



Research article

A multi-approach assessment of land use effects on groundwater quality in a karstic aquifer

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ABSTRACT

Groundwater represents almost half of the drinking water worldwide and more than one third of water used for irrigation. Agro-industrial activities affect water resources in several manners; one of the most important is leaching of agrochemical residues. This research identifies the major contributors of changes in groundwater quality comparing two contrasting land uses in a karstic area of the Yucatan peninsula as case study. Using a multiple approach, we assess the impact of land use with physicochemical data, multivariate analyses, hydrogeochemistry and nitrate isotopic composition. We confirmed that agricultural land use has a greater impact on groundwater quality, observed in higher concentration of nitrates, ammonium, potassium and electrical conductivity. Seasonality has an influence on phosphates and the chemical composition of the groundwater, increasing the concentration of dissolved substances in the rainy season. There was a clear effect of manure application in the agricultural zone and the nitrate isotopic composition of groundwater points toward recharge in certain areas. We consider that seasonality and land use effects are intertwined and sometimes difficult to separate, likely because of land use intensity and hydrogeochemical process at a local scale. Finally, we observed poor groundwater quality in the agricultural area during the wet season; thus, it is desirable to maintain non-agricultural areas that provide groundwater of appropriate quality.

1. Introduction

Groundwater supply almost half of the population worldwide, it represents about 30% of the global freshwater reserves and it is widely used for irrigation (Zektser and Everett, 2004; Cozzarelli and Weiss, 2007; Siebert et al., 2010). Groundwater is stored in geological reservoirs (aquifers) made of rocks and deposits from different geological ages and types (Freeze and Cherry, 1979). Aquifers consisting namely of carbonate and evaporite rocks with unconsolidated sediments that originate from the deposition of geological material through weathering are referred to as karst aquifers (Perry et al., 2002; Escolero et al., 2005; Ford and Williams, 2007). In shallow karst aquifers, the vadose zone has an average thickness of 10–20 m with fractures and fissures influencing infiltration rates (Bauer-Gottwein et al., 2011). This characteristic gives karst aquifers high hydraulic conductivity, which facilitates the vertical and horizontal flow of water; and together with a thin soil layer permits the infiltration of water. In general, groundwater quality is influenced by

three main factors: natural processes (such as weathering), anthropogenic activities, and atmospheric input (Helmer and Meybeck, 1996; Jiang and Yan, 2010), being the anthropogenic input the most important from our point of view. It might involve changes in the percolation rate of the unsaturated zone (Harter, 2004), modification of redox processes, sorption of solutes, dissolution and precipitation of mineral and other substances (Vissers, 2006).

The evaluation of groundwater quality is commonly associated to nitrate concentration and prevalence of pathogens (Pacheco and Cabrera, 1996; Leal-Bautista et al., 2013; Rosiles-González et al., 2017); however, legacy effects of agrochemicals is an increasing concern (Gonzalez-Herrera et al., 2014; Saint-Loup et al., 2018). Several studies have found that nutrient concentrations are related to land use and application of agrochemicals (Muñoz et al., 2004; Espino et al., 2007; Graniel-Castro et al., 2009; Boy-Roura et al., 2013; Lawniczak et al., 2016; Fronczyk et al., 2016). The measured variability in the concentration of dissolved substances are commonly related to water level fluctuations and

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seasonality (Elango and Rajmohan, 2005; Long et al., 2018). The excessive use of agrochemicals in agriculture creates a surplus of nutrients not assimilated by crops that can infiltrate into groundwater systems, with nitrates being one of the most prevalent contaminants of surface and groundwater (Pacheco and Cabrera, 1996; Menció et al., 2011). Stable isotopes of nitrate have been used as tracers to differentiate sources (Kendall and Aravena, 2000) and the effects of land use in aquifers (Vystavna et al., 2017).

The National Water Commission (CONAGUA) states that groundwater in Mexico represents almost 40% of the total water allocated for consumptive usage (CONAGUA, 2017). In Mexico in 2014, there were 106 overexploited aquifers out of the total 653 aquifer systems (CONAGUA, 2017). As populations increase, so does the demand for water. A recent estimate stated the total national demand for water at more than 98 million cubic meters (CONAGUA, 2017). In southeastern México, groundwater it is the largest water resource and it occurs exclusively in karstic aquifers. The Yucatan Peninsula is a region with important economic zones for tourism and agriculture; and the only available fresh water resource in the peninsula is groundwater, located in karst aquifers. The permeable structure and thin soil layer of these systems exposes the vulnerable aquifers to contamination by the leaching of residues from anthropogenic activities (Bauer-Gottwein et al., 2011).

Land use is the modification of the terrestrial surface through anthropogenic activities; and can be the expansion or contraction of the original land cover or changes in the management of the existing land cover (Foley et al., 2005; Davis et al., 2019). Land use change from non-agricultural to an agricultural affects water resources in several ways. For instance, once native vegetation is removed the soil structure is altered, changing structure, porosity and water storage capacity (Lerner and Harris, 2009), which can result in rapid infiltration of surface water into the aquifer. These changes increase vulnerability of the groundwater systems to contamination (Scanlon et al., 2005). Since the agriculture sector uses more than half of the total amount of the concessional water, groundwater resources are stressed by agricultural activities. With agricultural development in recharge zones and karstic landscapes, groundwater is vulnerable to degradation without proper land management practices (Famiglietti, 2014). Knowing the changes in the hydrogeochemical and isotopic composition of water is essential for identifying and estimating the impact of processes occurring in water as it moves from the surface into the aquifers. Evaluating the effect of land use upon groundwater is crucial since most of the population in karstic areas relies on groundwater for all economic activities. This research shows the influence of land use on groundwater quality in karstic aquifers, using as case study the north-eastern Yucatan Peninsula. Our objective is to distinguish the effect of land use based on several assessment tools including statistical analyses, hydrogeochemistry and nitrate stable isotopes, in order to identify the major contributors of changes in groundwater quality in a tropical karstic aquifer. We hypothesize that precipitation enhances solutes movement in agricultural areas, measured as greater ions concentration in groundwater. To achieve our objective, we seasonally sampled groundwater in two areas with contrasting land use, analysed it for nutrients, mayor elements and nitrate stable isotopes. We compare these parameters with descriptive and multivariate statistics to find out differences and grouping by land use. Then, we used hydrogeochemical tools to identify the structure and composition of groundwater and used nitrate stable isotopes ($d^{15}NNO_3$ and $d^{18}ONO_3$) to explore most probable sources of nitrate. Lastly, we used a water quality index for finally integrate all this information to probe our hypothesis.

