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Connecting Water Quality and Ecosystem Services for Valuation and Assessment of a Groundwater Reserve Area in South-East Mexico

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Abstract: Even though the role of ecosystem services is known, the identification and assessment of water-related services is usually absent or often less represented as an ecosystem service. Progress in water quality indicator definition and compliance with regulations has been made; however, the relationship between water quality degradation and benefits to individuals and ecosystems remains little recognized. Here, we present an assessment of water quality and identification of ecosystem services in south-east Mexico. This study was performed within the geohydrological reserve zone of the Ring of Sinkholes, Yucatán Peninsula. Thirteen ecosystem services provided by the aquifer were identified. Water quality was evaluated in sinkholes based on national and international norms, considering different sinkhole uses. Results show a dynamic system, without saltwater intrusion and good to excellent water quality. The research demonstrates the relationship between ecosystem services and water quality, showing pressure in services related to uses for aquatic life protection and to a lesser extent those related to consumption. Current productive activities showed no pressure at this time. Principal Component Analysis (PCA) and Analysis of Variance (ANOVA) exhibited a significant difference in parameters and campaigns, but not between sinkholes. A long-lasting monitoring program for water quality is necessary to accurately evaluate the status of ecosystem services provided by the aquifer. Moreover, it is necessary to assess aquifers as ecosystems with economic, ecologic and socio-cultural importance. Effective water governance requires a balance of interests between all parties, within a legal and institutional framework.

Keywords: groundwater; ecosystem services; protected areas; water quality

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1. Introduction

Humans depend on ecosystems and the services provided are vital for their well-being and existence on Earth. Societies are closely linked to water where they live [1], but an ecosystem's role is often not recognized until it is degraded or destroyed. Freshwater supports societies and ecosystems in two forms, the water in rivers and aquifers (blue water) and the soil moisture that supports all non-irrigated vegetation (green water) [2].

The Millennium Ecosystem Assessment [3] has four categories of ecosystem services (ESs): (1) provisioning, (2) cultural, (3) regulating and (4) habitat or supporting. Groundwater-dependent ecosystems provide services and functions, like nutrient recycling, water storage and purification, bioindicators, maintaining the environment and the resources for a population, and conferring aesthetic and cultural benefits to humans [1,4]. Ref. [5] highlight the importance of understanding how groundwater-dependent ecosystems are affected by changes in groundwater quantity and quality, as severe changes have been observed in many regions.

Humans' right to water and sanitation was acknowledged by the General Assembly of the United Nations in 2010 [6]. The 17 Sustainable Development Goals (SDGs) adopted by the United Nations in 2015 incorporate the SDG6, seeking to guarantee the availability and sustainable management of water and sanitation for all [7]. At present, there is pressure on groundwater (quantity and quality), due to increases in demand for different uses, causing changes in aquifers worldwide [8]. Nowadays, the water scarcity problem is one of the most important environmental challenges of Mexico. The National Water Commission [9] highlights that groundwater overexploitation occurs in some regions of Mexico and water quality degradation places water availability at risk. The effects of climate change are more visible every day; water balance changes are expected due to precipitation reduction and temperature increase [10,11]. In the Yucatán Peninsula, the impact of rural land use on water quality has received little attention as most of the water quality studies have been conducted around urban areas [12–14]. Bakalowicz [15] revealed that land use (e.g., agriculture, urban) and the nature of rocks has an influence on the recharging of karst aquifers; this was also shown by [16] in Yucatán State. To protect the recharge zones and to prevent aquifer contamination, [17] recommended the creation of a "hydrogeological reserve zone". The amount of water is relevant for Yucatán State because it is entirely dependent on groundwater.

Refs. [16,18,19] were the first to propose a hydrogeological reserve area at the west of Mérida City, but the proposal was not a decree. Ref. [20] proposed a reserve area with the results of the project funded by a CONACYT grant. In order to protect and ensure the drinking water supply for Yucatán State, the reserve area proposed was extended and decreed by the Government of the State of Yucatán in 2013, published in the Official Gazette as a geohydrological reserve of the Ring of Sinkholes [21].

The aim of the study was to assess the water quality and to identify the ecosystem services in the geohydrological reserve area of the Ring of Sinkholes decreed by the Yucatán State government.

2. Materials and Methods

2.1. Site Description

The hydrogeological reserve area for Yucatán State was delimited inside 13 municipalities with a surface of 219,208 ha. and a volume of approximately 108,200,000 m^3 (Figure 1). The decree of the reserve area subdivided the recharge zone into northern and southern zones [21]. The southern zone (Tekit, Tecoh, Homún, Cuzamá, Huhí, Sanahcat and Xocchel) had a mean annual rainfall of between 900 and 1000 mm. The northern zone (Acanceh, Seyé, Hocabá, Hoctún, Timucuy and Tahmek) had a mean annual rainfall of between 800 and 900 mm [22,23]. The thirteen municipalities had a total of 97,704 inhabitants in 2010 [24] and an increase of between 4 and 11% in the 2020 census was observed, with 104,011 inhabitants [25]. The municipalities have a young population, between 25 and 59 years old, representing 48% of the population, with the potential to carry out economic activity. Regarding schooling, around 15% of the population $\leq$15 years old is illiterate, 46% speak the Mayan language and Spanish and 54% speak only Spanish, reflecting a loss of identity or origin [23]. All the municipalities of the reserve area have a medium or high degree of marginalization [26]. The municipalities of Huhí, Timucuy, Hoctún, Tecoh, Xocchel, Cuzamá and Hocabá are part of the list of the 1000 most marginalized municipalities in Mexico. The mean population density is 52 inhabitants per square kilometer. A total of

70% of the population is in poverty and at least 10% are in extreme poverty. Only 28% are economically active, where 73% are men and 27% are women [26].

Sinkholes, caves or caverns in the Yucatán Peninsula have been recognized for present and pre-Hispanic cultures as ceremonial (sacred spaces) and in some cases shelter places. These features have prevailed through time in the Mayan culture. From the upper Pre-Classic to the late Post-Classic eras, Mayan cities were planned with a close relationship to natural cavities like sinkholes, allowing for the existence of human settlements until today [27,28]. In some caverns of Yucatán State, vestiges of ancient rituals have been discovered [29]. Eleven sinkholes were selected in four municipalities of the reserve (Sanahcat, Tekit, Tecoh and Cuzamá) (Figure 1). The selection was based on their location (groundwater recharge area), the productive activities carried out, the accessibility and the population density of the municipalities.

