

Topics of limnological research in Mexico



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Analysis of the Ionic Quality of the Water in the North Aquifer and Cozumel Island, Quintana Roo, Mexico

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Abstract

he Yucatan Peninsula comprises the states of Yucatan, Campeche, and Quintana Roo in the southeast of Mexico. Although it heavily relies on the aquifer as the primary source of water for socioeconomic and ecological needs, quality and quantity remain mostly unknown. Being a karstic region, the aquifer's recharge depends solely on precipitation with discharge occurring mostly through natural features like cenotes. The objective of this study was to characterize water quality from various sites from the northern part of the Yucatan Peninsula and to identify extraction region's potential on Cozumel Island. Ground and surface water quality from water bodies such as wells, cenotes, flooded caverns, and extraction wells within the central-northern Quintana Roo and Cozumel Island were analyzed to determine ion concentration (Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO³⁻, Cl⁻, SO₄²⁻ and F⁻), electrical conductivity, temperature, dissolved oxygen, pH, salinity, and chlorophyll-a. Results show heterogeneity in the environmental characteristics of all analyzed systems (n=231), with 55 % Ca-Mg bicarbonate type, 24 % mixed type, and 21 % Na-K & Cl-SO₄ type. A high concentration of Cl-SO₄ in the coastal areas are a sign of seawater mixing with freshwater and can be used as indicators of possible intrusions at inland wells. Sites with mixed water types should be monitored to ensure their viability for socioeconomic water use. Water quality monitoring and potential extraction volumes from various sites must complement each other for sustainable water resource management. This analysis enhanced understanding of the hydrological behavior and heterogeneity of the karst aquifer.

Keywords

Wells, sink holes, groundwater, karst, Yucatan Peninsula.

Introduction

Groundwater is one of the most important sources of drinking water, supplying approximately 20-50 % of all demand worldwide (Steube et al., 2008; Brinkmann & Parise, 2012; Hartmann et al., 2015). In Mexico, groundwater covers 39.2 % of the total volume granted for all consumption uses, approximately 34,839 hm³ per year as of 2018 (Conagua, 2019). The Yucatan Peninsula is located in the southeast of Mexico, and it is constituted by the states of Yucatan, Campeche, and Quintana Roo. The whole aquifer is the most viable source in the region to fulfill water needs of the population and for economic activities. According to the National Water Commission (Conagua), the region is divided into four main aquifers: Cerros y Valles, Xpujil, Yucatan Peninsula, and Cozumel (Conagua, 2020b). The four aquifers have an estimated annual water availability of 13,200 mm³/year and an extraction volume of 2,120 mm³/year; meanwhile only in the North of the state of Quintana Roo, the yearly water availability is estimated in 561.1 mm³ with extraction volumes of 486.8 mm³/year (Conagua, 2021).

Cozumel is the third largest island in Mexico located in the state of Quintana Roo, approximately 17.5 km off the coast of the city of Playa del Carmen (Zack & Lara, 2003). It has a total surface area of 473 km², with an average length of 30 km and an average width of 16 km (Conagua, 2020a), with an average elevation of 5 m and some hills up to 10 m in the south (Ward, 2004). On the island, population has increased from 1,500 inhabitants in 1936, to almost 90,000 inhabitants in 2015 with the urban area concentrated mainly in the western sector of the island (Hernández, 2001; Frausto-Martínez et al., 2016; INEGI, 2017). Tourism is the most important economic activity with a recorded arrival of 575,055 tourists and 3,391,241 visitors in 2015 (Segrado-Pavón et al., 2017).

