Physical and Biogeochemical Characterization of a Tropical Karstic Marsh in the Yucatan Peninsula, Mexico.

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Abstract

Karstic wetlands provide important ecosystem services such as maintenance of hydrological balance, flood regulation, drinking water supply and nutrients cycling. It is important to conserve and maintain karstic wetlands due to its interaction with groundwater systems and its socioeconomic relevance. The objective of this research was to generate base-line knowledge of the microtopography, hydroperiod and biogeochemical characteristics of poorly known tropical karstic marshes by testing two hypotheses, the phreatotrophic nature of tropical karstic marshes, and the alteration of its biogeochemistry by a highway dividing the marsh. The study site is located in the north of the state of Quintana Roo (Mexico), in pseudo-paludal depressions associated to fractures. The water level varied from few centimeters below the ground to more than 100 cm. We demonstrate that the wetland is groundwater-fed with differences among groundwater, interstitial and surface water in almost all parameters measured. The water is calcium bicarbonate type; the main processes occurring are recharge, evaporation and rock dissolution. Our results suggests active denitrification, low phosphates attributed to Ca- and Fe/Al-bound P, elevated alkalinity and sulfate reduction due to anaerobic conditions in water and soil. The soil reflect its sedimentary origin, the bulk density is low with very high water retention capacity. We do not have enough evidence of the highway modifying the biogeochemistry or hydrology of the marsh. These karstic wetlands provide important provisioning and supporting ecosystem services that should be studied, acknowledged and maintained.

Introduction

Wetlands are transitional zones between terrestrial and aquatic ecosystems. They are characterized by the presence of standing water and/or saturated soils for long time during the growing season, a condition that enhances the development of aquatic vegetation and hydric soils (National Research Council 1995; Mitsch and Gosselink 2007). Karst is a term used for characteristic landscapes, landscape features, and phenomena developed in water soluble and porous carbonate rocks on surface and underground (Beltram 2016). While most karst systems are characterized by a lack of integrated surface drainage systems, surface wetlands do occur in karst (White 2002). Some surface karstic wetlands are groundwater-fed and exhibit modern or fossil tufas; whereas other karstic systems are closed basins called sinkholes or dolines (Pipan and Culver 2019), formed at major joints or cracks in the bedrock. Some sinkholes form from the surface enlargement of joints by dissolution, others form when underground voids collapse leaving an opening to the surface.

Karstic landscapes and their associated wetlands have important socioeconomic values including maintenance of general hydrological balance and flood regulation, drinking water supply, and water for grazing animals or agriculture. Karstic aquifers and wetland remain a significant source of drinking water all over the world and may play an especially vital role in ensuring adequate water supplies for human communities in generally dry surface landscapes (Beltram 2016, Wilson et al. 2019).

The Ramsar Convention is an important tool in the protection of karstic wetlands. A total of 130 karstic wetlands comprising more than 105,000 km² are listed, including poljes, permanent surface water features, large ecoregions, and cave systems. Almost one fourth of all karstic Ramsar sites in the world are designated in the Yucatan Peninsula in Mexico (Beltram 2016). In the state of Quintana Roo (México), it has been identified 2890 karst depressions occupying an area of 1147.05 km², being uvalas the most abundant and poljes the more extensive (Fragoso-Servón et al. 2014). Sinkhole wetlands are also important, but they have received much less attention (Cejudo and Herrera-Caamal 2019) and we do not know how many they area. Sinkholes and uvalas are present across the entire state, whereas poljes are present mainly in valleys. The complexity of karstic wetlands, their values, and ecosystem services are still not fully recognized. To conserve and maintain karstic wetlands, it is important the knowledge of their main characteristics and understanding of the functioning and processes that form and sustain these ecosystems. Recognizing the interlinkage and interaction of exokarstic structures with groundwater systems, as well as their ecosystem services, is crucial to conserve and sustain wetlands within their catchments.

The aim of this study was to generate base-line knowledge of the physical and biogeochemical characteristics of poorly known tropical karstic marshes, testing two hypotheses: 1) the tropical karstic marshes locally called *sabanas* are phreatotrophic wetlands, (i.e. groundwater-fed), and 2) the highway dividing the marsh into two sections alters the biogeochemistry of the portions of the marsh.