2. Materials and methods

2.1. Study sites

The Yucatan Peninsula is one of the largest karstic environments in Central America and the Caribbean. It is a geological structure largely consisting of a limestone platform with an approximated size of 165,000

km², including the states of Quintana Roo, Yucatan and Campeche, and part of Chiapas (Mexico) in addition to portions of Belize and Guatemala (Graniel-Castro and Gil-Garcia, 2010). It is a porous geological structure of Pleistocene and Tertiary rock; the first 120 m of the geological structure consists of recrystallized calcites of high permeability and argillaceous and coquinoide limestones; deeper layers consists namely of evaporites, dolomites, anhydrites and halite from the Paleocene and Eocene (Andrade-Gómez et al., 2019). The permeable geological structure throughout serves as a conduit for the geo-hydraulic processes such as groundwater flow, and aquifer recharge/discharge (Cabrera Sansores et al., 2002). Apart from carbonates and evaporates, the Peninsula also consist of anhydrites precipitated from the Miocene (23.03 million years ago) and Cretaceous periods 145.5 million years ago (López-Ramos, 1973). The aquifer is unconfined and shallow with an average depth of 30 m, in which groundwater flow patterns mainly run from inland toward the north and east coast (Perry et al., 2002).

This area has a plain relief with practically no mountain cover. The climatic condition is tropical sub-humid with an average rainfall of 1432.3 mm per year and temperature ranging from 23–28 °C (CONAGUA, 2017). For the purpose of this research we identified three seasons using historical data (1949–2016); namely dry season (December to May) with less than 100 mm monthly precipitation, wet season (June to October) with more than 100 mm and cold front season (January to March) with less than 50 mm. The area has thin soil layers. There are four main soil types: leptosols (shallow soils with weak structure), histosols (mainly of organic matter about 40 cm in thickness), vertisols (composed of clays), and gleysols (saturated, mostly with groundwater; Fragoso-Servón et al., 2017). The vegetation cover is mainly composed of tropical secondary growth forests, halophile vegetation and mangrove zones are present in coastal zones.

2.2. Sampling and analytical methods

This study includes an agricultural area and a non-agricultural area, located in the states of Yucatan and Quintana Roo respectively (Figure 1). The agricultural area includes three municipalities on the northeast region of Yucatan (Tizimín, Sucilá and Panabá), where dominant land use in pasture and crops such as corn and soybean. This region is the leading producer of cattle in the state of Yucatan (INEGI, 2017). The non-agricultural area is a well field located in the Municipality of Benito Juárez (North of Quintana Roo); the land use is largely secondary vegetation with the city of Cancun situated east from the well field. All water samples were collected from wells based on the following criteria: currently in used (for irrigation or supply), not exposed to surface runoff and minimum 12 m deep to screen. In the agricultural area, the selected wells (n = 14) were drilled by CONAGUA as part of a project installing deep wells for irrigation. Within the urban zone, the wells (n = 16) are operated through a government concession; all drilled to an approximate depth of 16 m. Sampling was completed seasonally in October 2017 (wet season), February 2018 (cold fronts) and May 2018 (dry season).

The flowchart in Figure 2 shows the summarized research methodology. Water samples were collected in 250 ml HDPE bottles previously washed with phosphate-free detergent. Samples were collected directly from outlets and faucets installed at the pumping system. Physicochemical parameters recorded in situ were temperature (°C), pH, electrical conductivity (mS/cm), redox potential (mV) and total dissolved solids (mg/l) with previously calibrated HANNA sondes models HI98129 and HI98130. Samples were stored cold for 24 h. Upon arrival to the laboratory, the samples were filtered (0.45 µm Pall membrane) and sub-sampled for alkalinity, nutrients and ions. Total alkalinity was measured by acid titration (NMX-AA-036-SCFI-2001 and Method 310.1 Alkalinity Titrimetric). The analyses of nutrient were conducted using colorimetric methods with a UV-VIS spectrophotometer (Eppendorf BioSpectrometer). Nitrites were quantified following Strickland and Parsons (1972), ammonium with the salicylate-hypochlorite method (Bower and Holm-Hansen, 1980) and orthophosphates following the

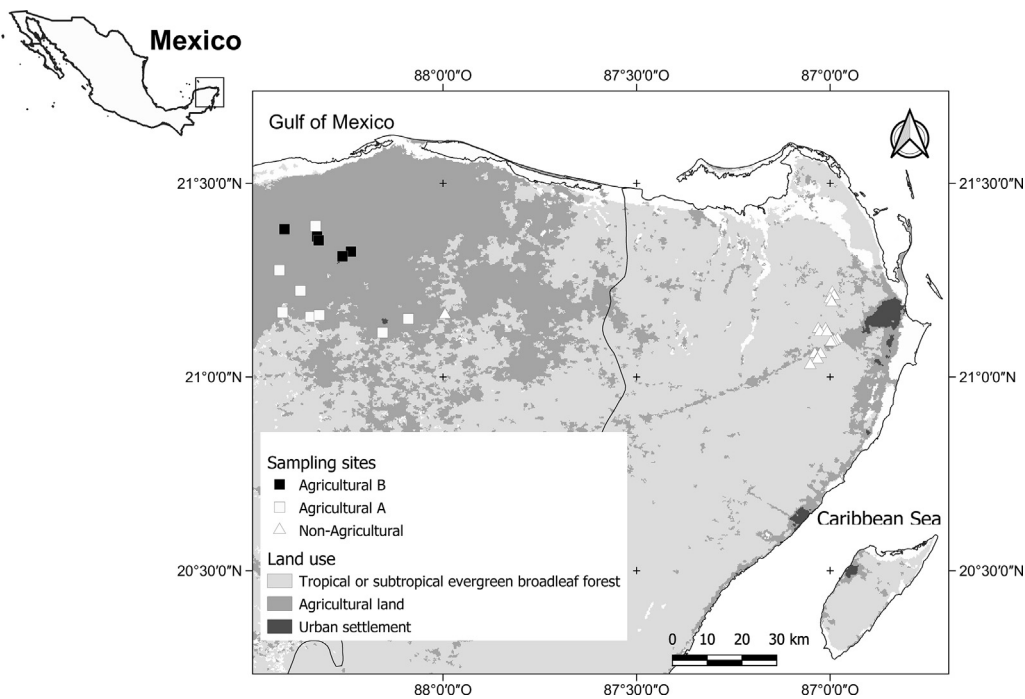


Figure 1. Study area in the northeastern Yucatan Peninsula. Land use vector data provided by INEGI.

procedure EPA 365.3. Nitrates, sulphates, chloride and cations (Na^+ , K^+ , Mg^{2+} and Ca^{2+}) were quantified by ion chromatography using an Ion Chromatograph 822 IC (Metrohm), with a limit of detection of 0.1 mg/l. It is important to mention that dissolved oxygen was not measured because all samples were collected from pumping wells; thus, aeration might cause biased results.