Although the state of Quintana Roo is generally conceived as a region with high water reservoirs due to its large amounts of yearly rain and low hydric pressure (Conagua, 2019; 2020b), it is also very vulnerable. It has been reported that poor water quality reduces the possibilities of water use (as for drinking), resulting in health and environmental consequences, as well as a reduction in availability (Mishra et al., 2021). Chemical contaminants from human activities (estrogen, soap, fertilizers, pesticides, and petroleum products) in groundwater are one of the biggest threats to the available fresh water as recent studies suggest their presence in the Peninsula's aquifer (Medina-Moreno et al., 2014; Torres et al., 2014; Long et al., 2018); which along with a national 15.7 % of increase in national groundwater extraction from 2009 to 2018, compromise available water for future consumptive and non-consumptive use (Gondwe et al., 2011; Conagua, 2019).

As rainwater infiltrates into the aquifer and flows through the underground sediments, it accumulates elements (such as soluble ions) with which it comes into contact.

Piper Diagrams are known to be used to describe chemical water characteristics, which aid in the identification of 1) rainfall composition and infiltration, 2) sewage contamination, 3) dissolution of carbonate and minerals, and 4) mixing with saltwater (Back & Hanshaw, 1971). Ion analysis through piper diagram is important as it can provide a reference for water origins, status, flow, and recharge dynamics (Lagomasino et al., 2015). The aim of this study is to characterize water quality from the northern aquifer of the Yucatan Peninsula and to identify vulnerable water extraction regions in Cozumel through water concessions.

In this study, vulnerability was addressed based on the type of water (in relation to the ions present), its location, and in the case of Cozumel, the volumes of extraction granted within the Public Registry of Water Rights (REPDA).

Materials and Methods

The analyzed area is the region called "Acuífero Norte de Quintana Roo" or Northern Aquifer of Quintana Roo, it is included in the polygon bounded from Cancún, Cozumel, Tulum, Cobá cities; and towards the West of Cobá, and Nuevo Xcán cities, into the geographic coordinates 20°15'N-86°44'W; 21°15'N-87°40'W, Quintana Roo, Mexico (Fig. 1).

Determinations of ionic content in natural waters that were made intermittently between 2008 and 2019 by local administrations, or by us (in the project QROO 2005-2008-01-19177 "Geohydrological Study and Evaluation of Polluting Sources of the Northern Aquifer of Q. Roo, Mex"), were also considered. These determinations were electrical conductivity, dissolved oxygen, and salinity concentration, done *in situ* with a calibrated multiparametric probe (Hydrolab-DS5x), by following standardized testing methods described in NMX-AA-007-SCFI-2013 (Secretaría de Economía, 2013) or by the American Public Health Association (APHA et al., 1996).

The considered source of data included coastal and lagoon areas, urban and rural areas, and catchment areas of rainwater for drinking water supply, which are under local administrations (Fig. 1). The physical and chemical characterization of water in the months of March and July to September of 2008-2019 was carried out through the analysis of water samples for cations and anions, such as Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻, Cl⁻, SO₄²⁻ and F⁻. A total of 231 sampling points were considered, 188 in the continent and 43 in Cozumel. For some of the sites, additional measurements of temperature, dissolved oxygen, pH, salinity, and chlorophyll-a (Chl-a) were taken.

To allow the comparison of the chemical results to the Mexican standard of drinking water and other official regulations, and because they are characteristic ions of karstic aquifers; the concentrations of Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻, Cl⁻, SO₄²⁻ and F⁻ were considered.

The cation and anion concentrations were determined by certified laboratories where accuracy of the chemical analyses was controlled by the ion charge balance, proposed

by Fetter (2001). Ion concentrations were determined in the laboratory of the Technical University of Berlin, Department of Hydrogeology, or proceed from the records in the National Measurement Network on Water Quality (Red Nacional de Medición de Calidad del agua –RENAMECA-, and SINA). These certified laboratories use ion chromatograph, mass spectrometer, and flame atomic absorption spectrometer to calculate ionic concentration. Then, the reliability of these data was performed using the general criteria for the quality control of the analytical results (Secretaría de Economía, 2015) while Chl-a concentration was estimated using colorimetric methods (APHA et al., 1996).