Materials And Methods

Study Area

This research was completed in a tropical karstic marsh located in the community La Esperanza, municipality of Lázaro Cárdenas, state of Quintana Roo (Mexico). The climate is warm sub-humid (Aw), with annual mean temperature of 24.7°C, and annual mean precipitation of 1249.5 mm (884-2734.2 mm; 1951–2010 historical records; INEGI 2016). The marsh is located in a pseudo-paludal environment (Fragoso-Servón et al. 2019), the geological setting is a carbonate platform dominated by Neogene and Quaternary sedimentary calcites (INEGI 2009), the soil in the elevated land is mostly Leptsol; however, inside karstic depressions it can be Gleysol (Fragoso-Servón et al. 2017, 2019). Tropical karstic marshes locally named *sabanas* are common landscapes of the Holbox Fracture Zone, characterized for wetlands established in solution depressions related to faults and fractures (McKay et al. 2020). The marsh (north limit 20.977274° N, 87.418609° W; south limit 20.964197°N, -87.423740° W) is divided by a state highway in two sections, identified as north and south portions. We established two transects in each portion, in order to capture the spatial variability of the marsh and the potential effect of fragmentation upon the biogeochemical characteristics of the marsh (Fig. 1). We estimated the area using a Sentinel-2 image with 0% cloud cover from January 10th 2019 (Sentinel-2 - Tile: T16QDJ Acquisition Date:07-JAN-19 for Scene: L1C_T16QDJ_A009604_20190107T161737). The image was further edited in QGIS 3.8.3-Zanzibar. The GIS was trained defining wetland and non-wetland areas for a supervised classification

and vectorization of the polygons. We obtained three main polygons with a total wetland area of 777,385.14 m². The sampling transects were located in polygons A and B.

Microtopography and hydroperiod

The microtopography of the study site was measured by leveling the microrelief with a mobile arm with a bubble level attached to a 1 m² aluminum square to determine the difference in height of a cross-section from east to west in polygon A (north of the state highway). This method is an alternative to the level hose previously reported (Flores-Verdugo et al. 2007). The leveling was done with respect to the surrounding-elevated terrain and not respect to the mean sea level. The hydroperiod of the wetland was recorded between the months of October 2019 and November 2020, with PVC pipes (1/2" width) buried 30 cm into the soil. Measurements in the same site were not completed from September to November 2020 due to disappearance of the pipes from the site (likely stolen); thus, we completed measurement of the water level at random locations inside the marsh.

Soil

Soil properties were assessed by the edaphic factors gravimetric (ω) and volumetric water content (θ), bulk density (D_a), porosity (P) and saturation (S , Campos-Cascaredo and Moreno-Casasola 2009). In eight samples, we analysed ferrous iron (Fe^{2+}) by a modification of the method by Heaney and Davison (1977) using α,α -bipyridyl as colorimetric indicator in soil aqueous solutions. This measurement is a proxy of the redox status of the soil, as its presence indicates anoxic soil conditions (Kutzbach et al. 2004). A qualitative analysis of the elemental composition of the soil was performed by X-ray spectroscopy with a scanning electron microscope (SEM) in sub-samples of dry soil. The sample support was a Double-Sided Carbon Tape (Electron Microscopy Sciences®) so that C and O were detected in the same proportion in all samples; therefore, they were eliminated from the analysis. The SEM conditions for the acquisition of spectra was 35° elevation of spectrum acquisition, 20.00 kv acceleration, resolution greater than 45 eV, with count / variable of spectra. The values express the percentage of each element with respect to the total sample. We assume that the elemental composition would not change significantly during the study period, so we only analysed the samples from October 2019.

Water chemistry

The physicochemical parameters of surface and pore water were measured at five points in each study site. The temperature (° C), pH, electrical conductivity (mS/cm) and content of total dissolved solids (g/L) were measured with a Hanna® Temp / pH / EC / TDS probe (HI98129); while the oxide reduction potential (mv) with a Hanna® ORP / PH H198121 probe. The probes were previously calibrated with buffers and calibration standards. We aimed to collect a total of 20 surface water and 20 interstitial water samples per sampling event; however, water was not available at all sampling points in October 2019 (saturation below 20 cm from ground surface). All samples were collected at the same points where hydroperiod and physicochemical parameters were measured. Surface water was sampled directly, interstitial water was sampled from 20 cm deep with a 5/16-inch perforated copper tube hose attached to

a manual peristaltic pump. The water samples were stored cold (approximately 4 ° C) in Nalgene® high-density polyethylene bottles. Within the next 6 h, samples for nutrients and ions were filtered with a 0.45 µm pore size Pall® nitrocellulose filter.