Descriptive statistics were performed with Minitab 18. An Anderson Darling normality test was conducted for identifying data distribution. Data did not have normal distribution ($p \leq \alpha$); thus, we used the non-parametric Kruskal Wallis test to distinguish differences in land use by season. Box plot graphs were produced with SPSS 13. We explored multivariate analyses in order to evince grouping relative to land use. A Non-parametric multidimensional scaling ordination (nMDS) and cluster analyses were done for grouping locations within same land use in order to identify spatial differences. To evaluate physicochemical parameters

between the agricultural and non-agricultural zones a one-way crossed permutational multivariate analysis of variance (PERMANOVA) was used. The PERMANOVA was performed using a Bray-Curtis similarity matrix build. The statistical significance of the PERMANOVA was tested with 10,000 residual permutations under a reduced model and type II (conditional) sums of squares (Anderson et al., 2008). The dissimilarity contribution of physicochemical parameters between the agricultural and non-agricultural zones was estimated using a one-way similarity percentage analysis (SIMPER); multidimensional analyses were conducted in Primer V6 and PERMANOVA+ (Clarke and Warwick, 2001).

Once we obtained the grouping identified with the nMSD, we created a trilinear Durov plot with direct comparison of the total dissolved solids (TDS) and redox potential (ORP) using the software AquaChem 2011.1. Selected groundwater samples from the agricultural area ($n = 12$) and from the non-agricultural area ($n = 9$) were analysed for nitrate stable

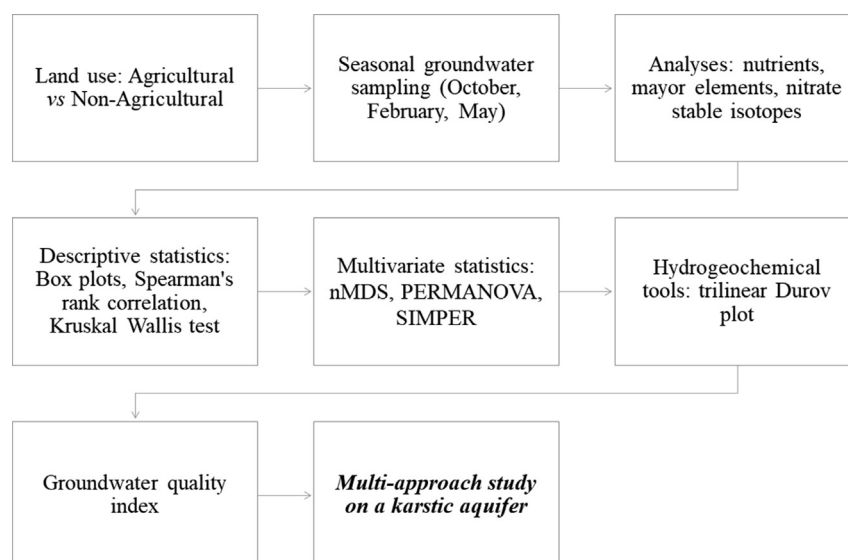


Figure 2. Flowchart showing the research method used in this multi-approach assessment of land use effects on groundwater quality in a karstic aquifer.

isotope composition. Analyses for the $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ were obtained by chemical denitrification as described by [Mcilvin and Altabet \(2005\)](#). Isotopic analyses of nitrate were completed in the University of Waterloo in duplicate using a GV Trace Gas preconcentrator system coupled to a GVIsoprime mass spectrometer. Stable isotope ratios were converted to delta notation (δ) expressed per mil (‰) relative to atmospheric air with an analytical precision of $\pm 1\%$ for ^{15}N and $\pm 0.5\%$ for ^{18}O . Two in-house standards were used, EGC-1 (13.8‰ $\delta^{15}\text{N}$, 28‰ $\delta^{18}\text{O}$) and EGC-17 (25.6‰ $\delta^{15}\text{N}$), USGS-34 (-1.8‰ $\delta^{15}\text{N}$, -27.9‰ $\delta^{18}\text{O}$), USGS-25 (2.7‰ $\delta^{15}\text{N}$, 57.5‰ $\delta^{18}\text{O}$) and IAEA-NO-3 (4.72‰ $\delta^{15}\text{N}$, 25.6‰ $\delta^{18}\text{O}$) as check standard.

Finally, we evaluated the Water Quality Index developed by [Sánchez et al. \(2016\)](#) to assess the groundwater quality of the study area. This WQI use seven parameters (pH, TDS, total hardness, Na^+ , Cl^- , SO_4^{2-} and NO_3^-) as mandated by Mexican regulations. We did not quantify hardness; thus, we use alkalinity.

3. Results

3.1. Descriptive statistics

The Box plot graphs showed in Figures 3 and 4 resume the trends and dynamics of physicochemical properties and dissolved substances observed within seasonal cycle in the two study areas. Temperature and total dissolved solids were lower and more stable in the non-agricultural zone. There were slightly alkaline values (max = 8.22 in the agricultural zone) common in karstic aquifers. Higher electrical conductivity and TDS in the agricultural zone represent greater dissolved substances in this type of land use. The redox potential (Eh) had clear seasonal behaviour, moderately reductive in the wet and cold seasons, with reductive

conditions in the dry season (See *Supplementary material* for complete descriptive statistics).

Regarding the concentration of dissolved substances, we noticed that values were higher and the dispersion was greater in the agricultural area during the wet season. As expected, nitrate was always higher in the agricultural zone. Sulphate was slightly higher in the non-agricultural zone and chloride and bicarbonate were the dominant anions in both areas. We also measured higher concentrations of magnesium, sodium and potassium in the agricultural zone. Spearman's rank correlation (r_s) shows that the variables temperature, TDS, nitrate, magnesium and alkalinity correlate with land use, whereas seasonality is highly correlated with redox potential (Table 1). The ammonium and potassium correlation is considered the result of manure application whereas the correlations among ions (Cl^- , SO_4^{2-} , Mg^{2+} , Na^+) are likely the expression of rock dissolution (see section 3.3).

Considering land use as the only variable (without seasonal distinction), there were statistical differences between the agricultural and non-agricultural zones. The parameters which were different are temperature ($H = 38.5$, $p < 0.001$), TDS ($H = 40.22$, $p < 0.001$), pH ($H = 15.8$, $p < 0.001$), nitrates ($H = 59.1$, $p < 0.001$), ammonium ($H = 7.9$, $p = 0.005$), magnesium ($H = 59.9$, $p < 0.001$), chloride ($H = 8.5$, $p = 0.004$) and sodium ($H = 4.18$, $p = 0.041$). When we evaluated the data within each land use, we observed the seasonal differences showed in Table 2. Higher concentrations of nutrients were associated to wet season, whereas cations had variable behaviour.