The Cozumel water sample lacked HCO₃-, Na+ and Mg²⁺ ion content; an average of 314.4 (mg/L) alkalinity was estimated by considering reports from 183 sites within the Yucatan peninsula from 2012-2018 provided by *Sistema Nacional de Información del Agua* (*SINA*) from Conagua. According to an official water analyze norm, NMX-AA-036-SC-FI-2001 (Secretaría de Economía, 2001), alkalinity is to be estimated as CaCO₃ mg/L by national institutions in Mexico. Bicarbonate ion (HCO₃-) content was estimated according to Lind (1985). Cozumel's sodium and magnesium ions were estimated by calculating an average value of water samples carried out by *Comisión de Agua Potable y Alcantarillado* (*CAPA*) from 90 wells in the catchment basin for every month from 2005-2019.

A Piper diagram was elaborated with the ion content information with the aid of an Excel (Microsoft 365) template published by Zenodo (Stosch, 2022). According to how water sites were positioned within the Piper diagram due to its ionic content, water samples were classified into one of the following three types and a specific dot color was assigned: Ca-Mg Bicarbonate (blue), Mixed (yellow) and Na-K & Cl-SO₄ (purple). Water sample sites were then positioned on maps of the state of Quintana Roo and Cozumel Island, using Open Source Software QGIS 3.34.1 'Prizren'.

Finally, Conagua was consulted about information from users registered in the REP-DA in Cozumel 2023. For each user, their geoposition, volume of water granted for annual extraction, and assigned use for extracted water were obtained. With this information, a map was created to locate each user within the island, depending on use.

With the granted extraction volumes and the location, a map was developed using Inverse Distance Weighting (IDW) to identify the areas with the greatest individual user potential for pressure on the aquifer due to the extraction volumes.

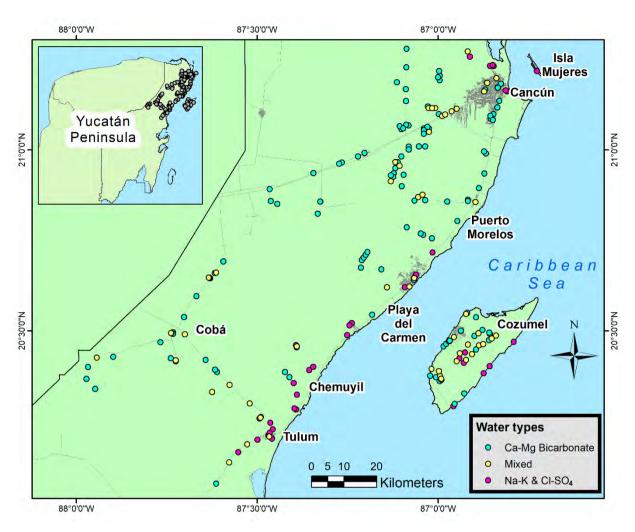


Figure 1. Water Types and Location of Sampling Sites.

Results

A total of 231 water samples from within the state of Quintana Roo were analyzed and grouped according to their ion concentration within the Piper diagram. Water samples were sorted within one of three water type groups: 1) Ca-Mg bicarbonate being the one with most samples (n=127), 2) Mixed type (n=56) and Na-K & CI-SO₄ with the least (n=48).

As shown in Table 1, temperatures, dissolved oxygen concentrations, and pH showed very slight variations on their values among the different water types. As for Chl-a values, the lowest concentration was found in bicarbonated water type (\bar{x} =0.7±0.9 mg/L) while it was almost 6 times higher in the other two water types described in this study.

Fresh, bicarbonated water: The North and West of the surveyed aquifer in the Yucatan Peninsula, with low Electrical Conductivity (EC) for the groundwater representing the best water quality. The EC ranges (Table 1) from 20 to 4,060 μ S/cm (\bar{x} =890±540). Most of the sites correspond to deep wells (\sim 92 %) that are in the areas of rainwater catchment basins (blue dots in Fig.