Total alkalinity was measured by acid titration. Chemical oxygen demand (COD) was analysed using low range Chemetrix ® COD vials (0-150 mg/L) following the ASTM D 1252-06 test method B. Nitrite, ammonium, orthophosphates and silica were quantified with spectrophotometric methods using UV-Vis spectrophotometer. Nitrites were quantified with modifications of the Strickland and Parsons (1972) method, using three milliliters of sample volume and adapting the operating range from 0.01 to 0.5 mg N-NO₂⁻/L. The ammonium ion (NH₄⁺) was quantified with the salicylate method (Bower and Holm Hansen 1980) with a range of 0.01 to 2.0 mg N-NH₄⁺/L. Orthophosphates (PO₄³⁻) were quantified with the USEPA method 365.3 (EPA 1978) with a range of 0.01 to 1.2 mg P-PO₄⁻³/L. Silica (SiO₂) was quantified by the molybdosilicate colorimetric method (NMX-AA-75-1982).

Nitrate and all ions (Cl⁻, SO₄⁻², Na⁺, Mg²⁺, K⁺, Ca²⁺) were quantified by ion chromatography using an Ion Chromatograph 822 IC (Metrohm) with a limit of detection of 0.1 mg/L. Calibration curves were prepared with Fluka and Sigma Aldrich standards; the integration of results was completed using the software MagIC Net. All results were expressed in mg/L and meq/L of each chemical species. An ionic balance was carried out to verify the accuracy of ion quantifications.

Hydrochemistry

Hydrogeochemical relations were explored to find out water–rock interaction processes, and saturation indexes were estimated to identify dissolution or saturation of mineral. Piper, Chadah and Gibbs diagrams were produced to identify the water family and dominant processes in surface and interstitial water, compared with groundwater from two nearby production wells.

Statistical Analyses

Graphs were made with SPSS 13. In order test our first hypothesis (the phreatotrophic regime of the marsh), we analysed differences between sampling events and water sample origins with two-way ANOVA tests, applying a Tukey HSD post hoc test ($\alpha = 0.05$) for assessing differences in surface, interstitial and groundwater. Once we identified similarities and differences in the three sources of water, we tested our second hypothesis, the effect of the division of the marsh by a highway. We performed two-way ANOVA tests per sampling event (October 2019 and February 2020), for assessing the variability of the parameters by section of the marsh (north and south), and the origin of water samples. In this stage, we compared only surface and interstitial water because we consider that, at this scale, groundwater is regionally stable. Hydrochemistry diagrams were produced with Diagrammes Versión 6.73

Results

Microtopography and hydroperiod.

The microtopography of a representative east-west cross-section with the dominant vegetation is showed in Fig. 2. This cross-section of the marsh is located in the north portion of the marsh, it spans 198 m and the shallowest point from the surrounding uplands was 0.8 m. The steep slopes from 2 to 30 m (east), and then again from 140 to 160 m (west), corresponded to rock outcrops, creating step-like sections that remain moist or saturated, with vegetated patches. The water level (Fig. 3) varied from few centimeters below the ground level to more than 100 cm in November 2020 after the hurricanes Delta and Zeta (October 2020).

Soil

The properties of the soil (bulk density, gravimetric, volumetric content, porosity and saturation) were different between sampling events ($F = 6.368$, $p = 0.016$) and between the north and south portions of the marsh ($F = 14.137$, $p = 0.001$). The bulk density is low as expected in saturated soils, with a very high gravimetric water content and a volumetric content that reflect the same amount of water and soil in this marsh. Table 1 shows the results.

Table 1
Edaphic and physicochemical parameters of the tropical karstic marsh soil: bulk density (D_a), gravimetric (ω) and volumetric (θ) water content, percentage porosity (P) and percentage saturation.

Event	Portion		D_a (g cm ⁻³)	ω (g g ⁻¹)	θ (cm cm ⁻³)	P (%)	S (%)
October 2019	N	Avg	0.23	5.77	1.02	91.30	111.10
		s.d.	0.11	3.17	0.15	4.47	14.15
	S	Avg	0.14	7.87	1.03	94.60	109.50
		s.d.	0.05	2.17	0.12	1.90	13.80
February 2020	N	Avg	0.42	2.95	1.06	84.20	127.20
		s.d.	0.20	1.11	0.08	7.32	10.50
	S	Avg	0.19	6.73	1.05	92.90	112.90
		s.d.	0.08	2.92	0.06	3.00	7.16

The quantification of ferrous iron is showed in Table 2. Its quantification assume total extraction of Fe^{2+} from the soil and it is presented as mg Fe^{2+} / L. We noticed that highest concentrations of Fe^{2+} were found in the south portion of the marsh. The elemental analysis of the samples showed that Ca is the dominant element, followed by Si, Al and Mg, the latter was slightly lower in the north section. The most important differences were the presence of sulfur solely in the south portion, and chloride and iron only in the north portion (Fig. 3).