3.2. Multivariate statistics

According to the nMSD performed (87% similarity, 2D stress = 0.09), there were not only two distinctive groups according to land use; there

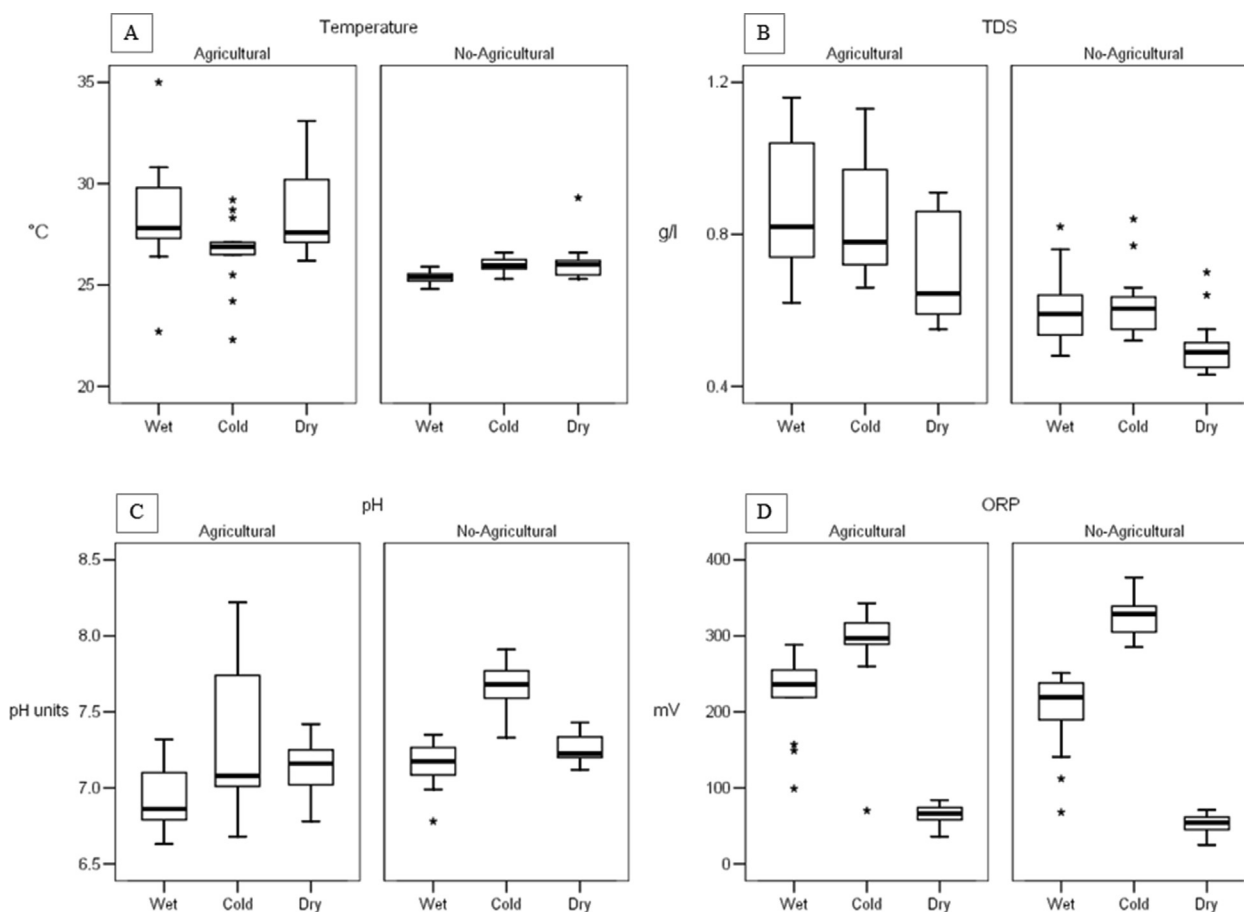


Figure 3. Box plot of temperature (in °C, A), total dissolved solids (TDS in g/L, B), pH (C) and redox potential (Eh in mV, D) in two contrasting land use areas in the Northern Yucatan Peninsula. Temporality represented wet (October 2017), cold (February 2018) and dry season (May 2018).

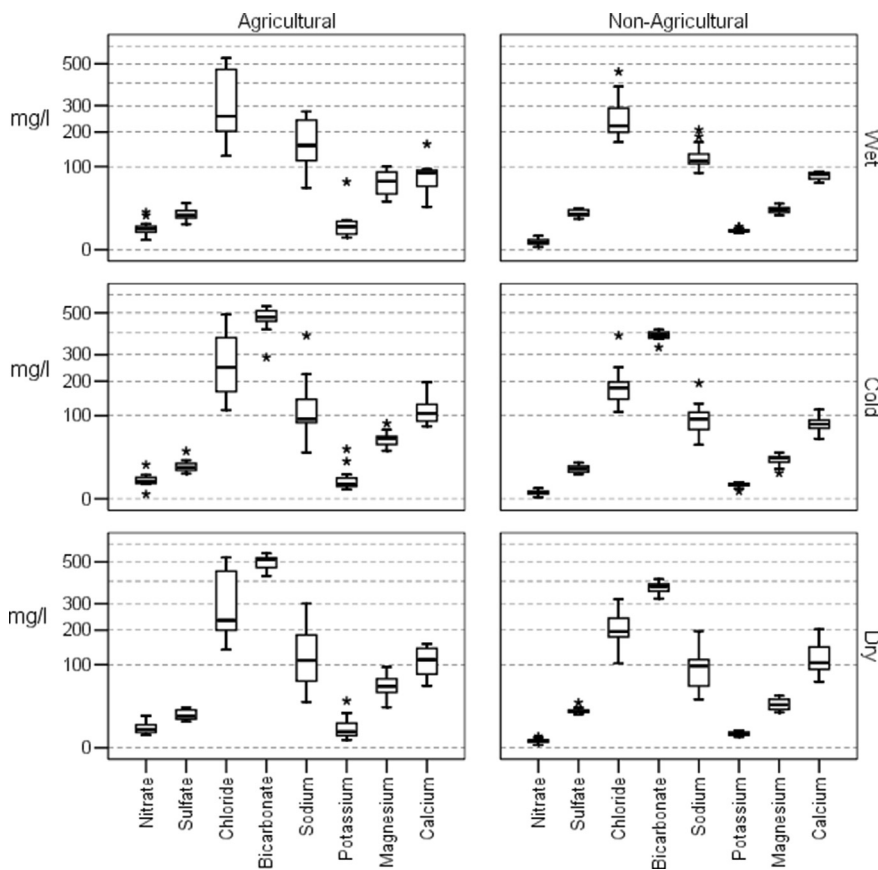


Figure 4. Box plot of nitrate and mayor elements in two contrasting land use areas in the Northern Yucatan Peninsula. Concentrations expressed as nitrate (mg NO₃/L), sulfate (mg SO₄²⁻/L), chloride (mg Cl⁻/L), bicarbonate (mg HCO₃⁻/L), sodium (mg Na⁺/L), potassium (mg K⁺/L), magnesium (mg Mg²⁺/L) and calcium (mg Ca²⁺/L). The Y axis is on power scale (0.5). Temporality represented are wet (October 2017, upper panel), cold (February 2018, central panel) and dry seasons (May 2018, lower panel).

was a separation among agricultural sites (AA and AB) yielding three distinctive groups (Figure 5). The grouping is based on the PERMANOVA analysis (Table 3). It is important to mention that a sampling site spatially located within the agricultural zone (NA14), ended up grouped with the Non-Agricultural sites. The PERMANOVA showed that the differences among agricultural and non-agricultural locations are in temperature, electrical conductivity, nutrients, bicarbonate, sulphate and magnesium.