1) which subsequently go towards the urban areas of Cancún and Playa del Carmen. A smaller percentage is made up of epicontinental freshwater bodies like lakes and lagoons (~8 %).

According to the Piper diagram (Fig. 2), the water type that dominates in this region is the Ca-Mg Bicarbonate type. Such catchment basins are located within 5 to 20 km of the urban areas. In Cozumel, this type of water is found in the north-central region of the catchment area and in epicontinental lagoons to the east of the Island.

Mixed type waters: With EC values from 1,090 to 2,490 μ S/cm (\bar{x} =1,447±582); mixed type, showed to be the second most classified systems as by their cation and anion content (yellow dots in Fig. 2) dominate in the Cozumel Island catchment area and some deep wells in the catchment area of Cancún and Playa del Carmen. Mixed waters are also part of superficial lakes and lagoons in this region.

Na-K & Cl-SO₄ type: This water type has EC values ranging from 1,020 to 53,321 μ S/cm (\bar{x} = 5,667±8,384) and represent the most saline (\bar{x} =3.2±6.8 ups) when compared to bicarbonate (\bar{x} =0.6±0.2 ups) and mixed (\bar{x} =0.8 ± 0.2 ups) types. They are represented by purple dots, the least abundant of all analyzed water types in this study and are located near the coastline.

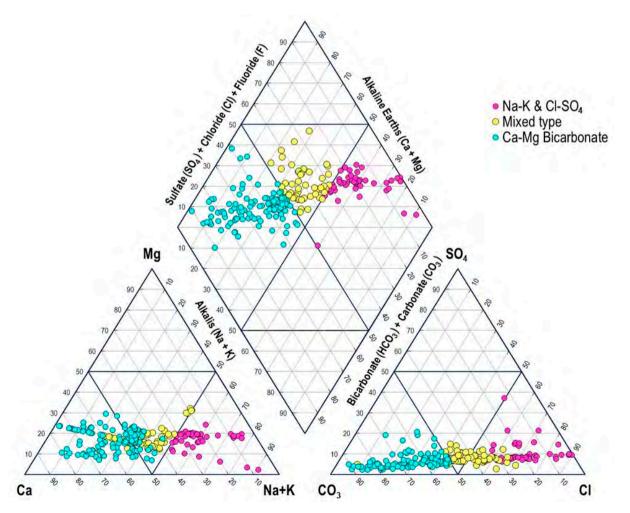


Figure 2. Piper Diagram with Samples Sorted by Water Type.

Table 1. Water Type Quality Parameters. (EC=Electrical Conductivity; Chl-a=Chlorophyll-a; SD=Standard Deviation)

1M242 4220	Ö	a-Mg E	Ca-Mg Bicarbonate	nate			_	Mixed				Na-K	Na-K & CI-SO ₄	04	
water type	Average	SD	Min	Мах	n	Average	SD	Min	Мах	u	Average	SD	Min	Мах	u
Ca²⁺ (mg/L)	111	28	25	166	127	130	32	40	191	26	171	84	40	585	48
Mg^{2+} (mg/L)	21	6	2	37	127	32	8	20	99	99	126	230	23	1,416	48
Na⁺ (mg/L)	62	35	4	153	124	133	45	61	258	54	946	1,704	122	10,090	47
K⁺ (mg/L)	5	4	_	19	109	9	3	3	14	38	32	46	4	199	41
HCO ₃ - (mg/L)	361	90	117	629	127	348	88	200	266	26	377	112	187	780	48
CI- (mg/L)	114	73	7	510	125	265	103	13	622	22	1,691	2,973	195	17,603	48
SO_4^{2-} (mg/L)	31	18	9	100	124	99	24	12	113	99	300	441	43	2,542	48
F- (mg/L)	1	1	0	2	45	1	1	0	2	17	1	1	0	8	7
EC (µS/cm)	897	540	20	4,060	127	1,448	582	20	2,490	42	5,668	8,384	1,020	53,321	48
Temperature (°C)	26	7	24	32	109	26	2	23	32	38	26	2	25	31	4
Dissolved Oxygen (mg/L)	3	2	0	8	109	3	2	0	7	38	3	2	0	9	41
Hd	7	0.4	7	6	127	7.4	0.5	8.9	8.8	26	7.5	0.4	7	6	48
Salinity (ups)	9.0	0.2	0.2	0.8	89	8.0	0.2	0.5	1.3	23	3.2	6.8	6.0	35.7	25
Chl-a (mg/L)	0.7	6.0	0.1	4.1	89	4	15.8	0.1	2.92	23	4.3	9.1	0.16	36.1	25