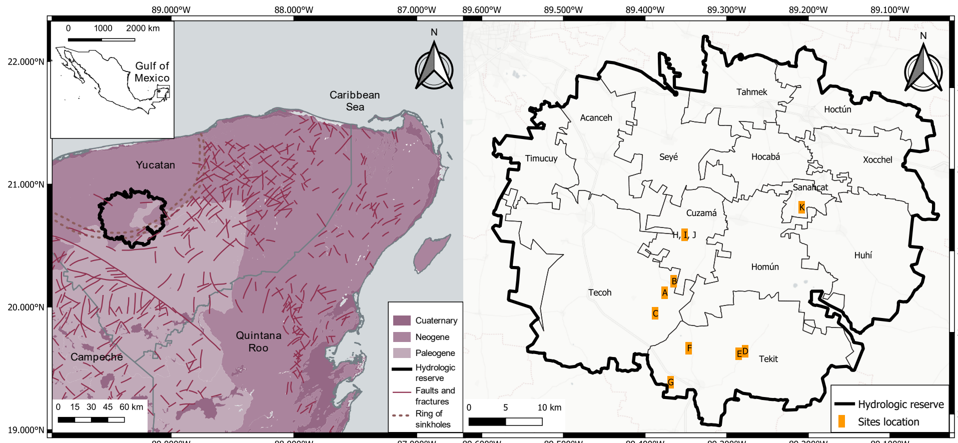

Figure 1. The geohydrological reserve area, the study sites and meteorological station locations.

2.2. Hydrogeological Framework

Yucatán Peninsula sprawls over an emerging portion of a limestone platform of limestones, dolomites and evaporites [30]. In the northwest portion of the Yucatán Peninsula there is a fracture zone called "The Ring of Sinkholes", which is the sole surface expression of the buried crater structure. The Chicxulub crater formed after the impact of an asteroid that hit the Yucatán Peninsula at the end of the Cretaceous period [31]. The ring forms a semicircle with a 160 km diameter [32] and plays a key role in the regional hydrology of the peninsula. Research studies have been conducted on the buried Chicxulub impact crater [33–35]. The exploration has revealed the features of the K/T Chicxulub impact crater in the northwestern part of the peninsula, with a probable age of 65.96 m.y. [31,36]. Several hypotheses have been proposed to explain the Ring of Sinkholes formation of the surface feature by the Chicxulub impact crater [37]. Geophysics and geological studies showed that the Ring of Sinkholes was developed in a high permeability zone [36], with preferential flow paths occurring at different scales, with fracture zones and dissolution conduits [38].

Sinkholes are locally known as cenotes, from the Maya language d'zonot. In this study, the selection of sinkholes was made according to certain characteristics (water uses), the type of sinkhole, even if was not in the selection criteria, is important in the analysis of the results; four sinkholes are covered (water is not exposed to the surface), five are semi-open (some permeable rock still covering the sinkhole) and two sinkholes are open (exposed water, cover-collapse) [39]. The studied sites are located in the recharge zone of the geohydrological reserve [21], with high surface permeability, with the second highest density of sinkholes per square kilometer in the State of Yucatán, with high hydraulic heads and high hydrological variability and important short-term changes in preferential flows.

Sinkholes, fractures and caverns are the most evident manifestations of the karstic system, due to dissolution of the limestone rock [40,41].

2.3. Survey Design

A survey was designed and divided into two sections: (1) general data, (2) knowledge of the aquifer and the study area (perceptions and preferences). The survey included open questions, multiple choice questions and some closed questions. The survey was not probabilistic [42], since the objective was to have the participation of a specific segment of water users in the study area. The sample size was calculated using the formula proposed by [43,44]:

$$n = \frac{z^2 p(1-p)}{e^2}.$$

In order to maintain the error levels, the number of surveys needed is 270, defined as follows:

$z =$ confidence level of 90%, equivalent to $z = 1.645$.

$p =$ population proportion expected to be found; as it is unknown, a 50% value was assigned.

$e =$ maximum error margin of 5%.

The standard error of the sample was calculated according to:

$$\sqrt{\frac{p(p-1)}{n-1}}$$

The maximum error margin can be calculated as follows $\frac{0.98}{\sqrt{n-1}}$ or with $\frac{1}{\sqrt{n}}$. The population of Mérida was selected, because it is the inhabitants of the state capital who will have to pay to maintain the environmental services provided by the reserve area. The target population should comply with the following:

- They should live in Yucatán, considering at least 80% of the sample (250 of the approximately 300 participants), represented by the City of Mérida habitants.
- They should meet the minimum age of 18 so they can work legally and have the opportunity to receive a salary (261 of the approximately 300 participants).
- Applicants must have visited a cenote, assuring a real experience (253 of the approximately 300 participants).

2.4. Ecosystem Service Identification

Observational records were conducted in order to identify the ecosystem services in the area. The services provided by the aquifer were classified according to the Millennium Ecosystem Assessment [3]: provisioning, cultural, regulating and habitat or supporting services. Interviews were performed during sampling campaigns in May (2015 and 2016), with local people, authorities (formal and informal), NGOs and members of cooperatives in order to complete the identification of ecosystem services. For better identification of the ecosystem service, an image of the geohydrological reserve area was presented with the question: What services do you consider that sinkholes, caves or caverns of this reserve provide to habitants for their wellbeing? The four municipalities where sinkholes were studied have 35% of the total population at the reserve. Tourism and recreational use are the main activities in seven sinkholes and four sinkholes are used for irrigation, livestock and recreational use.

2.5. Water Sample Collection and In Situ Measurements

Thirteen parameters associated with water use (human consumption, agricultural irrigation, recreational use, livestock and aquatic life protection) were selected for water quality condition evaluation vis-à-vis the threshold limits established by two national regulations [45,46] and one international by the World Health Organization [47], considering that uses can be simultaneous and can vary according to users and needs. Water sample collection and in situ measurements were carried out in two campaigns in May (2015 and 2016). Water samples were collected in Nalgene® (Sigma Aldrich, Toluca, Mexico) high-density polyethylene bottles, using a Van Dorn-type horizontal bottle. Samples collected for nutrients were filtered with a 0.45 μm Millipore syringe disc. To determine the alkalinity, 250 mL of water was collected without filtration, avoiding air bubble formation. The samples were stored at −4 °C in coolers and transported to the laboratory. For total and fecal coliform determination, 100 mL of water was collected in a sterile bottle with sodium thiosulfate as inhibitor. Bacteriological analyses were carried out the same day as the collection. The in situ measurements were made with a multiparameter sonde YSI® series 6600 (Xylem, Inc., Milford, OH, USA) with a precision: ±0.1 mg/L dissolved oxygen, ±0.001 mS/cm electrical conductivity (EC), ±0.15 °C temperature, ±1% salinity and ±0.2 unit for pH.

2.6. Laboratory Analysis

Analyses to determine nitrite, nitrates, phosphates, chloride and sulfate were performed at a laboratory with an Ion Chromatograph Metrohm 882 Compact IC Plus (Metrohm AG, Herisau, Switzerland) with a conductivity detector. Ammonia concentration was determined via spectrophotometry UV-Vis with a LaMotte Smart 2, using the 3649-SC Nesslerization method. Alkalinity was quantified via acid-base titration method 8203 HACH, (Hach, Tlalnepantla, Mexico) with an automatic titrator model 16900. Total coliform and fecal coliforms (*Escherichia coli*) amounted to MPN/100 mL; these were detected via the chromogenic substrate method Colisure (IDEXX, Westbrook, ME, USA), incubation at 37 °C, 24 h [48]. Laboratory analyses were conducted in the Water Science Unit of Centro de Investigación Científica de Yucatán.