From the comparison of two groups within the area (AA and AB), it was found that their differences were based on electrical conductivity, chloride, sulphate and sodium (Table 3). It is important to mention that

redox potential and potassium were differentiation factors when comparing sites of the group AB, all of them located in the same municipality. Likewise, the cluster analysis (Figure 6) points that groups AA and AB are not as related between them as expected, despite they both are agricultural groups; rather, the AA group have greater resemblance to the Non-Agricultural area.

The SIMPER analysis shows that, in the Non-Agricultural area, the largest contribution for aggregation was from the variables bicarbonate, chloride, redox potential and sodium (83.5% cumulative contribution) and not from nutrients. It is important to highlight that the groups Non-

Table 1. Spearman's rank correlation coefficient (r_s). Correlation significance *p = 0.01 and **p = 0.05.

	Season	Land Use	Temp	EC	pH	ORP	NO ₂	NO ₃	NH ₄ ⁺	PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	Mg ²⁺	Ca ²⁺	Na ⁺	K ⁺
Land Use	-0.015															
Temp	0.152	-0.663*														
EC	-0.317*	-0.676*	0.419*													
pH	-0.298*	0.396*	-0.126	-0.217**												
ORP	-0.899*	-0.028	-0.123	0.288*	0.204											
NO ₂	-0.297*	0.262**	-0.345*	-0.036	0.193	0.292*										
NO ₃	0.091	-0.82*	0.627*	0.514*	-0.477*	-0.062	-0.285*									
NH ₄ ⁺	0.183	-0.3*	0.095	0.243**	-0.359*	-0.106	-0.042	0.337*								
PO ₄ ³⁻	-0.159	-0.195**	0.04	0.323*	-0.366*	0.244**	0.339*	0.247**	0.364*							
SO ₄ ²⁻	0.347*	0.139	-0.061	0.1	-0.155	-0.413*	-0.048	-0.012	0.212**	0.051						
Cl ⁻	0.157	-0.311*	0.16	0.532*	-0.27*	-0.189	-0.008	0.283*	0.274*	0.213**	0.622*					
Mg ²⁺	0.107	-0.826*	0.652*	0.706*	-0.356*	-0.051	-0.325*	0.664*	0.229**	0.141	0.033	0.372*				
Ca ²⁺	0.217**	-0.155	0.124	-0.068	-0.129	-0.164	-0.237**	0.079	-0.087	-0.338**	-0.063	-0.068	0.181			
Na ⁺	0.044	-0.218**	0.134	0.611*	-0.22**	-0.07	0.083	0.167	0.367*	0.333*	0.533*	0.702*	0.291*	-0.311*		
K ⁺	0.047	-0.18	0.184	0.348*	-0.252**	-0.05	0.164	0.263*	0.509*	0.45*	0.458*	0.391*	0.208	-0.181	0.477*	
Alk	0.02	-0.798*	0.578*	0.589*	-0.384*	0.053	0	0.698*	0.321**	0.267**	-0.173	0.205	0.687*	0.076	0.124	0.143

Table 2. Kruskal Wallis tests for the three seasons evaluated per land use area in the northeast Yucatan Peninsula.

Land use	Parameter	Z value			H, p
		Wet	Cold	Dry	
Non-Agricultural	Temperature	-4.48	2.37	2.11	20.12, <0.0001
	E.C.	1.35	2.45	-3.79	14.81, 0.001
	pH	-3.95	5.47	-1.52	31.86, <0.0001
	ORP	-0.07	5.6	-5.53	41.31, <0.0001
	Ammonium	4.18	-3.89	-0.28	21.8, <0.0001
	Phosphate	5.06	-0.78	-4.29	29.74, <0.0001
	Sulphate	2	-4.7	2.7	22.2, <0.0001
	Chloride	2.23	-2.41	0.16	7.25, 0.027
	Potassium	5.53	-2.84	-2.69	30.62, <0.0001
	Sodium	3.57	-2.17	-1.41	12.94, 0.002
	Calcium	-3.38	-0.04	3.43	15.39, <0.0001
Agricultural	Temperature	1.26	-2.51	1.2	6.3, 0.043
	E.C.	1.21	1.26	-2.45	5.99, 0.05
	pH	-2.84	1.65	1.18	8.19, 0.017
	ORP	0.99	4.16	-5.07	29.41, <0.0001
	Ammonium	2.4	-1.6	-0.8	6.06, 0.048
	Phosphate	5.2	-2.8	-2.5	26.8, <0.0001
	Calcium	-2.67	1.67	1.03	7.28, 0.026

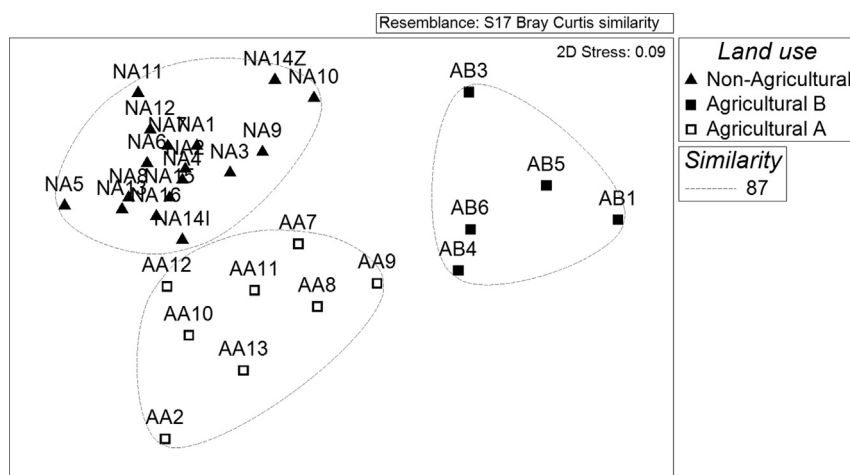


Figure 5. Non-metric multidimensional scaling (nMDS) with superimposed clusters from the cluster analysis at a similarity level of 87% (dashed line) for grouping locations within same land use.

agricultural and AB have the same four explanatory variables but with different weight (bicarbonate, chloride, sodium and redox potential). The only different explanatory variable between the agricultural sites is the dominant cation, calcium or sodium (Table 4). The differences in ORP were namely seasonal, reductive in the dry season and moderately reductive in wet and cold seasons.