Table 2
Ferrous iron (mg Fe²⁺/L) from the tropical karstic marsh soil (n = 8).

Event	Portion	Fe ²⁺ (mg/L) ± s.d.
October 2019	N	0.058 ± 0.034
	S	0.104 ± 0.035
February 2020	N	0.756 ± 0.355
	S	0.213 ± 0.024

Water

When exploring the physicochemical parameters by comparing means (and standard deviations) among groundwater (GW), interstitial (IW) and surface water (SW) by sampling event, we noted that almost all parameters had differences between events and among the origin of water samples. In order to test our first hypothesis, we analysed differences between sampling events in the three water samples (surface, interstitial and groundwater). The results are showed in Table 3. We did not observe consistent trends in similarities or differences among groundwater (GW) relative to surface (SW) or interstitial water (IW). For instance, electrical conductivity was similar in GW and IW, possibly because similar amount of dissolved solids, lower in SW due to dilution from rain. pH was similar between GW and SW, more acidic conditions in IW might be attributed to elevated organic acids in the rhizosphere. Moderately reduced condition in GW (≈ 250 mV) but reduced conditions in SW (≈ 90 mV) and IW (≈ -16 mV). Reductive conditions in the rhizosphere (SW and IW) are also supported by low nitrates and sulfates concentration, together with high alkalinity in IW. Mg and Ca were also different (greater in GW and IW), but we interpret these results as the interaction with rock (GW) and precipitation and biogenic carbonates (IW).

After identifying differences among the three types of water, we explored the differences between the two portions of the marsh, relative to dividing the highway as a physical barrier. When comparing the two portions of the marsh only of SW and IW, we found that IW was higher in electrical conductivity, slightly more acidic and with reducing conditions compared to SW. Interestingly; pH was different by comparing the portions of the marsh, lower in the south. In case of the nutrients, ammonium was greater in IW water, assumed the result of intense organic matter decomposition, but was not different by portions. The DIN had a different trend; it was higher in the surface water in October 2019, the opposite February 2020 (higher in in the interstitial water).

Silica was very variable among samples, but the COD was similar between SW and IW; however, in February 2019 (with higher flood level) we observed higher silica in the north portion, and higher COD in IW. Alkalinity was always higher in IW, not different by portions. The ions were also mainly different by water origin, only chloride was different in February 2020, higher in the south portion. Sulfates were higher in SW in October 2019, but the opposite in February 2020 (SW < IW). Mg and Ca were always

higher in IW, regardless of the portion. The two-way ANOVA tests results are showed in Table 4 and the complete results are provided in Supplementary Table 1. Box-plot graphs of redox potential (Fig. 5), bicarbonates (Fig. 6), sulfates (Fig. 6) and calcium (Fig. 7) are showed by origin of water, without considering separation by portions of the karstic marsh.

Table 3

Results of the two-way ANOVA test of water by sampling event (October 2019 and February 2020) and origin (groundwater, interstitial and surface water) in the tropical karstic marsh of La Esperanza, Quintana Roo, México. Water samples with different letters (Tukey HSD) were statistically different ($\alpha = 0.05$). *n.s.* = non-significant.

Parameter	Sampling event	Origin	Tukey HSD
Temperature	F = 6.29, p = 0.014	<i>n.s.</i>	
E.C.	F = 8.397, p = 0.005	F = 59.287, p < 0.001	GW = IW ^a > SW ^b
pH	F = 4.402, p = 0.04	F = 81.97, p < 0.001	SW = GW ^a > IW ^b
ORP	F = 16.72, p < 0.001	F = 64.663, p < 0.001	GW ^a > SW ^b > IW ^c
Nitrites	F = 19.512, p < 0.001	<i>n.s.</i>	
Nitrates	<i>n.s.</i>	F = 4.252, p = 0.02	GW ^a > IW = SW ^b
Ammonium	F = 5.008, p = 0.029	<i>n.s.</i>	
TP	F = 6.839, p = 0.017	<i>n.s.</i>	
COD	F = 29.098, p < 0.001	<i>n.s.</i>	
Silica	F = 4.844, p = 0.031	<i>n.s.</i>	
Alkalinity	F = 4.019, p = 0.049	F = 20.286, p < 0.001	IW ^a > GW = SW ^b
Chloride	F = 14.177, p < 0.001	<i>n.s.</i>	
Sulfates	F = 19.525, p < 0.001	F = 11.537, p < 0.001	GW ^a > IW = SW ^b
Magnesium	<i>n.s.</i>	F = 20.004, p < 0.001	IW ^a > GW = SW ^b
Potassium	F = 5.928, p = 0.028	F = 7.053, p = 0.018	
Calcium	<i>n.s.</i>	F = 16.915, p < 0.001	IW ^a = GW ^{ab} = SW ^b