2.7. Color Code for Water Quality Evaluation

A color code was developed considering the compliance of the results with water quality thresholds established in national and international regulations depending on main water uses in the study area: (1) the ecological criteria established for recreational use with primary contact, agricultural irrigation, livestock use and the protection of aquatic life in freshwater [46], (2) the Official Mexican Standard [45] for human consumption and (3) World Health Organization standards of water for human consumption [47]. In some cases, there is no value and this appears as a blank box. All the thirteen variables selected have the same weight and the color code defines three ranges of compliance of each parameter with limits established in the norms and criteria for different uses. For example, when the site is in red it means that half of the threshold limits were not accomplished for the parameter. So, the color code is established as follows: red (≤50% compliance, poor water quality), yellow (>50% and ≤75%, a treatment is needed for drinking water supply) and green (>75%, water can be used after a disinfection process). When compliance is lower than 50%, there is a risk for human and ecosystem health; therefore, this is the strictest limit.

2.8. Color Code for Water Quality and Ecosystem Services Provided

This color code was developed in order to associate the quality of the water with the ecosystem service provided, a visual comparison can be seen about the level of observance. Maintaining a water quality from good to very good ensures the stability of the ecosystem service provided by the aquifer in the reserve area. The color code includes the percentage of compliance with the permissible limits according to the ecosystem service provided and they were associated with three ranges: red (≤50%), yellow (>50% and ≤75%) and green (>75%) . The selected parameters have the same weight and when the site is in red it means that half of the parameters studied for that site do not meet the limits established in the legislation and therefore do not provide the ecosystem service, meaning poor water quality.

2.9. Economic Valuation

The Method of Contingent Valuation (MCV) was selected to assign a value to the ecosystem services provided by the aquifer in the reserve area. The method considers use and non-use values based on interviews. The method is based on asking the users how much they are willing to pay for ecosystem services [49,50]. The survey designed included a question of willingness to pay for water conservation in the study area.

2.10. Statistical Tools and Methods

An exploratory analysis was carried out in order to identify dependencies between parameters, which can be explained by the existence of chemical compounds and processes. The statistical methods were the following: Pearson's correlation analysis is applied in order to see the possible dependencies by means of correlation coefficient, which measures the linear correlation between variables; Principal Component Analysis (PCA) is applied to identify the uncorrelated variables which explained the largest percent variance, to reduce the dimensionality of the multivariate data with minimal loss of information and to understand how concentrations vary between sampling sites; using PCA results, k-means clustering was carried out, which involves unsupervised classification to find the possible groups for the variables; finally, Blocking Factorial Design was applied in order to analyze the significant impact of the variables, the sinkholes and the campaigns, by means of Analysis of Variance (ANOVA) and applying the Least Significant Difference (LSD) test for multiple comparisons.

The statistical analysis was carried out using the programming language R (version 3.6.1) and the functions used were the following: `cor()` function for Pearson's correlation analysis; `prcomp()` function for PCA; `kmeans()` function for *k*-means clustering; `aov()` function for ANOVA and `LSD.test()` function for the LSD test. In addition, to visualize the two relevant PCA outputs the ggplot2 package is used, which shows the individual projections of correlation matrix eigenvectors on the first two principal components and classification of variables according to the sampling campaign through a biplot.

3. Results and Discussion

3.1. Survey Analysis

The target population was the 892,363 inhabitants of Mérida city, in Yucatán State [24]. Approximately 300 surveys were applied. The calculated sample size was 270 surveys with an error margin of 6% and a confidence level of 90%. The sample size guaranteed the representativeness of the socioeconomic variables (age, gender, education). A total of 95% of interviewed persons resided in Mérida City; in total, 59% were women and 41% men. The income of 37% of the participants surveyed was between 8000 and 16,000 Mexican pesos; the salary of 21% was lower than 8000 Mexican pesos and 11% declared no remuneration. A total of 50% of the participants had finished high school and 30% had completed higher education studies. Experts on the theme were also included in the survey, including officials from the municipalities of the study area, academics, representatives of civil society and some members of COTASMEY (local groundwater committee). The exercise allowed to document the opinion and rank of the ecosystem services.

3.2. Ecosystem Service Identification

Figure 2 shows answers of almost 300 persons interviewed. It is important to highlight that most participants knew the sinkholes or had visited them before and they could choose more than one option. Participants consider water recharge and rainwater collection as the most important and biodiversity conservation in second place. Even if livestock is a main activity in the region, the ecosystem service appears in last place.

Thirteen ecosystem services were identified in the reserve area after observational campaigns, meetings and interviews (Table 1). Regarding cultural ecosystem services, recreational activities take place in seven out of the eleven studied sites: sinkholes A, B and C (Tecoh), sinkholes H, I and J (Cuzamá) and sinkhole K (Sanahcat). Tourism, in particular the ecotourism in sinkholes, has a direct benefit to the cooperatives' members; some associates are relatives (father, son, nephews) and they have a close relationship with transportation services (trucks) from one sinkhole to another. The Cuzamá Truck Cooperative has 47 members and the Chunkanan Truck Cooperative has 33 members [51]. However, even if the inhabitants of the area identify the visit to the sinkholes as a business opportunity, there is a lack of management vision and capacity building as suppliers of services. In Yucatán State, the SEDUMA (Environment Secretary of Yucatán State government) published a regulatory framework of sinkholes named "Reglamento de la Ley de Protección al Medio Ambiente en Materia de Cenotes, Cuevas y Grutas, la Alianza de Colaboración Intermunicipal para la Gestión Integral de la ZRGHAC" [52].

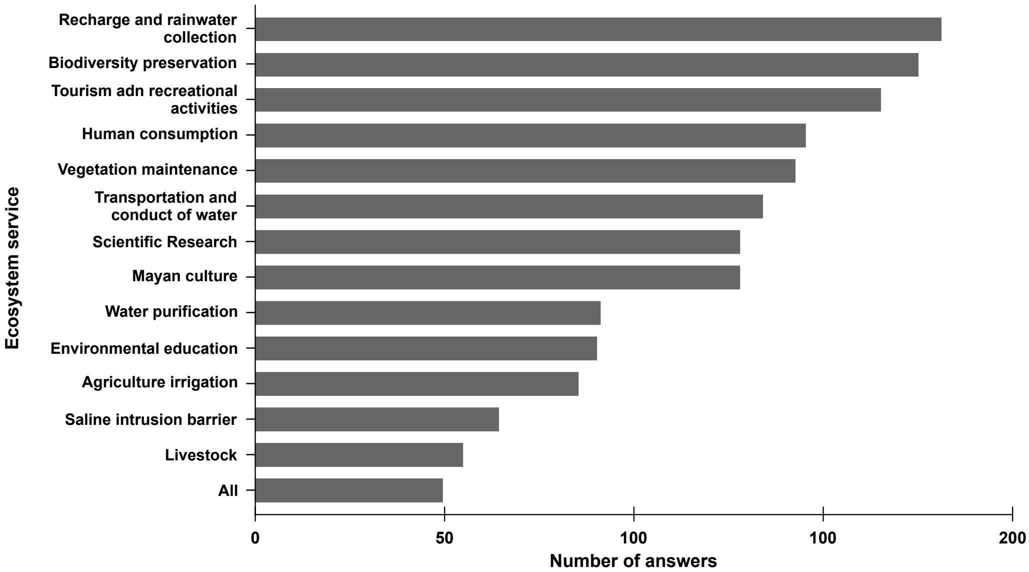

Figure 2. Ecosystem services identified by the participants interviewed.