3.3. Hydrogeochemistry

The hydrochemical structure of the groundwater water in the study area is showed in Figure 7. The Durov plot shows that there is greater dispersion in the chemical composition of the agricultural zone (rectangles). The non-agricultural zone as a more defined composition with bicarbonate and calcium as dominant ions; yet, during the dry season there was a slight enrichment in calcium and/or loss of sodium (triangles). The agricultural zone had greater dispersion during the cold front season (ORP from +73 to +343 mV). In this zone, we observed dispersion in the cations due to the high concentrations of potassium. Therefore, the dominant cation is not calcium but the sum of sodium and

potassium, while bicarbonate and chloride are the dominant anions. The distribution of the data points in TDS plot separates the two agricultural areas; being the non-agricultural area similar to the agricultural area A (AA, Figure 5). The ORP dispersion correspond to seasonal variations, moderately reductive conditions in the wet and cold seasons, shifting to reductive conditions in the dry season (0 to +100 mV).

3.4. Nitrate isotopic composition $\delta^{15}N$ and $\delta^{18}O$

The isotopic composition of the nitrate measured in selected samples confirm our hypothesis that agriculture have a clear impact on groundwater quality (Table 4). Our results showed two main trends, the first one is the effect of manure in the agricultural zone ($\delta^{15}N$ NO_3 from 7.5‰ to 17‰ in cluster AA). The second one is the $\delta^{18}O$ NO_3 characteristic of nitrate in precipitation measured in samples from the non-agricultural zone, an area with low human impact and likely recharge area ($\delta^{18}O$ NO_3 from 22‰ to 61‰, cluster NA), Figure 8). However, there were some samples from the non-agricultural zone that suggest nitrate from natural sources or manure ($\delta^{15}N$ from 5 ‰ to 15‰).

Table 3. Results of one-way PERMANOVA based on Bray-Curtis similarity matrix. Significant p values ($\alpha = 0.05$) are indicated in bold.

Parameter	NA - AA	NA - AB	AA - AB
Temp (°C)	0.0001	0.0001	0.6292
EC (mS/cm)	0.0003	0.0001	0.0001
pH	0.0045	0.1672	0.6340
ORP (mV)	0.3324	0.0226	0.0662
N-NO ₂ mg/l	0.0001	0.0012	0.9725
N-NO ₃ mg/l	0.0001	0.0001	0.2450
N-NH ₄ ⁺ mg/l	0.0044	0.0117	0.7488
P-PO ₄ ³⁻ mg/l	0.3676	0.0931	0.2847
HCO ₃ ⁻ mg/l	0.0001	0.0001	0.5055
Cl ⁻ mg/l	0.9595	0.0001	0.0001
S-SO ₄ ²⁻ mg/l	0.0059	0.0008	0.0008
Na ⁺ mg/l	0.8190	0.0001	0.0012
Mg ²⁺ mg/l	0.0001	0.0001	0.4619
Ca ²⁺ mg/l	0.1693	0.5934	0.6850
K ⁺ mg/l	0.0586	0.0001	0.0890

3.5. Water quality index

According to the WQI developed by Sánchez et al. (2016) and modified to our results (using alkalinity instead of hardness), the water quality in the northeastern region of the Yucatan Peninsula, varied from excellent year-round in the non-agricultural zone (<50), to good (50 to <100) and marginally poor (100 to <200) in the agricultural area. The water quality was particularly ill qualified during the wet season (Table 5) due to the greater concentration on nitrate and ions during this season.

4. Discussion

With the results obtained through the multivariate statistics, the hydrogeochemical differences and the isotopic composition of nitrate, we were able to distinguish changes in the groundwater quality due to land use and seasonality. We measured higher concentration of nutrients and ions in the agricultural area during the wet season and we found significant correlation among several physicochemical parameters with land use and seasonality. Both statistical and hydrogeochemical evidence support our hypothesis that the use of agrochemicals together with precipitation and irrigation influence the biogeochemical structure of the groundwater by enhancing solutes movement and modifying its quality. The Spearman correlations confirm that agricultural land use influence

the groundwater quality observed as differences in nitrite, nitrate, phosphate, chloride, magnesium and sodium. The N species and phosphate are namely introduced by agrochemicals (Pacheco et al., 2001; Jiang et al., 2008; Aranda-Cirerol et al., 2011; Gonzalez-Herrera et al., 2014); whereas other ions and alkalinity responded more to water-rock interaction.

Nitrates had greater influence by land use and not so significant by seasonality. In the agricultural zone, concentration reached 8 mgN-NO₃/L, much higher than in the non-agricultural zone, which did not exceed 1 mgN-NO₃/L. The nitrate isotopic composition ($\delta^{15}\text{N-NO}_3$) from the agricultural groundwater also confirm the impact of manure application in groundwater (Choi et al., 2003; Matiatos, 2016). Lower nitrates concentration in the cold front season compared to the dry season are assumed to be because of differences in temperature influencing the microbial activity responsible for the oxidation of ammonium (Groeneweg et al., 1994).

In the non-agricultural zone, we consider that nitrates are of natural origin because of its low concentration, the $\delta^{15}\text{N-NO}_3$ common in soil organic matter and the $\delta^{18}\text{O-NO}_3$ typical of precipitation (Kendall, 1998). The NO₃/Cl⁻ ratio was approximately 0.25, lower than the ratio established for nitrate of urban origin (Pacheco et al., 2001); the slight increase in the rainy season could be due to surface runoff followed by infiltration. However, the nitrate isotope composition of some samples (NA 11 and NA14Z) suggest influence of septic systems given that there is not agriculture in the area. Perhaps we did not measure greater nitrate concentrations, but there might be septic leaking or fertilizers inputs from irregular settlements and nearby ranches. Ammonium had both seasonal and land use influence, greater concentrations in the agricultural zone and variable by season. This may be due to the application of agrochemical fertilizers and decomposition of organic matter. In the case of the non-agricultural zone, concentrations are much lower and are attributed to natural conditions.

Phosphate was not influenced by land use, but by seasonality. Phosphate in both zones had a higher concentration in the rainy season than in other seasons. The soil in the Yucatan Peninsula has a low sorption and phosphate might remain in the soil until rain or irrigation mobilizes it to the aquifer (Siemens et al., 2004). Jeong (2001) found that anthropogenic inputs influence not only groundwater nutrients concentration, but also the concentrations of the inorganic constituents.