Table 4

Results of the two-way ANOVA test of water by portions (north and south), and origin (groundwater, interstitial and surface water) in the tropical karstic marsh of La Esperanza, Quintana Roo, México. *n.s* = non-significant ($\alpha = 0.05$).

Parameter	Sampling event	Portion	Origin
Temperature	October 2019	<i>n.s</i>	<i>n.s</i>
	February 2020		F = 4.83, p = 0.034
E.C.	October 2019	<i>n.s</i>	F = 38.47, p < 0.001
	February 2020		F = 313.22, p < 0.001
pH	October 2019	F = 5.64, p = 0.025	F = 54.34, p < 0.001
	February 2020	F = 6.34, p = 0.016	F = 110.7, p < 0.001
ORP	October 2019	<i>n.s</i>	F = 28.2, p < 0.001
	February 2020		F = 65.23, p < 0.001
Ammonium	October 2019	<i>n.s</i>	<i>n.s</i>
	February 2020		F = 9.38, p = 0.004
Phosphates	October 2019	<i>n.s</i>	<i>n.s</i>
	February 2020		
DIN	October 2019	<i>n.s</i>	F = 5.04, p = 0.033
	February 2020		F = 9.25, p = 0.004
COD	October 2019	<i>n.s</i>	<i>n.s</i>
	February 2020		F = 6.23, p = 0.017
Silica	October 2019	<i>n.s</i>	<i>n.s</i>
	February 2020	F = 4.75, p = 0.036	
Alkalinity	October 2019	<i>n.s</i>	F = 73.79, p < 0.001
	February 2020		F = 7.62, p = 0.009
Chloride	October 2019	<i>n.s</i>	<i>n.s</i>
	February 2020	F = 5.074, p = 0.030	
Sulfates	October 2019	<i>n.s</i>	F = 44.93, p < 0.001
	February 2020		F = 74.01, p < 0.001
Magnesium	October 2019	<i>n.s</i>	F = 14.53, p < 0.001
	February 2020		F = 27.771, p < 0.001

Parameter	Sampling event	Portion	Origin
Calcium	October 2019	<i>n.s</i>	F = 36.76, p < 0.001
	February 2020		F = 7.56, p = 0.009

Hydrochemistry

The chemical composition of the water is of calcium bicarbonate type, with a chemical composition of cations $\text{Ca}^{2+} > \text{Mg}^{2+} \geq \text{Na}^+$. The anions were $\text{HCO}_3^- \gg \text{Cl}^- > \text{SO}_4^{2-}$ (Fig. 8). As a unit, the marsh has a single type of water; however, there are slight differences between SW and IW. The composition of IW appears to be more homogeneous in low flood conditions (October 2019), whereas in high flood conditions (February 2020) its chemical composition was more variable. The most evident increase the HCO_3^- concentration while SO_4^{3-} has a slight decrease. GW plots slightly lower in K but higher in Na^+ ; yet, within the same quadrant than all other samples; suggesting that all the water have the same origin, most likely groundwater.

Saturation index

The minerals aragonite, calcite and dolomite showed oscillation between saturation and under-saturation, whereas anhydrite, gypsum and halite in both sampling events were under-saturated (Fig. 8). Thus, the dissolution of carbonate rocks is the dominant process in this tropical karstic marsh. Although, it alternates in a very slender threshold depending on the origin of the water (SW or IW) and showed certain temporal variability. The Chadah diagram (Fig. 9) indicates that both SW and IW in both sampling events plot together with GW and both fall into the section of recharge processes. Finally, the Gibbs diagram (Fig. 10) pointed towards two dominant processes, evaporation and rock dissolution.