Regarding provisioning ecosystem service, the availability of water provided by the aquifer was identified, either to the inhabitants of the reserve area living near the sinkholes or the inhabitants of urban areas, who receive drinking water from a distribution system. The largest consumption is related to agricultural and multiple-use activities with 257 hm^3/year, followed by the urban public sector with 197 hm^3/year and livestock with 6.8 hm^3/year [21]. Agriculture and livestock are the main activities of the primary sector; farming activities (corn, henequen, orange, lemon, papaya, etc.) are carried out, some as self-consumption crops. Pasture cultivation occupies the first place (19,617 ha, equivalent to 74% of hectares occupied for seeding), for cattle feeding, modifying the use of land [23]. Regarding livestock, spaces for raising pigs, cows and birds were identified in the study area, mainly for self-consumption or local sale. For the secondary sector, the main activities are textiles, pottery and plastics industry [23,51].

Concerning the ecosystem-regulating services, the sinkholes and channels allow the availability of freshwater [40,41]. According to the National Water Commission, the volume extracted for various uses in the Ring of Sinkholes is 495 hm^3 [21]. The regulating service can be affected by the volume of water extraction demanded for supply (industry, irrigation system, drinking, etc.) or by over-extraction that attains the halocline and causes mixing of fresh and saltwater. In the reserve area, there is a preferential groundwater flow which prevents the infiltration of seawater into the continental area [11]. The presence of halocline in near-shore sinkholes is common and can be detected through differences in conductivity, temperature or with water column profiles. In this study, the halocline was not observed. Aquifers filter and transform the residues or organic loads that are discharged into the groundwater and control the presence of pathogens [11]. The infiltration of rainwater avoids possible flooding and contributes to the nutrient and water cycles; the groundwater extraction volume is equivalent to 1.4% of annual precipitation [53]. Yucatán Peninsula is almost flat, with slight elevation, the surface runoff is another source of recharge from rainfall [38].

Habitat or supporting services were also identified in the karst system of the Yucatán Peninsula aquifer. Biodiversity maintains the stability of the main processes that occur in the Ring of Sinkholes; there are more than 41 endangered wild species and more than 15 endemic species, freshwater fish, amphibians, reptiles, birds, mammals and bats, among others [54,55]. The surrounding vegetation at the sinkholes provides shelter and food for various organisms [56]. Maintenance of vegetal cover is a key support service, since it maintains the hydro period in the area [57].

Table 1. The ecosystem services identified in the study area (cultural, regulating, provisioning, habitat or supporting).

Ecosystem Service	Description	
Cultural	Recreation (tourism)	Income for tourism, tourist numbers, tours numbers, labels or certifications
	Environmental education	Workshops, introduction of sustainable practices in communities
	Research	Number or project research, monitoring network, water quality indicator, public policies
	Mayan Cosmo-vision (caves and sinkholes)	Mayan traditions preservation, tangible and intangible benefits
Provisioning	Water drinking supply	Compliance with regulations
	Water for irrigation	Volume of water, irrigation surface, Income for agriculture
	Water for livestock	Income for livestock activities Available surface
Regulating	Water transportation	Mapping of sinkholes, caves and fractures Porosity and permeability studies
	Water purification	Biogeochemical cycles
	Saline intrusion barrier	Halocline lens measurements, depth
	Aquifer Recharge	Water volume available Water quality Water table
Habitat or supporting	Vegetation cover maintenance	Management plans in forestry and vegetation areas Presence/absence vegetation cover related with water volume
	Biodiversity preservation	Species monitoring, endangered and protected species

3.3. Socioeconomic Variables and Ecosystem Services

To identify relationships between some socioeconomic variables and ecosystem services, some independent variables were analyzed with chi-square statistics. Subgroups were defined for the analysis: age, education, gender and residence place.

In the age variable, two groups were considered:

Group 1. Millennial and generation Z, because they are critical people, familiar with technology and multitasking. They are characterized for being entrepreneurs; they value participation and collaboration; they prefer sharing over owning, and promote new values such as sustainability, transparency and social commitment. This group covers the ages of 18–33 years of the surveyed persons.

Group 2. The generation X and baby-boomers who grew up in a period of prosperity, with a good educational level, with a consumerist attitude that contributed to strengthening the world economy, were little worried about the environmental impacts generated by the industry. This group consists of the ages of 34 to 72 years.

For education level, the following classification was established:

Group 1. Preparatory completed except for 3 who only finished high school.

Group 2. University completed.

Group 3. Master's or doctorate completed.

In the variable on residence were the following groups:

Group 1. The people who reside within the reserve area

Group 2. The people who live in Mérida.

Group 3. The people who reside in any other municipality that does not form part of the reserve area or who live in the City of Mérida.

In the gender variable, the following two options were used: male or female.

In Table 2, chi-square statistics is computed to see independence between two random variables. Since independence implies non-correlation, this statistic allows one to test the following hypothesis:

- There is a relationship between the identification of water recharge and rainwater catchment ESs and age.
- There is a relationship between the identification of all ESs and age. There is a relationship between the water recharge and rainwater catchment identification as the most important ESs and age.
- Education and rainwater catchment and water recharge ES identification are related.
- Education and the identification of water recharge as the most important ESs are related.
- The gender and identification of all ESs are related.

Table 2 shows in gray the significant relationship values. The identification of the ESs of recharge and rainwater capture has a significant relationship with the age and schooling of the participants; so it is recommended that these two socioeconomic variables be considered in the analysis of economic value and in future studies on ecosystem services. There was also a significant relationship between the identification of the 13 services provided by the aquifer with gender and age. The identification of the 13 ESs provided by the aquifer is important since the perception of the value of the aquifer is integral even when men and women do not benefit directly from each service.

Table 2. Relationship between ecosystem services of the reserve area and the social variables by means of chi-square statistic ($\alpha = 0.05$) (– not significant; in gray, the most significant).