Potassium was influenced by land use and not by seasonality. In the non-agricultural zone, low values (<1 mg K⁺/L) suggest natural origin (Appelo and Postma, 2005) and Perry et al. (2002) reported values as high as 4 mg K⁺/L for coastal locations of Yucatan Peninsula. Variations in sodium and potassium in a karstic aquifer due to human activities was already reported by Lang et al. (2006), who showed that water-rock

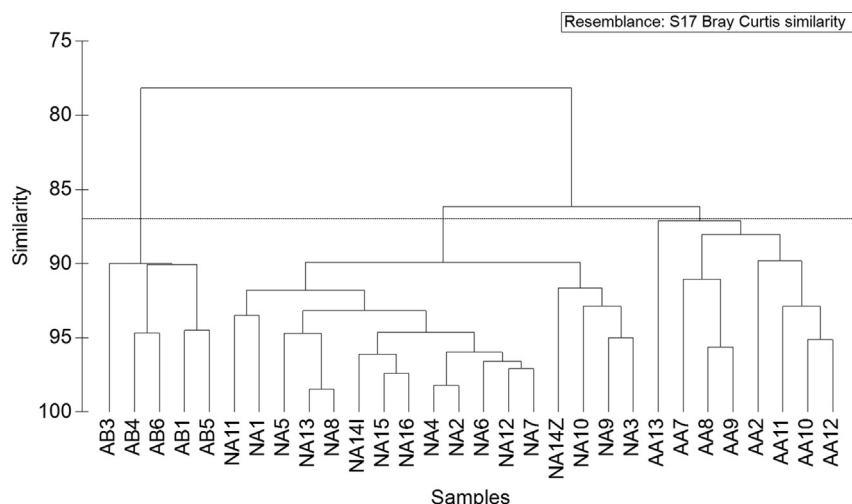


Figure 6. Cluster analysis for grouping locations within same land use (gray line similarity level of 87%).

Table 4. The physicochemical parameters that contribute more strongly to the similarity (SIMPER) between the agricultural and non-agricultural zones. Avg. Sim. = Average similarity.

Group	Explanatory variables	Contribution %	Cummulative %
Non Agricultural Avg. Sim: 92.24 %	HCO ₃ mg/l	37.35	37.35
	Cl ⁻ mg/l	18.81	56.16
	ORP (mV)	18.64	74.8
	Na ⁺ mg/l	8.75	83.54
Agricultural A Avg. Sim: 89.09%	HCO ₃ mg/l	42.12	42.12
	ORP (mV)	16.76	58.88
	Cl ⁻ mg/l	15.94	74.82
	Ca ²⁺ mg/l	8.36	83.18
Agricultural B Avg. Sim: 90.96%	Cl ⁻ mg/l	31.34	31.34
	HCO ₃ mg/l	30.81	62.14
	Na ⁺ mg/l	13.24	75.38
	ORP (mV)	9.75	85.13

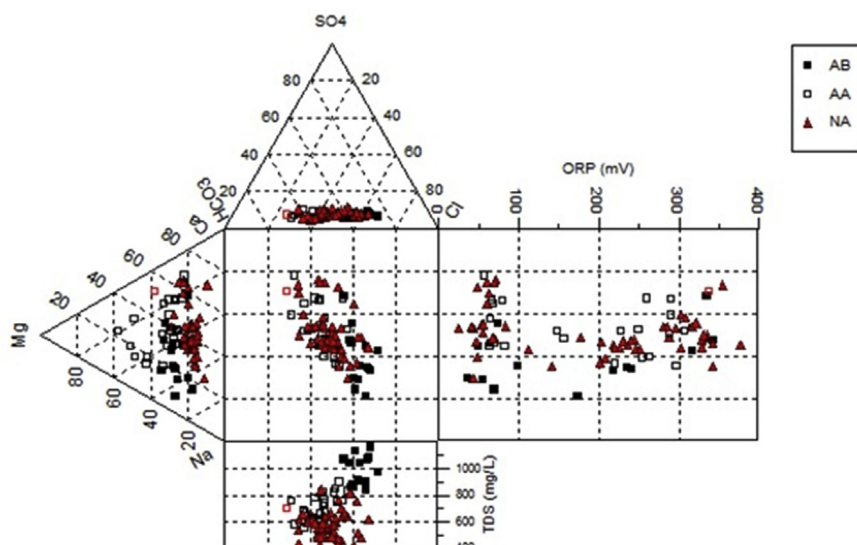


Figure 7. Durov plot showing the hydrogeochemical dispersion of the agricultural sites (squares AA and AB) and the non-agricultural sites (triangles NA). TDS (mg/L) assist in distinguishing the effect of land use and redox potential (mV) suggest differences by seasonality (see Supplementary material for details).

interaction can be influenced by seasonality. In the agricultural zone, measured potassium values indicates intense use of agrochemical fertilizers or manure. Manure is as an important biogeochemical fingerprint in the agricultural region because of the relatively high potassium content

in cattle manure, as high as 2.5 % by weight (López-Martinez et al., 2001). The maximum value measured (66.7 mg K⁺/L) is concurrent with the correlation between ammonium and potassium ($r_s = 0.509$; $p = 0.01$) as ammonium likely also leaks into the aquifer after manure application as it is commonly applied by end of the dry season and rains would mobilize it and promote their entry into the aquifer. Sulphate concentrations are typical of groundwater so we can attribute mostly natural origin from water-rock interaction (Appelo and Postma, 2005; Delgado et al., 2010).

Some parameters were expected to increase in concentration with increased infiltration, whereas others might be reduced due to dilution (Gonzalez-Herrera et al., 2014). Despite the fact that there are differences in the chemical composition of water due to land use, the type of water is dominated by seasonality. The multivariate analyses shows that the agricultural locations separate into two groups, supported by the dispersion from the Durov diagram, confirming that the grouping of groundwater were both spatially and seasonally distinguished. We think that changes in calcium, sodium, chloride and sulphate result from frequent irrigation in the agricultural zone that mimics precipitation, increasing concentrations of exchangeable base cations (Yavitt et al., 1992) and carbonate weathering (Chao et al., 2017). The relation between hydrogeochemistry and land use is likely intertwined with surface geology, which might be similar in most agricultural sites and its

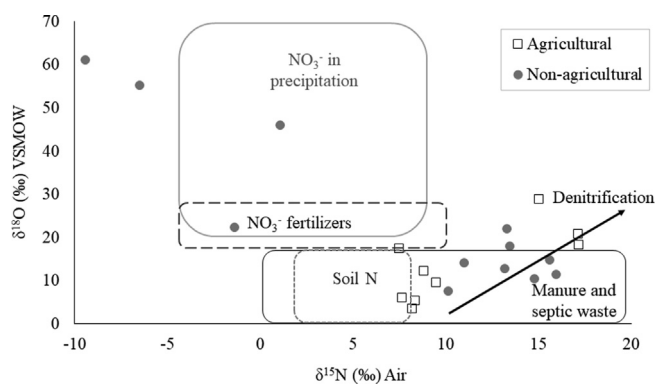


Figure 8. Nitrate stable isotopes composition δ¹⁵N-NO₃ and δ¹⁸O-NO₃ (in ‰) in selected water samples of the agricultural (open squares, n = 12) and non-agricultural zone (grey circles, n = 9) Boxes drawn after Kendall and Aravena (2000).

Table 5. Groundwater Quality Index of the Northeastern Yucatan Peninsula. This WQI considers seven parameters (pH, TDS, total hardness, Na⁺, Cl⁻, SO₄²⁻ and NO₃). WQI modified from Sánchez et al. (2016). SI_i: parameter sub index.