Discussion

We accept our hypothesis that tropical karstic marshes locally called sabanas are phreatotrophic wetlands, the hydrochemical data demonstrated that groundwater is the dominant water source in this marsh. Stein et al. (2004) reported that faults may be the conduit responsible for water delivery into wetlands; thus, supporting the assumption of GW provenance for this tropical karstic marsh. The water of the marsh of La Esperanza is calcium bicarbonate type regardless the origin of the sample. We consider that the homogeneous chemical conditions in low flood conditions reflect stable hydraulic conditions, which changed in response to seasonal events (such as frontal rains), the presence of vegetation (Yang et al. 2008) and hydrodynamics (Karstens et al. 2015). It is important to mention that all GW eventually was in the ground surface short after it precipitated, so the SW and IW plotting in the recharge section of the Chadah diagram is attributed to the transit of water from the surface to the vadose zone and the into the shallow aquifer. The water moving through the vadose zone into the saturated zone, interacts with sedimentary rock, dissolving carbonates and as HCO_3^- and Ca^{2+} (Ravikumar et al. 2017) as showed by

the saturation indexes. IW has a more defined chemical composition, the carbonate minerals are around equilibrium, but it also acquired characteristics of infiltrating water that has passed through the soil, such as acidic pH, reductive conditions and organic matter decomposition (Craft et al. 1991). Similar electrical conductivity in GW and IW is assumed as comparable amount of dissolved solids was found in those compartments; the former due to the water-rock interaction (Smith et al. 2020), the latter due to the solubilisation of several substances around the rhizosphere (Raghavendra et al. 2016). In summary, this marsh is a good site to evaluate in detail the water infiltration process and the chemical changes that occur in the water during this process.

Changes in EC in SW are interpreted as entrance of precipitation with the consequent dilution effect in the previously existent surface water (McDonough et al. 2020). Slightly more acidic pH in IW might be attributed to elevated organic acids and secreted substances by organisms in the rhizosphere (Lynch et al. 2012). The water oxidation-reduction potential, together with the behaviour of redox-sensitive species and ferrous iron in the soil, give additional hints of the most probable processes occurring inside the marsh. For instance, moderately reduced condition in GW (≈ 250 mV) enable nitrates and sulfates presence in GW; whereas reduced conditions in SW (≈ 90 mV) and IW (≈ -16 mV) indicate that most nitrate has been reduced, supported by very low $\text{N-NO}_3^-/\text{L}$ concentrations measured in SW and IW (Close et al. 2016). In addition, ammonium concentrations increase in SW and IW because of organic matter decay, mineralization, retaining or transformation of NH_4^+ (Gribsholt et al. 2006). Ammonia could also be a product of nitrogen fixation, since high nitrogen fixation (expressed as nitrogenase activity) has been described in karstic marshes (Rejmánková and Komárková 2000). DIN in low flood conditions (October 2019) was higher in SW, but changed to higher DIN in IW with greater flood conditions (February 2020). We are not able to estimate N transformation rates; however, we consider that high DIN in SW is the result of water evaporation from the marsh, yielding greater concentration of N in a reduced water volume. The water saturated, anoxic soil supported by the ferrous iron tests in soil, provides evidence of reductive conditions in the rhizosphere, which allowed sulphate reduction; thus, promoting high alkalinity in IW (Norton et al. 1988, Pester et al. 2012). To the best of our knowledge, high alkalinity (≥ 10 mM HCO_3^-) can inhibit growth of some plants (Cartmill et al. 2008); the alkalinity in this marsh was around $6.2 (\pm 2.4$ mM HCO_3^-) and did not seem to affect the growth of grasses and sedges. High alkalinity in wetlands has been identified as a sink of atmospheric CO_2 (Saderne et al. 2021) accounting for an overlooked component of the C cycle and storage in wetlands.

Low phosphates concentrations in karstic ecosystems is attributed to Ca- and Fe/Al-bound P, as they vary spatially and seasonally (Gao et al. 2019). With the measured pH-Eh, the expected P species is H_2PO_4^- (di-hydrogen phosphate ion, Takeno 2005). With oxygen deficiency and stagnant conditions, phosphorus can be released back from sediments to the water column and with oscillating flood conditions; sediments rich in Fe and Mn are capable of becoming sinks again (Karstens et al. 2015).