Among the sampling sites located on Cozumel Island, 18 were identified which belong to the Ca-Mg bicarbonate type, 18 to the mixed type, and 7 to the Na-K & Cl-SO $_4$ type (Fig. 3). It is important to highlight that in the center of the island, in the rain catchment area, there were 3 Na-K and Cl-SO $_4$ type samples.

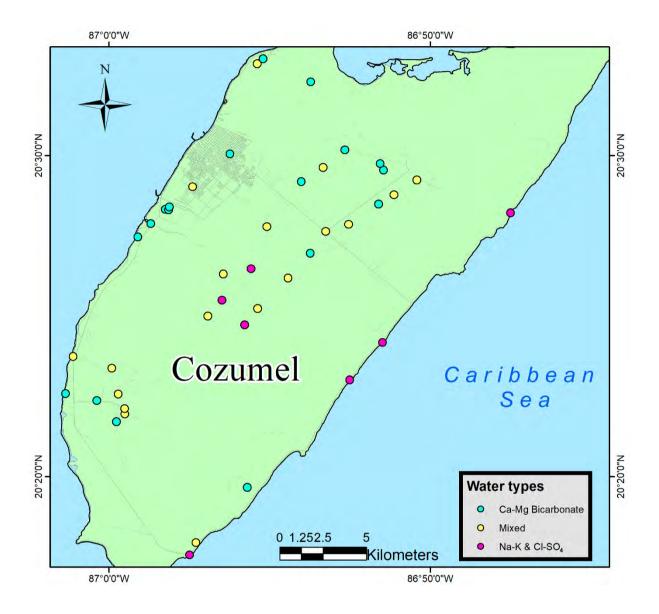


Figure 3. A Close Up of Water Types from Samples Taken in Cozumel.

Regarding the information of users registered at REPDA, Fig. 4 represents the 454 records that were identified within the Cozumel polygon, since a same user can be eligible for different extraction points with the same grant. A total of 56 sites were positioned outside the geographical limits of Cozumel, thus not considered in this study. The highest density of users was found in the center of the island and along the transversal highway.

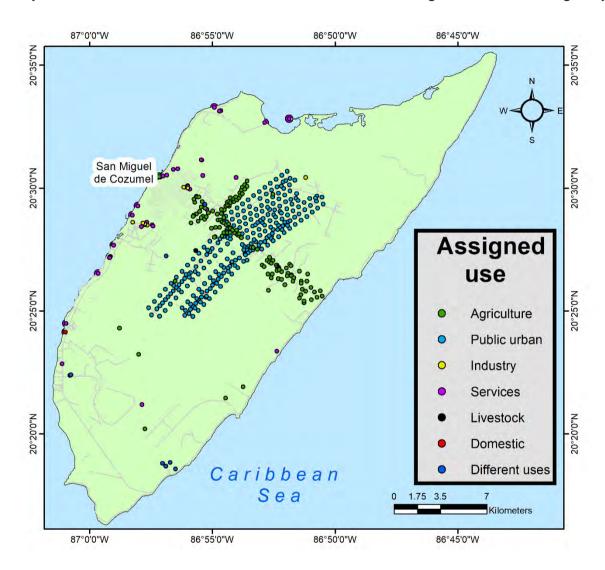


Figure 4. Location of Users Registered with REPDA and with the Concession for Water Extraction in Cozumel.