Description Questions (Yes/No)	Age	Educational Level	Gender	Residence Location
Sinkholes visit	–	0.75	0.62	–
Water recharge identification as ES	0.007	$p < 0.05$	0.002	–
Identification of all ES	0.04		0.002	–
Water recharge identification as the most important ES	$p < 0.05$	$p < 0.05$	0.08	0.75

3.4. Water Quality of Sinkholes

Results show that sulfate, chloride, nitrite, phosphates, fecal coliforms and pH meet the threshold limits of legislation for all water uses. Ammonia, nitrate, dissolved oxygen and alkalinity have a regular compliance and total coliforms and total dissolved solids do not meet the norms (Table 3). In general, the water quality is good to very good and meets the permissible limits established in the Mexican regulations and those of the World Health Organization for water consumption (Table 3) and guarantee allocation for different uses. Similar results were reported by [20,58]. The differences can be associated with seasonality, sinkhole characteristics such as depth and type (open, closed or semi-open), and rainfall. Ref. [58] showed that a sinkhole's water chemistry in the geohydrological reserve area is controlled by carbonate rock dissolution (Ca, Mg and HCO_3) and can explain the non-compliance of the TDS in some sites.

Table 3. Analyzed parameters and threshold limits in legislation for comparison [45–47].

Parameter	WHO (2011) Water Drinking Standards	N.O.M-127-SSA1(1994) Modif 2000	CE-CCA-001/89 (DOF 1989)				
			Water Drinking Supply	Recreative w/Primary Contac	Agriculture Irrigation	Livestock	Aquatic Life Protection (Freshwater)
Sulfate (mg/L)		400	500		130		0.005
Chloride (mg/L)	250	250	250		147.5		250
Nitrate (mg/L)	50	10	5			90	
Nitrite (mg/L)	3	0.05	0.05			10	
Ammonia (mg/L)		0.5					0.06
Phosphates (mg/L)			0.1				0.025
Alkalinity (mg/L)	500	500	400				
Fecal coliforms (MPN/100 mL)	Absence	Absence	100	200	1000		200
Total coliforms	Absence	Absence					
Temperature (°C)			Natural condition +2.5		Natural condition +1.6		
Total dissolved solids (mg/L)	1000	1000	1000				
pH	6.5–8.6	6.5–8.5	5–9		4.5–9		
Dissolved oxygen (mg/L)			4				5

Table 4 shows water quality compliance with the code established. Overall, the compliance level of water quality at the sinkholes is higher than 75% (green), the water meets the regulations for different uses. The chlorides, phosphates, sulfates, nitrites, fecal coliforms (Escherichia coli), temperature and pH results reflect a very good water quality (green) in all sinkholes. Regarding ammonia and nitrates, no variations between campaigns and between study sites were found (yellow), both parameters reveal good water quality, although water was not recommended for human consumption and a purification treatment is needed. Dissolved oxygen presented a more variable behavior, influenced by sinkhole characteristics (open, semi-open or closed). One sinkhole (H) in Cuzamá municipality remains with a yellow color code in both sampling campaigns. Two sinkholes located in Tecoh (B, A) and one sinkhole in Sanahcat (K) municipality present the best water quality conditions (green) and meet regulations used for comparison. There is no pH guideline value, but pH is considered an important and functional parameter of water, because some processes depend on pH [47]. Total coliform presence can be due to activities in the area like livestock, pigs, poultry breeding and untreated wastewater spills; a monitoring strategy is needed. Total coliform densities in water of the studied sites results in poor water quality (red). Using Escherichia coli as an indicator of fecal contamination is considered a well-established practice and is commonly used for drinking water quality evaluation. For recreational activities, *E. coli* is the only reference indicator included in Mexican water quality criteria [46].

Table 4. Water analysis results of different parameters (value in each case), and legislation compliance using the color code: Red ≤ 50%; Yellow > 50 and ≤75%; Green > 75% (1: sampling campaign 2015; 2: sampling campaign 2016; ND: no data).

Sinkole	Campaign	Parameter												
		Sulfate (mg/L)	Chloride (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)	Ammonia (mg/L)	Phosphates (mg/L)	Alkalinity (mg/L)	Fecal Coliforms (MPN/100 mL)	Total Coliforms (MPN/100 mL)	Temperature (°C)	Total Dissolved Solids (mg/L)	pH	D.O (mg/L)
A	1	18.4	100.9	19.9	<LDM	0.43	<LDM	480	<1.0	1011.2	26.6	1325	7	3.4
	2	12.6	42.2	17.1	<LDM	0.21	<LDM	481.9	<1.0	691	26.4	660	7.3	4.4
B	1	16.1	107.6	13.9	<LDM	0.09	<LDM	386	<1.0	1011.2	25.9	1553	7.2	4.2
	2	26.9	131.3	20.3	<LDM	0.11	<LDM	446	<1.0	4	26	890	7.2	5.8
C	1	17.7	109.9	36.7	<LDM	0.11	<LDM	201	<1.0	1011.2	26.3	1533	7.3	4.6
	2	10.8	134.7	11.4	<LDM	0.3	<LDM	289	ND	ND	25.6	1090	7.5	6.9
D	1	15.7	58.8	14.3	<LDM	0.24	<LDM	240	<1.0	1011.2	26.9	1242	7.1	5.1
	2	28.3	76	14.4	<LDM	0.26	<LDM	487.9	<1.0	173.3	26.7	790	7.2	4.1
E	1	15.6	65.1	15.7	<LDM	0.18	<LDM	440	<1.0	1011.2	26.8	1300	6.9	3.9
	2	27.7	68.2	17.3	<LDM	0.11	<LDM	505.8	<1.0	1011.2	26.7	780	7.5	5.1
F	1	15.7	58.8	14.3	<LDM	0.24	<LDM	240	<1.0	1011.2	26.9	1242	7.1	5.1
	2	28.3	76	14.4	<LDM	0.26	<LDM	487.9	<1.0	173.3	26.7	790	7.2	4.1
G	1	46.6	101.5	15.9	<LDM	0.13	<LDM	367	<1.0	1011.2	27	1420	6.9	4.4
	2	16.6	110.3	7.2	<LDM	0.09	<LDM	184	ND	ND	26.8	1080	7.3	6.1
H	1	6	21	14.1	<LDM	0.3	<LDM	515	<1.0	249.5	24.8	1110	7.9	1.3
	2	14.6	46.2	14.6	<LDM	0.19	<LDM	460.9	<1.0	263.1	25	640	7.4	1.6
I	1	6.3	27.9	12.9	<LDM	0.32	<LDM	305	<1.0	<1.0	26.9	1120	7.8	2.1
	2	19.9	81.4	21.9	<LDM	0.11	<LDM	475.9	<1.0	424.5	26.8	690	7.5	6.7
J	1	19.4	109.8	23.4	<LDM	0.12	<LDM	383	<1.0	1011.2	27.1	1430	7.4	3.9
	2	19.2	135.8	17.8	<LDM	0.21	<LDM	309	<1.0	173.1	26.8	1160	7.1	5.4
K	1	12.1	59.1	20.3	<LDM	0.18	<LDM	441	<1.0	<1.0	25.4	1220	7.7	4.7
	2	24.2	75.3	21.2	<LDM	0.15	<LDM	457.9	<1.0	691	25.6	740	6.8	5

3.5. Water Quality and Ecosystem Service Relationship

Ecosystem services, water use for human consumption and saline intrusion barrier, associated with the available freshwater volume, exhibited a compliance with legislation [45,47] between 60% and 88% (in yellow and green) (Table 5). The saline intrusion barrier service remains without change, because no saline intrusion was present in the studied sites. Tourism was identified as an ecosystem service associated with recreational use of sinkholes, showing full compliance with water quality criteria [46] (100%, green). Water for agricultural irrigation and water for livestock use, both directly associated with ecosystem services, obtained a 100% (green) compliance with Mexican criteria [46]. Current productive activities are for self-consumption mainly, not pressure at this time.