The similar COD between SW and IW reveals that with stable hydraulic conditions, the water in the rhizosphere and above the ground had similar amount of organic matter. This situation changed in

February 2019 (higher flood level), when higher COD in IW indicated increase in dissolved organic matter in the rhizosphere. High COD has also been associated to elevated sulfate reduction and inhibition of some trophic groups by H_2S (Barber and Stuckey 2000). This situation was likely occurring in the karst marsh as low sulfate concentrations were measured with high flood. High COD/N ratio (600 to 1800 in La Esperanza marsh) relates to very active denitrifiers, yielding the low nitrate conditions observed, due to high availability of organic matter as electron donor (Hou et al. 2018).

In case of silica, its variable concentration can be related to the hydrology of the marsh and the dominant plant species. Both Grasses (Poaceae) and sedges (Cyperaceae) are Si-accumulating species (Struyf and Conley, 2009) which can release it back to the environment after biomass decay. Marshes are recognized as silica recyclers and re-suppliers (Struyf et al. 2005). We do not know microalgae Si demand, but it is reported that some microalgae can regulate fluxes and DSi concentrations in aquatic environments for as long as six months (Sigmon and Cahoon, 1997). We cannot provide plausible explanations because we ignore the microalgae composition. The knowledge of Si cycling in wetlands is incomplete (Struyf et al. 2005); this topic requires further research, especially due to the relevance of Si as groundwater tracer.

The under-saturation of the evaporitic minerals (anhydrite, gypsum and halite) suggest that those rocks are not dominant underlying this marsh; however, the trend might be opposite in southern areas of the Holbox Fracture system, where other geological formations are dominated by gypsum (Perry et al. 2002). Aragonite, calcite and dolomite had variable trends, there might exist precipitation, deposition and resuspension of biogenic carbonates (Morse 1986) as observed for the variability in saturation indexes between sampling events. The Chadah diagram clearly points towards recharge processes. Additionally, the Gibbs diagram associates some water samples with rock dissolution. Rainwater is the main entrance of water into the aquifer, large part of the precipitation rapidly infiltrates until reaching the saturated zone of the aquifer (Lases-Hernandez et al. 2019). Then, as the phreatic level rises because of increases in the hydraulic head, the GW already in contact with sedimentary rock, increases its interaction with calcite and dolomite, enhancing water erosion (Dai et al. 2017), increasing the dissolved solids in IW and even in SW as the water table elevates above the ground level. Finally, as indicated by the Gibbs diagram, evaporation is another dominant process in the marsh. This evaporation is supported by the increase in dissolved solid in SW during low flood conditions. It is important to mention that, what we consider SW, is a combination of groundwater discharged into the marsh (Gondwe et al. 2010) in addition to intercepted precipitation inside the marsh; thus, the evaporation process affects SW after the combination of the two main processes above-mentioned, yielding water subject to evaporation and rock dissolution.

Regarding our second hypothesis, we have less evidence that the highway had an influence on some parameters in the marsh. For instance, ferrous iron in soil was present in both portions, with higher concentration in the south portion, suggesting prolonged or predominant anoxic conditions. Nonetheless, X-ray spectroscopy suggested that iron (and chloride) were present only in the north portion. This last piece of evidence could be inferred as the effect of surface runoff from the highway. Road traffic has been related to the production and deposition of dust with metals and elements related to engine combustion and tires wear (Adachi and Tainosho 2004, Aguilera et al. 2018). The production of these

residues, together with the preferential flow northward of the water (Perry et al. 2002, McKay et al. 2020), help explaining its presence only in one side of the road, partially supporting our hypothesis that the highway caused changes in the biogeochemistry of the marsh. We were not able to find effects of the highway in the hydrology of the marsh, the similar flood level in both sides of the road suggest that there is not any apparent hydraulic cut so far. We cannot discuss the fact that the largest polygon located at the north of the highway has something to do with changes in the groundwater flow, discharge or changes in the microtopography.

The soil of this tropical karstic marsh has very high water retention capacity, holding as much as seven grams of water per gram of soil. This condition is not exclusive of marshes; it is a common feature across all types of wetlands (Campos et al. 2011). The soil in these marshes do not develop deep profiles (Fragoso-Servón et al. 2020). Assuming that the mean soil depth in the marsh is 50 cm, with an average apparent density of 0.25 g m^{-3} (250 kg m^{-3}), there are approximately 97,173,142.5 kg of soil in the marsh with an average gravimetric water capacity of 5.8 kg of water per kg of soil. This represents an estimated water retention capacity in the soil of this marsh of $563,604 \text{ m}^3$ of water (563.6 million liters). When the water column is above the ground such as in November 2020 (1 m flood level after Hurricanes Delta and Zeta), the micro-basin of this karstic wetland would store at least $700,000 \text{ m}^3$ of surface water, in addition to the water stored in the soil. This goes to show the magnitude and relevance of the provisioning and supporting services that tropical karstic marshes provide just by existing, and the importance of maintaining in good conditions for keeping these environmental services, commonly acknowledged but barely understood and quantified (Shepard et al. 2011).