Figure 5 shows the potential water extraction granted for each user yearly. The greatest pressure can be identified in the North-West and South-West areas of the island.

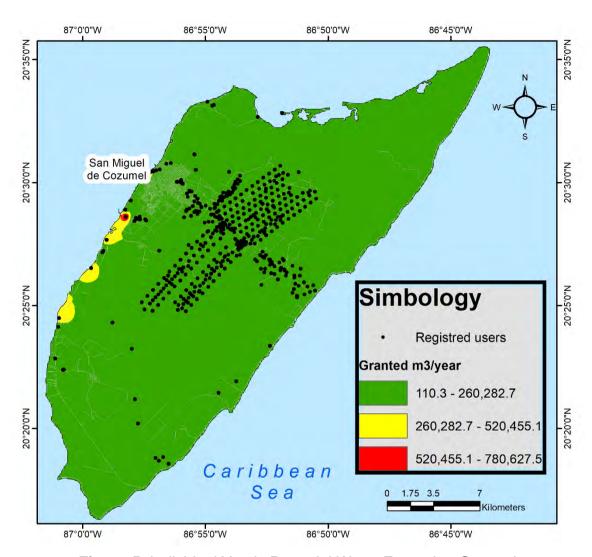


Figure 5. Individual Yearly Potential Water Extraction Granted to Users Subscribed to REPDA in Cozumel.

Discussion

Although the Yucatan Peninsula hosts 4 main aquifers, according to Conagua's classification, the northern continental region of the state of Quintana Roo is part of aquifer 3105 "Yucatan Peninsula," while the aquifer on Cozumel Island is 2305 "Cozumel Island". Three main water types were identified on aquifers 3105 and 2305: Calcium-bicarbonate, Mixed, and Sulfated-Sodium-chlorinated. Conagua reports that the majority of the state of Quintana Roo contains calcium bicarbonate waters while on the coastal line they are sodium chloride type. Only south-central of the Yucatan Peninsula (around Xpujil) has calcium sulfate water been recorded (Conagua, 2021). The Conagua reports provide a good overall picture; but with the detailed analysis done here, it was possible to identify at least three different types

of water (only in the North of Quintana Roo), their location, and with an accurate ion charge balance, ranged between -4.99 to +5.0 % in the surveyed samples.

The westerly region of the investigation area showed low EC in the region where Ca-Mg bicarbonated waters were dominant. These types of waters are presumed to be originated by the dissolution of the carbonates that constitute calcareous rocks due to the dominant presence of evaporites and gypsum (Conagua, 2021). Further water quality analysis should be performed to determine if water within this type and location meets the criteria established within NOM 127 (Secretaría de Salud, 1996) which would make it suitable for potabilization processes. If the water does not meet the minimum standards established for potabilization, other uses could be suggested, such as agricultural or industrial, depending on the results of water quality analysis.