For the aquatic life protection Mexican water quality criteria [46], the main ecosystem services identified (biodiversity preservation, freshwater transportation, vegetation cover maintenance, water mass purification, research and environmental education) showed a lower compliance (≤50%, red and 67%, yellow) . The sinkholes A, H and K presented a compliance level ≤50% for all sampling campaigns. A trend in the color code was observed; in red appeared the ecosystem services related with aquatic life protection use and in yellow-green the ecosystem services related with consumption; in other words, the pressure on the water is reflected in both ecosystem services (Table 5). Analyzing inter-annual variability, with the color code, there was higher compliance in the 2016 campaign compared with 2015. The differences can be influenced by climatological changes, but systematic monitoring needs to be established in order to confirm these differences. Likewise, according to the results obtained, in the reserve area it is important to have compliance higher than 60% for water consumption ecosystem services and to reduce the pressure in the supporting service in order to change from red to yellow in the color code (Table 5). The ecosystem services produce multiple and intertwined values [59]; some services provide benefits to users, controlling their offer and demand. In general, the color code must remain in green-yellow for provisioning, regulating and supporting services and to establish actions to reverse the trend in the services currently in red.

Table 5. Compliance level of ecosystem services related with water quality of the sinkholes, using the following color code: Compliance: Red ≤50%; Yellow > 50 and ≤75%; Green > 75% (1: sampling campaign 2015; 2: sampling campaign 2016; ND: no data).

Ecosystem Service with Direct Relationship	Provisioning/Regulating Human Consumption						Cultural (Recreational: Sinkholes Visit)		Provisioning (Agriculture)		Provisioning (Livestock)		Habitat or Supporting (Biodiversity Conservation)	
	WHO (2011) [47]		NOM-127-SSA1(1994) Modif. 2000 [45]		Mexican Water Quality Criteria CE-CCA-001/89 [46]									
					Drinking Water Supply		Recreational with Primary Contact		Agriculture Irrigation		Livestock		Aquatic life Protection (Freshwater)	
Sinkhole	1	2	1	2	1	2	1	2	1	2	1	2	1	2
A	75%	87%	70%	80%	64%	82%	100%	100%	100%	100%	100%	100%	50%	50%
B	75%	87%	70%	80%	82%	82%	100%	100%	100%	100%	100%	100%	50%	67%
C	65%	83%	70%	67%	82%	80%	100%	ND	100%	ND	100%	100%	50%	67%
D	75%	75%	70%	80%	82%	82%	100%	100%	100%	100%	100%	100%	67%	50%
E	75%	75%	70%	70%	64%	82%	100%	100%	100%	100%	100%	100%	50%	67%
F	75%	87%	70%	80%	82%	82%	100%	100%	100%	100%	100%	100%	67%	50%
G	75%	83%	70%	80%	82%	80%	100%	ND	100%	ND	100%	100%	50%	67%
H	63%	87%	60%	70%	64%	73%	100%	100%	100%	100%	100%	100%	50%	50%
I	87%	87%	80%	80%	73%	82%	100%	100%	100%	100%	100%	100%	50%	67%
J	75%	75%	70%	70%	73%	82%	100%	100%	100%	100%	100%	100%	50%	67%
K	87%	87%	80%	80%	73%	82%	100%	100%	100%	100%	100%	100%	50%	50%

3.6. Statistical Exploration

An exploratory analysis of data was carried out by means of a Pearson correlation matrix (Table 6), with the three highest correlations being between chloride and DO (0.6325), sulfate and pH (−0.5649), and alkalinity and TDS (−0.5243). These three correlations are considered as moderate. Runoff over limestone can explain the negative correlation between alkalinity and total dissolved solids. Low positive correlation was found between sulfates and temperature (0.3792) and between sulfates and chloride (0.3718). The correlations can be explained by the processes occurring in the sinkholes and confirms the dependency of these variables. The oxygen concentrations may decrease as a result of the lower solubility of oxygen when temperature increases, but also because of the physical characteristics of the sites.

Table 6. Pearson's correlation matrix ($n = 22$, $p = 0.05$). TDS: total dissolved solids; T: temperature °C; DO: dissolved oxygen.

	Sulfates	Chlorides	Nitrates	Ammonia	Alkalinity	Temperature	TDS	pH	DO
Sulfates	1	0.3718	0.1199	−0.3490	0.1812	0.3792	−0.0612	−0.5649	0.259
Chlorides		1	0.2130	−0.3028	−0.3290	0.2111	0.3186	−0.3827	0.6325
Nitrates			1	−0.2722	0.0158	0.0042	0.2134	−0.0769	0.0659
Ammonia				1	0.1284	−0.0749	−0.0203	0.1262	−0.3934
Alkalinity					1	−0.3193	−0.5243	0.0924	−0.3344
Temperature						1	0.2083	−0.3724	−0.3155
TDS1							1	−0.1303	−0.0586
pH								1	−0.2814
DO									1

A Principal Component Analysis (PCA) and a classification method were implemented for variables and sinkholes, considering the eigenvalue decomposition of correlation matrices. It is important to highlight that the database complies with the assumption of multivariate normality, which is necessary to be able to apply the PCA method. A multivariate normality test was carried out, obtaining satisfactory results via two different methods (skewness: 164.3947, p-value: 0.4987; and Kurtosis: -0.7648, p-value: 0.4444). Although the accumulated variability between the first two principal components reaches only 50.5% (which is relatively low), Figures 3 and 4 were made in order to visualize their behavior. The direction given by PCA of each variable and the corresponding classification by the k-means clustering algorithm is shown in Figure 3. In order to identify the optimal k-parameter, a cross-validation method was implemented obtaining two different groups. It can be observed that the classification is strongly influenced by the projection of the variables on the first dimension. Cluster 1 includes three parameters, alkalinity, ammonia and pH. Cluster 2 includes six parameters (temperature, dissolved oxygen, nitrate, sulfate, TDS and chloride).