The elemental composition of the soil clearly reflect its sedimentary origin, with calcium as the element comprising 90% of the mineral fraction. The presence of Si and Mg are also result of rock weathering (Cejudo et al. 2020). In case of Al, kaolinite is naturally present in young and intermediate karstic landscapes (Bautista et al. 2011) and it is commonly in aluminosilicates and oxide minerals. Its availability do not depend of the redox potential of the environment and is one of the most prevalent contaminants directly attributed to human activities and potentially toxic to aquatic biota (Gensemer and Playle, 1999). Its deposition in the soil is considered result of weathering and mobilization of clays (Cabadas et al. 2010). This element and Si deserves much more attention in wetlands biogeochemistry.

Conclusions

The tropical karstic marshes of the Yucatan peninsula called *sabanas* are groundwater-fed wetlands in which reductive conditions regulate processes such as denitrification, sulfate reduction, alkalinity production, high organic matter and elevated content of minerals from sedimentary rock dissolution. Low PO_4^{3-} concentrations are attributed to Ca-bound P deposited in sediments. The hydrochemical diagrams showed recharge processes together with evaporation and rock dissolution. This means that precipitation infiltrates into the phreatic aquifer (*i.e.* groundwater recharge). Once the water table elevates above the ground level, it controls the hydroperiod and hydrodynamic of the marsh, showing the water-rock

interaction of the discharged groundwater, in which there is evaporation of the water exposed at the surface. This marsh is a good site for studying infiltration and recharge processes, as well as the chemical changes occurring to water as it recharges local aquifers. We did not find a negative effect of the highway on the hydrology of the marsh. This marsh provides important provisioning and supporting ecosystemic services as it can store of 563,604 m³ of water in the soil and around 700,000 m³ of surface water; in addition to intense nutrient cycling (N and P), likely with effective N removal. The Si and Al cycles deserves much more attention in tropical wetlands.

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Data availability: The dataset generated and analyzed during the current study is available in the [Institutional Repository CICY] *upon acceptance*.

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Figures

Figure 1

Study site, tropical karstic marsh “La Esperanza”, Quintana Roo, Mexico

Figure 2

Microtopography and dominant vegetation from an east-west cross-section in the tropical karstic marsh of La Esperanza, Quintana Roo, Mexico. Shaded areas represent 25 m sections with dominant plant species

Figure 3

Hydroperiod of the tropical karstic marsh of La Esperanza, Quintana Roo, Mexico. Hurricanes Delta (October 7th) and Zeta (October 27th)

Figure 4

Elemental composition of soil by X-ray spectroscopy measured from the tropical karstic marsh of La Esperanza, Quintana Roo, México

Figure 5

Box-plot of redox potential (mV) in surface, interstitial and groundwater in the tropical karstic marsh La Esperanza, Quintana Roo, México.

Figure 6

Box-plot of bicarbonates (mg HCO₃⁻/L) (mV) in surface, interstitial and groundwater in the tropical karstic marsh La Esperanza, Quintana Roo, México.

Figure 7

Box-plot of sulfates (mg S-SO₄³⁻/L) in surface, interstitial and groundwater in the tropical karstic marsh La Esperanza, Quintana Roo, México.

Figure 8

Box-plot of calcium (mg Ca²⁺/L) in surface, interstitial and groundwater in the tropical karstic marsh La Esperanza, Quintana Roo, México.

Figure 9

Piper diagram of surface, interstitial and groundwater in the tropical karstic marsh La Esperanza, Quintana Roo, México.

Figure 10

Saturation index of minerals from surface, interstitial and groundwater in the tropical karstic marsh La Esperanza, Quintana Roo, México. Arg-aragonite, Cal-calcite, Dol-dolomite, Anh-anhydrite, Gp-gypsum, Hl-halite.

Figure 11

Chadah diagram of surface, interstitial and groundwater in the tropical karstic marsh La Esperanza, Quintana Roo, México.

Figure 12

Gibbs diagram of surface, interstitial and groundwater in the tropical karstic marsh La Esperanza, Quintana Roo, México.