As previously mentioned, in the Yucatan Peninsula, sulfated natural waters are in the geohydrological zone of South Campeche and Quintana Roo and the chlorinated water type is described to be located usually along the coastal zone. In these coastal lines, the influence of seawater produces a mixing zone among them and the groundwater (Conagua, 2021). Fig. 1 shows that in the surveyed area, the Cl-SO₄ type waters are found along the coastal area: the wide range of EC of this water type (1,020-53,321 µS/ cm) confirms that the presence of SO_4^{2-} can be due to the dissolution of sulfate-rich minerals anhydrite (CaSO₄) and gypsum (CaSO₄·2H₂O) as reported by Lagomasino et al. (2015), and to a greater extent, due to the influence of seawater causing a mixing among them and the groundwater. The presence of seawater is notable in the underground area of the east coast of the studied area. This influence of seawater towards the interior apparently presents a wedge shape: from the south of Tulum to the north of Playa del Carmen (in fact, these cities are above the area of seawater entry), as well as on the east margin of Cozumel Island. There is evidence of saltwater intrusion in the state of Quintana Roo and in Cozumel Island due to pumping rates and with a saline interface 22 m inland (Cardoso, 1993). According to Deng et al. (2017) considering the Quintana Roo aguifer with a 1 m rise in sea level, it is projected that inland saltwater intrusion could extend as far as 150 km under head-controlled conditions and 1 km under flux-controlled conditions. This entry of seawater into the underground region of the continental area occurs in recent Quaternary deposits (Sánchez & Pinto et al., 2015), both on the eastern margins of the Peninsula and the island; but it also occurs in the oldest deposits on the western edge of the island. Evidence about penetration of the seawater towards the continent in the coastal regions of Yucatan Peninsula, has been described by Steinich et al. (1996), and Steinich and Marin (1997), who have reported seawater penetration up to 110 km from the coast.

Black and Hanshaw (1971) have concluded that the primary factors influencing the chemical composition of water in the Yucatan Peninsula are the dissolution of carbon-

ate minerals and the blending of freshwater with underlying saline water, with seawater sites located at the right end of the triangle in the Piper diagram (Back & Hanshaw, 1971). Mixed-type waters should be evaluated according to parameters described in the NOM 127 (Secretaría de Salud, 1996) to confirm whether they are viable for use by institutions that provide domestic drinking water services. Although the chemical nature of mixed-type waters may not be suitable for potable use, perhaps (depending on their composition) they could be processed through techniques such as reverse osmosis which would allow their use as potable water. Additionally, they could also be used for other purposes such as agriculture or industry, as the quality requirements are not as stringent for these uses, although always considering that they do not contain compounds that could be harmful to human health. Unfortunately, water from Na-K & CI-SO₄ type tend to be more of the saline-like type with average salinities of 3.2 ups, conductivities of 5,667 µS/cm, and an elevated Chl-a content when compared to Ca-Mg Bicarbonate type, so their use is limited since they are not recommended for purification or agricultural use.

Cozumel shares characteristics with the Caribbean coast of the Yucatan Peninsula from the northern cape to Tulum such as upper Pleistocene eolianite, elevation, sedimentology, stratigraphy of subaerial and shallow-marine limestones (Ward, 2004). Miocene Pliocene are the sedimentary rocks present both, in the state of Quintana Roo from Chetumal to Cancun and on Cozumel Island (Ramos, 1975). For this reason, the island shows eolianites on the East which show classic terra rosa paleosol and vegemorph development, while from North to West there are eolanites without well-developed vegemorphs (Kelley et al., 2011). This might explain the prevalence of Ca-Mg bicarbonate type waters within the studied area.

Although a clear pattern of Na-K & CI-SO₄ water types near the coastline of Quintana Roo was observed, the distribution is not so evident for the samples taken on the island, even though they occur around the east coast and in the center (Fig. 3). The center of the island is known to be reserved as an area for the recharge of the aquifer and the extraction of water to supply the needs of the inhabitants (Hernández-Flores et al., 2021). The presence of a water type associated with the influence of seawater mixing in this area could represent a thinning of the freshwater layer due to extraction practices, as it is the area where water is extracted to supply most of the island population's needs. This hypothesis is supported by a recent study that reports an increase in the number of extraction dejected wells (2015-2018) in that area due to the increase in the concentration of chlorides present in water samples (Hernández-Flores et al., 2021). For this reason, further studies to characterize water quality dynamics in this area are suggested.