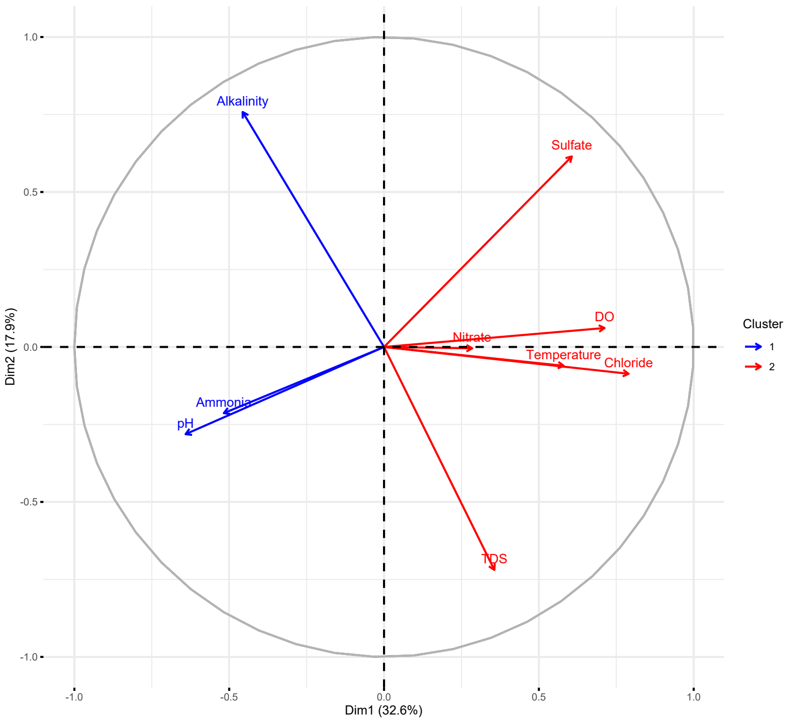

Figure 3. Plot of the eigenvector projections on the first two principal components and classifications by k-means.

Figure 4 shows the classification by fieldwork campaign (green and purple) and the corresponding projections on the first principal component. Campaign 1 (May 2015) is influenced by almost all the variables and campaign 2 (May 2016) is strongly influenced by alkalinity and TDS. Moreover, in campaign 1, sinkholes 15 and 17 show up, influenced by pH and ammonia projections, both sinkholes located in the same municipality (Cuzamá). Sinkholes 10 (E) and 22 (K) stand out in campaign 2, by alkalinity and sulfate projection, located in different municipalities (Tekit and Sanahcat). Campaign 1 lies entirely on the negative side of principle component 2, with the exception of sample 13 (Figure 4). In terms of direction, this would probably be attributed to the variables ammonia, pH and TDS.

The structure of Blocking Factorial Design takes into account the measurements as a dependent variable of the sinkholes and the fieldwork campaigns. Analysis of Variance (ANOVA) was performed, obtaining no significant difference between sinkholes and between campaigns (Table 7).

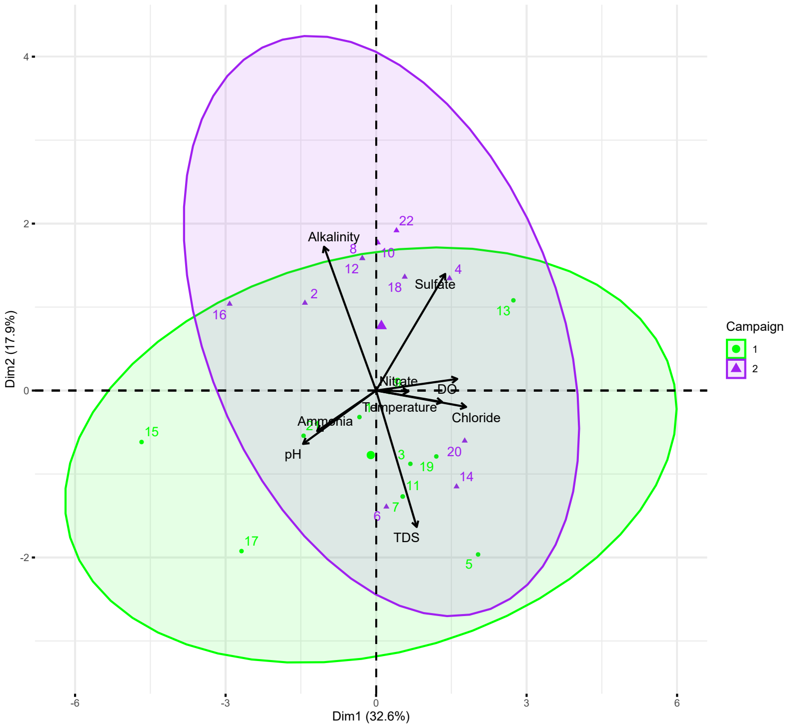

Figure 4. Biplot of the eigenvectors projections on the first two principal components and clustering by campaign.

Table 7. Analysis of Variance (ANOVA) summary for sinkholes and campaigns.

Analysis of Variance Test						
		Df	**Sum Sq**	**Mean Sq**	**F Value**	**P (>F)**
Sinkhole		10	47,035	4703	0.035	1.00
Campaign		1	98,390	98,390	0.741	0.391
Residuals		186	24,709,918	132,849		
Least Significant Difference Test						
		Mean	**Groups**			
Campaign						
	Campaign 1	203.24	a			
	Campaign 2	158.65	b			

Since the parameters and campaigns were significantly different, the Least Significant Difference (LSD) test was applied for multiple comparisons, with a confidence level of 99%. Two different groups of parameters are formed, symbolized by the letters a and b (Table 7). Results also show that campaigns are significantly different, then influenced by climatic conditions (Table 7).

Precipitation data between 2010 and 2017 are shown in Figure 5, at three different meteorological stations near the geohydrological reserve area, Acanceh (north), Cuzamá (center) and Sotuta (south), from meteorological stations of the CONAGUA. A gradient is observed with eight years mean annual average precipitation data, 1062.0 mm (Acanceh), 1027.9 mm (Cuzamá) and 971.3 mm (Sotuta). In 2014, one year before sampling campaigns of the study, high precipitations were presented in the region. A widespread precipitation condition has been present since 2012, with high water recharge and groundwater dilution. A dry period began in 2015, finishing in 2017, from which the differences between the two seasons may be due to lower recharge and concentration of minerals in the groundwater. Ref. [58] suggested that the recharge area was not only regulated by both the dissolution and precipitation of minerals. It seems that precipitation conditions caused lower ecosystem service quality in 2015 (yellow), compared to 2016 conditions (green) for water consumption and for aquatic life protection as presented in Table 5.

