquifer, the cation Na<sup>+</sup> is adsorbed replacing part of the Ca<sup>2+</sup> in the solid surface. The main result is the Na<sup>+</sup> adsorption in the solid phase and the liberation of calcium to the solution, changing the water composition from Mg<sup>2+</sup>-Cl<sup>-</sup> to Ca<sup>2+</sup>-Cl<sup>-</sup>.

Other way to identify a cationic exchange process is quantifying the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  excess ( the amount which source is not the carstification process) and relating it directly to the  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$ , concentration. If the excess exists, is due to an exchange

Bye the equation that takes place in groundwater is clear to observe that the species interfering are mainly the cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$ . The increase of some specie has as a parallel process the decrease of the other.

In the graph 6 it is shown the relation between bla with the difference bla in concentration and ionic deltas. The relation is negative between both parameters indicating an increase of calcium and magnesium and a decrease of sodium, confirming the cationic exchange.

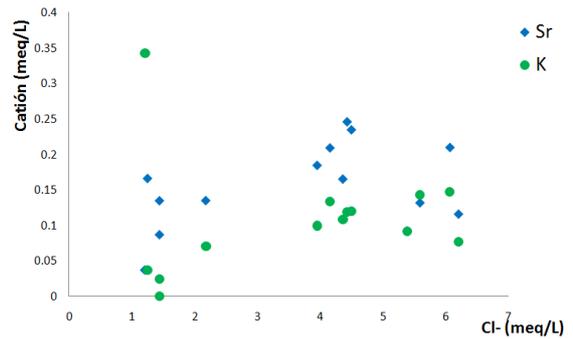


**Figure 6.** Relation between  $\text{Na}^+$  and the calculated excess of  $\text{Ca}^{2+} + \text{Mg}^{2+}$

### Strontium and potassium

In seawater the strontium and potassium have higher concentrations than groundwater. The concentration of them in groundwater is because of a saline intrusion or the aragonite dissolution.

For the groundwater samples of the Cenotes Ring, the values of  $\text{Sr}^{2+}$  are between 8-21 ppm, high concentrations for groundwater indicating a saline intrusion; its ratio with  $\text{Cl}^-$  is not completely lineal but there is a trend in both increases. The potassium has a similar behavior than the strontium.



**Figure 7.** Graph of  $\text{Sr}^{2+}$  and  $\text{K}^+$  for groundwater samples of the Cenotes Ring.

### Conclusions

The chemical composition analysis of cations and anions showed that groundwater from Cenotes Ring has the following trend:

- Cations: ( $\text{Mg}^{2+} \geq \text{Ca}^{2+} > \text{Na}^+ \geq \text{Sr}^{2+} > \text{K}^+$ )
- Anions: ( $\text{HCO}_3^- \geq \text{Cl}^- > \text{SO}_4^{2-}$ )

Hydrogeochemical tools like Piper and Stiff diagrams classify the groundwater samples in three main groups.

- Calcic-chloride (Ca-Cl)
- Magnesian -bicarbonate (Mg- $\text{HCO}_3$ )
- Magnesian - Chloride (Mg-Cl)

Because of the spatial distribution and the characterization by ionic relations and calculations of mixing line with seawater; the compositions of groundwater is due to:

- Saline intrusion
- Cationic exchange
- Host rock dissolution
- Sulphate reduction

The location of the caves (cenotes) in relation to the coast determines the possibility of seawater intrusion. In addition, the water-rock interaction will be determined by the mineralogical composition of the hosting rock.

There is not a clear trend in the zone, and a lack of homogeneity in the groundwater chemical composition; this makes the area not adecuate for the stablishment of an hydrogeological reserve.

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