Parameter	Agricultural Land use			Non-agricultural Land use		
	SI _i wet	SI _i dry	SI _i cold	SI _i wet	SI _i dry	SI _i cold
pH	3.3	3.3	3.4	3.4	3.4	3.6
TDS (mg/l)	0.0	0.0	0.0	0.0	0.0	0.0
Alkalinity (mg/l)	8.4	9.3	10.0	8.4	7.4	7.7
NO ₃ (mg/l)	67.4	53.2	48.8	9.2	6.2	5.3
Cl ⁻ (mg/l)	20.3	19.4	17.8	16.3	13.5	11.8
SO ₄ ²⁻ (mg/l)	1.6	1.3	1.3	1.6	1.6	1.1
Na ⁺ (mg/l)	13.4	10.1	10.0	9.7	7.2	7.2
∑SI _i	114.4	96.7	91.3	48.7	39.4	36.8
WQI	Poor	Good	Good	Excellent	Excellent	Excellent

geographic delimitation at small scale is not possible. Changes in ions concentration can also be interpreted as hydrogeochemical evolution in a flow path (Ledesma-Ruiz et al., 2015), but this is out of the scope of this research.

Long et al. (2018) found that not all water quality parameters changed during the rainy season, in some cases, groundwater was diluted in the rainy season due to the influence of flushing of the land surface. They also noticed that the shallow aquifer was more affected than the deeper aquifer. In the coastal aquifer of northern Yucatan, Martínez-Salvador et al. (2019) reported that NO₃ concentration increases with recharge (July to November), providing evidence, that recharge plays an important role in dissolved substances' behaviour. Wet and cold season correspond to dates where rains were present in the zone; thus, it is possible that there was recharge. We do not have enough evidence that points to preferential summer recharge in the north-eastern Yucatan Peninsula; however, the fact that higher concentrations of dissolved substances and δ¹⁸O–NO₃ characteristic of nitrate in precipitations were found in the wet season (NA3 and NA11), suggest that greater amount of water enters the aquifer during the wet season.

Chen et al. (2019) found that dissolved oxygen, chloride concentration and redox potential influenced the distribution of the microbial community in groundwater. Interestingly, redox potential was consistently among the explanatory variables for the SIMPER analysis. There is a straightforward relation between Eh and dissolved oxygen; yet, measuring redox potential of groundwater in field conditions has been a concern because reported Eh might be higher than the true Eh value due to contamination by atmospheric oxygen (Back and Barnes, 1965). Eh is a reliable indicator of oxidation potentials and it has been observed that it has seasonal variations in shallow aquifers (Back and Barnes, 1965; Kumar and Riyazuddin, 2012). From the chemical species hereby studied, ammonium, nitrite, nitrate and sulphate are considered redox-sensitive species. There was significant correlation between measured ORP and nitrite and sulphate, but not with ammonium and nitrate; the rest of the ions does not provide supporting information regarding oxidation potential in the aquifer. High Eh values has been associated to recently recharged water (Fetter, 2000) which would suggest that there was recharge during the wet and cold seasons (October and February), and most of the oxygen was consumed by the dry season sampling (May). Additional supporting information for aquifer recharge also comes from the nitrate isotopes. Bostic et al. (2018) found that forested lands retained large amounts of atmospheric nitrate; thus, the δ¹⁸O–NO₃ in the non-agricultural area in our research might be good indicator of local precipitation recharge (Wang et al., 2017) but also the result of water mobilization from other areas because of continuous pumping, irrigation or lateral flow (Pierre et al., 2016).

Due to the complexity of karstic agroecosystems and the variable outcomes from multi-tool assessments, approaches such as system dynamics (SD; Hashemi et al., 2019) include physical and non-physical factors, which can be evaluated with loops and feedbacks. When

hydrogeological parameters are well known, intrinsic vulnerability indexes such as DRASTIC can also be used for water management purposes (Jang et al., 2017; Hosseini and Saremi, 2018). We did not used a vulnerability index; however, the thin soil and porous epikarst features present in the study area, suggest that they are not acting as buffer zone (Martínez-Salvador et al., 2019); thus, they the movement of pollutants can occur fast. The shallow, unconfined aquifer (≤30 m deep) is embedded in a platform of carbonate sedimentary exposed rock (Andrade-Gómez et al., 2019), and this dominance of bicarbonate, calcium, sulphate and sodium indicate rock dissolution, a dominant hydrochemical process. However, the measured concentration of dissolved substances can also be influenced by the spatial location and intensity of irrigation. For instance, the two groups within the agricultural area (AA and AB) are clearly separated by the cations sodium and calcium, which are also distinguished by TDS in the Durov diagram, higher in the northern sites. These sites have the greatest concentrations (meq/L) of chloride, sulphate and sodium, resulting from greater rock interaction.

Regarding the Water Quality Index, the sites representing non-agricultural land use are of excellent quality and they are currently used for urban water supply. There might be some concerns about high chloride in some wells (385 and 458 mg Cl⁻/L), but the bulk water distributed to the urban area seems to not be currently compromised. On the other hand, the water in the agricultural area, especially during the wet season, is of poor quality and it is not recommended for human consumption. Most of the wells are used for irrigation; yet, some households rely on that water for domestic use. The use of indexes for assessing the suitability of water for drinking or agricultural use is a powerful tool for stakeholders as it provide information about declining quality relative to current and future land use or land management (Abbasnia et al., 2019; Delgado et al., 2010). Seasonal variability in water quality might be an issue in the near future should the current situation change and continuous monitoring may better establish some processes that also promote the affectation of groundwater quality, recharge and the origin of the contaminants. It is important to understand the synergistic influence that link the chemical composition of the water with land use management and seasonality, and interpret this information under the current climate change scenarios.

5. Conclusions

With the analyses performed and the statistical, hydrogeochemical and isotopic information obtained, we confirm that agricultural land use has a large impact on groundwater quality because the applied agrochemicals and manure are likely leaching into the aquifer with greater intensity during the wet season, impairing groundwater quality. We report physicochemical and isotopic indicators of groundwater recharge during the wet and cold seasons in both areas. The use of multiple tools such as multivariate statistics together with hydrogeochemical and

isotopic data highlight the scientific value of a multi-approach assessment, allowing us to identify differences related to seasonality and differences within areas with the same land use, likely the result of land use intensity and local scale surface geology. The groundwater quality of the study sites of the north-eastern Yucatan Peninsula is poor in the agricultural area during the wet season; we recommend maintaining non-agricultural areas as currently are for ensuring good groundwater quality for human and agricultural use and as high quality recharge areas. Our findings are thoroughly applicable for improving water management, promote renewable groundwater extraction and putting into practice best management practices in agroecosystems.

Declarations

Author contribution statement

Daniel N.I. Smith, Daniela Ortega-Camacho: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Gilberto Acosta-González: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Rosa Maria Leal-Bautista: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

William E. Fox III: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Eduardo Cejudo: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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