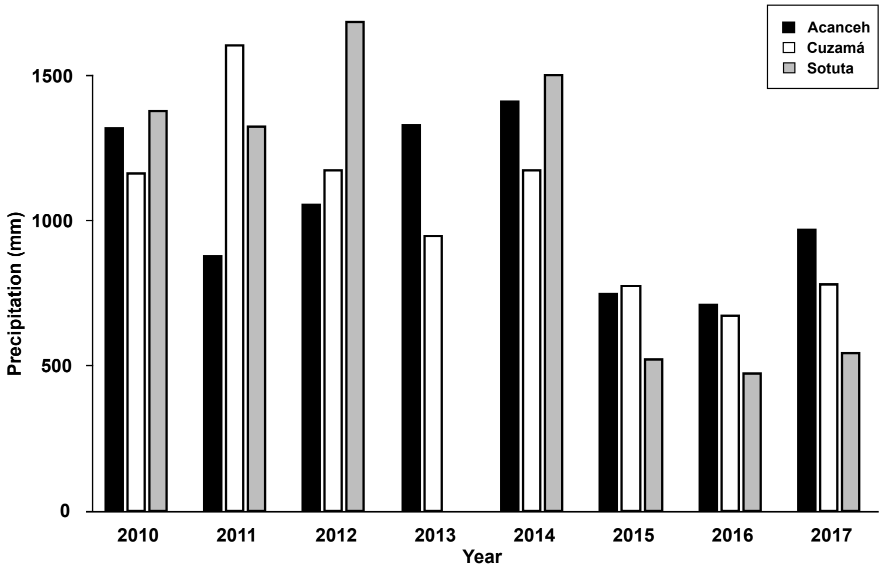

Figure 5. Total annual precipitation at each meteorological station for the years 2010 to 2017.

If authorities plan to adapt ecotourism to sinkholes as a low impact activity, water quality is essential [60] and they must pay attention to parameters like total and fecal coliforms. For human consumption, concerning the presence of total coliforms, nitrate and ammonia in the water of some sinkholes, purification treatment is necessary in order to meet drinking water standards legislation. For agriculture and livestock, the water quality condition varies, even though the amount of water required is greater in relation to other uses and depends on available supply and relative demand [61]. It is necessary to promote good environmental practices with tour operators that ensure the maintenance of water quality and to propose an integral value of the aquifer that considers the economic, ecological and socio-cultural aspects.

Ecosystem service demands have received less attention compared with offer estimations (related to degradation or loss of service). The environmental service of recharge and rainwater collection (in the livelihood classification) are the most representative and important of the reserve area and most recognized by population. The provision areas for human consumption and environmental service habitat or supporting will be the areas with more stress in which it is necessary to work, in order to advocate public policies and social actions for a complete purification, promoting the wastewater treatment for each use, in order to avoid sewage discharges to the ecosystem.

In Mexico, water recharge is established by CONAGUA (National Water Commission) for each one of the XIII hydrological-administrative regions (RHA). RHA XII, Yucatán Peninsula, has the highest average recharge per year (25,316 hm^3/year). Even when the indicators of water recharge and precipitation of the RHA Yucatán Peninsula are higher, they do not have the same value as poor water quality in the area. Ref. [61] indicates that in the case of provision services the demand generally exceeds the offer; in the area of study, this is not the case. The water allocation of Yucatán State was 4498.49 hm^3 [22], while in the reserve area municipalities, the extraction volume oscillates between 0.5 and 6.4 thousand cubic meters per day [62]. Ref. [20] declared that the water volume of the reserve area does not exceed current demand. On a global scale, the supply of ecosystem support or support services is greater than demand. However, under two climate change scenarios (low and high emissions), a water balance model estimation was conducted by [11], with a groundwater recharge reduction in the Yucatán Peninsula of 23% and 20%, respectively, which represent results that threaten the ecosystem services provided in the reserve area.

3.7. Economic Valuation: Willingness to Pay

Table 8 shows that women and men have similar behavior regarding willingness to pay for sinkhole conservation (77% women and 76% men). From 262 surveys, 200 persons have the disposition to pay and 117 out of 200 agree to pay $\leq$ 100 MX pesos per month. Nearly 80% of persons having a master's degree or doctorate agreed to pay more than 90 MX pesos (Table 8). An important disposition to pay from persons with lower education was observed and it could be related with the lack of infrastructure or water allocation and a close relationship with water or lack of resources (quantity and quality).

Table 8. Willingness to pay by gender and by degree of education.

		# of Surveys	Disposition to Pay	No Disposition to Pay	No Answer	Persons * (≤100 MX Pesos)
Gender	Women	154	118	34	2	65
	Man	108	82	24	2	52
			Surveys	**Disposition to Pay**		**Quantity**
			Persons	**Persons**	**%**	**$ MX pesos**
Education	Secondary and/or High School		125	96	77	86
	University degree		75	55	72	87
	Master's or Ph.D. degree		54	43	80	99
	None		7	6	86	87

Note: * Number of persons with disposition to pay less than 100 Mexican pesos.

The willingness to pay on average was 90 pesos per month per household. Compared to survey results included in Sanitation and Integral Management of Cenotes project, the cost of a trip to visit the sinkholes was 61 MX pesos per month; using the travel cost method and the contingent valuation method and an annual willingness to pay of 10,977 MX pesos, 149 MX pesos was obtained [51]. The results of this study was 29 MX pesos higher.

Two scenarios were proposed to calculate the profits by the willingness to pay for groundwater conservation of the reserve area, taking into account the 75% of households with water supply by a distribution system (180,884) [62]. A less optimistic scenario, achieving the payment of 10% of households, would be annually collecting 19,535,472 MX pesos. In a positive scenario, considering the participation of 70% of households, an income of 136,748,304 MX pesos per year can be attained. The willingness to pay groundwater users is a new topic in the area. Ref. [63] identified other key variables like sociocultural phenomena; further studies will be necessary to include more variables and other scenarios.

4. Conclusions

Thirteen ecosystem services were identified in the geohydrological area, highlighting their importance for conservation of the reserve area. The water quality in the study period was good to very good when related with selected parameters in legislation for comparison. A relationship between water quality and ecosystem services was established; a pressure was found in the ecosystem services related to use for aquatic life protection and to a lesser extent ecosystem services related to consumption. Current productive activities (agriculture and livestock) for self-consumption in the area showed no pressure. Analyzing the campaigns, higher compliance was observed for the 2016 campaign compared to 2015. We can infer that the differences are influenced by inter-annual variability, but systematic monitoring needs to be established in order to confirm these differences. The PCA analysis shows that campaign 1 is influenced by almost all variables and campaign 2 is strongly influenced by two variables only. Analysis of Variance (ANOVA) showed a significant difference in parameters and campaigns with a 99% confidence level, while no significant difference between sinkholes was found. The willingness to pay was 90 pesos per month per household. Considering a participation of 70% of the households that receive potable water service in Mérida, 136,748,304 MX pesos per year could be collected for conservation and preservation of the aquifer.

Ecosystem service analysis and their relationship with water quality can assist in understanding their importance and also increase their importance and at the same time, can help to accomplish a more comprehensive interpretation of data, not only related to parameters but with the uses, demand and availability of groundwater.

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