Geographic information on the ionic content and quality of water provides an idea of possible sources that allow the extraction and use of water for different purposes. By over-

lapping the information of Figs. 3 and 5, it is possible to identify sites that with increase in exploitation, could harm the Cozumel aquifer. Highly vulnerable areas could be identified by the presence of Na-K & CI-SO₄ water types with several water extraction sites nearby; in the case of Cozumel, it could be indicative of over-extraction and saline intrusion events in the aquifer, especially in the north-central part of the island. However, monitoring and updating the tools presented in this work are highly recommended, as the aquifer may be vulnerable to high extraction volumes and show indicators of degradation, such as the presence of brackish water. When Figs. 4 and 5 are combined, it is possible to see that the largest extraction of water volumes is found near the coastal area in the west of the island and those that belong to the "services use". According to the Dupuit–Ghyben–Herzberg model, the thickness of freshwater lenses reduces in correlation to the nearness of shoreline, then the over-extraction of freshwater in this area (bicarbonate, or mixed) could increase the risk of marine intrusion such as has been observed in Tulum by Gondwe et al. (2011).

The use of maps providing information about ions in water, maximum volumes granted for extraction, and their location allows triangulation of information to obtain a more comprehensive overview of the water resource and its utilization. It's important to note that although agricultural use accounts for 130 extraction points in Cozumel, the volumes are not as high. However, it is the service sector that has shown high volumes of water concessioned for extraction, locating itself near the coastline. In Figure 5, the maximum annual extraction volumes are observed, with those of greater volume located near the coastline. This somehow prevents the deterioration of the thickest layer of freshwater, which is found in the center of the island (Lesser et al., 1978). This is because near the coastline, the thickness of freshwater thins out, although it also increases vulnerability to saltwater intrusion due to proximity to seawater. Beyond being a relief, it is an incentive for the development of research that describes the effect of "small" extractions but with a high density of users in the island recharge zone, so research addressing the cumulative extraction volumes in a geographical area is encouraged. All this, along with the idea of proposing strategies that encourage actions which allow us to sustainably manage water resources. It is suggested that this method of triangulating information between water types and REPDA data be used on mainland, as it provides a more integrative vision for resource management.

The method presented in this study allows to consider water types, water extraction potential, and their geographical location. Therefore, we believe it can be a useful tool for decision-making related to the proper management of the resource, such as granting new extraction concessions or identifying new areas of possible water supply with sufficient quality for potabilization.

Conclusions

This study provides valuable insights into the water quality and extraction dynamics of the Yucatan Peninsula, particularly focusing on the northern Quintana Roo aquifer and on Cozumel Island. The analysis revealed three main water types: Ca-Mg bicarbonate, mixed, and Na-K & Cl-SO₄, emphasizing the heterogeneity of the aquifer's environmental characteristics.

The prevalence of Ca-Mg bicarbonate type water, along with physicochemical analysis of the water, especially in the rain catchment basins, suggests that the water extraction provided complies with NOM-127-SSA1-2021 (Diario Oficial de la Federación, 2021). However, the presence of mixed and Na-K & Cl-SO₄ types, particularly in coastal areas, raises concerns about seawater intrusion and the need for continuous monitoring. The research highlights the importance of considering both water quality and extraction sites for sustainable water resource management. The study underscores the importance of incorporating this geospatial information into future management strategies, encouraging a balance between water use demands and the preservation of aquifer integrity.

Ultimately, this research contributes to a better understanding of the hydrological behavior of the karst aquifer in the region, thanks to the characterization of physicochemical variables and extraction potentials. The combination of the information exposed in the figures of this study offers a foundation for informed decision-making and emphasizes the need for continuous research and proactive measures to sustainably manage water resources in the Yucatan Peninsula and Cozumel.

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Authors' Contributions

GHF conceived and designed the experiments, analysed the data, prepared figures and tables, and authored drafts of the paper. MAGA conceived and designed the experiments, prepared figures and/or tables, and authored drafts of the paper. ACM analysed the data and authored or reviewed drafts of the paper.

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