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Three-Year Follow-Up Assessment of Anthropogenic Contamination in the Nichupte Lagoon

Jorge Herrera-Silveira [1], Flor Arcega-Cabrera [2,*], Karina León-Aguirre [2], Elizabeth Lamas-Cosio [2], Ismael Oceguera-Vargas [2], Elsa Noreña-Barroso [2], Daniela Medina-Euán [1] and Claudia Teutli-Hernández [3]

1 Departamento de Recursos del Mar, CINVESTAV-Mérida, Km.6 Antigua Carretera a Progreso, Cordemex, Mérida 97310, Yucatán, Mexico; jorge.herrera@cinvestav.mx (J.H.-S.); daniela_medina96@hotmail.com (D.M.-E.)

2 Unidad de Química en Sisal, Facultad de Química, Universidad Nacional Autónoma de México, Puerto de Abrigo Sisal 97355, Yucatán, Mexico; kgla27@outlook.com (K.L.-A.); e.lamas89@hotmail.com (E.L.-C.); oceguera13@gmail.com (I.O.-V.); enorena@unam.mx (E.N.-B.)

3 Escuela Nacional de Estudios Superiores Unidad Mérida, Tablaje Catastral No. 6998, Carretera Mérida-Tetiz Km 4.5, Ucú 97357, Yucatán, Mexico; teutliclaudia@gmail.com

* Correspondence: farcega@unam.mx

Abstract: Tourism still represents a means of generating revenues in the coastal areas in the Mexican Caribbean, despite the growing concern about the social and environmental impacts. The Nichupte Lagoon System (NLS), the most representative lagoon of Quintana Roo State for being in the middle of Cancun's hotel development, has experienced a continuous drop-off in its water quality due to several factors, including dredging and wastewater discharges from different anthropogenic activities, which modify the flux of nutrients, increase the number of pathogenic microorganisms, and promote physicochemical changes in this ecosystem. Three sampling campaigns (2018, 2019, and 2020) were carried out in the NLS in August, which is the month of greatest tourist occupancy. To evidence the presence of anthropogenic wastewater in the NLS, the caffeine tracer was used, and to determine the water quality, 43 sampling stations were monitored for "in situ" physicochemical parameters (salinity and dissolved oxygen), and water samples were collected for the quantification of nutrients (NO_2^- + NO_3^-, NH_4^+, SRP and SRSi) and chlorophyll-a (Chl-*a*). For data analysis, the lagoon was subdivided into five zones (ZI, ZII, ZIII, ZIV, and ZV). Caffeine spatial and time variation evidence (1) the presence of anthropogenic wastewater in all areas of the NLS probably resulting from the tourist activity, and (2) wastewater presence is directly influenced by the coupling of the hydrological changes driven by anomalous rain events and the number of tourists. This same tendency was observed for nutrients that increased from 2018 to 2019 and the trophic state changed from oligotrophic to hypertrophic in all areas, as a result of previous anomalous precipitations in 2018, followed by normal precipitations in 2019. From 2019 to 2020, the nutrients decreased due to the drop in tourism due to COVID-19, promoting fewer nutrients in the lagoon, but, also coupled with an anomalous precipitation event (Cristobal storm), resulted in a dilution phenomenon and an oligotrophic state. The cluster analysis indicated that the least similar zones in the lagoon were the ZI and ZV due to their geomorphology that restricts the connection with the rest of the system. Principal component analysis revealed that wastewater presence evidenced by the caffeine tracer had a positive association with dissolved oxygen and chlorophyll-a, indicating that the arrival of nutrients from wastewater amongst other sources promotes algal growth, but this could develop into an eutrophic or hypertrophic state under normal precipitation conditions as seen in 2019. This study shows the relevance of monitoring in time of vulnerable karstic systems that could be affected by anthropogenic contamination from wastewater inputs, stressing the urgent need for efficient wastewater treatment in the area. The tourist industry in coastal karstic lagoons such as the NLS must have a Wastewater Treatment Program as a compensation measure for the anthropic pressure that is negatively changing the water quality of this highly relevant socio-environmental system.

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1. Introduction

The tourism industry has promoted direct and massive alteration of the coastal environment [1]. The state of Quintana Roo, Mexico, has been economically dependent on the tourism industry since the mid-1970s when Cancun and the Rivera Maya were created. Up to the late 1960s, Cancun was an uninhabited barrier island formed by dunes and unexplored beaches, within a landscape of mangroves and virgin rainforests [2]. The city of Cancun, State of Quintana Roo, is now a major hub for tourism activities, where many of them are carried out in natural protected areas, which are particularly vulnerable owing to the proximity of urban zones [3].

The Cancun hotel zone was built on a small spit, a relic fringing reef, separating the mainland of the peninsula with a shallow coastal lagoon: the Nichupte Lagoon [4,5]. The Nichupte Lagoon System (NLS) is an oligotrophic system that embraces an area of about 48 km^2, with depths varying between 0.3 and 4.5 m. It is located on the northeast coast of the Yucatan Peninsula on the coastline corresponding to the Caribbean Sea [6] it contains marine water and sandy sediments covered by seagrasses and algae and is one of the attractions that has made Cancun an important tourist place in Mexico [7].

Dismally, the NLS is subject to all the environmental negative changes typical of the urban development and recreational activities on the coastline, coupled with the growing urban expansion in the surroundings. Due to the hydrological connectivity underground that prevails in this karst system, it receives continental water discharges year round with a higher volume during the rainy season [8–10]. Incoming water carries out substances produced by land-based activities that have the potential to negatively change the water quality and ecosystem function [11].

The population growth in Quintana Roo state has caused an increase in the concentration of nutrients in the coastal aquifer, which are subsequently discharged into the coastal ecosystems of the area through the discharge of groundwater that maintains connectivity between inland anthropogenic activities and marine aquatic ecosystems [12]. One of the main activities that has affected Nichupte is the continual discharge of sewage, which has increased the amount of nutrients resulting in eutrophication [7]. This intense tourist activity gave rise to major environmental problems: loss of mangrove forests, swamps, sand dunes, and beaches; eutrophication of coastal lagoons; degradation of water quality; and changes in the coastline due to harbor and marina construction [13]. General changes in land use from the construction of hotels on these fragile coastal lands have resulted in increased sediment run-off, to which coral reefs are particularly sensitive, extensive deforestation, and the underground supply of water enriched with nitrogen and phosphorus from wastewater generated by hotels and golf courses, which result in alterations affecting the health of the ecosystem [1].

Currently, many parts of the NLS are seriously polluted and give off foul odors derived from the discharging of wastewater from hotels and shopping malls throughout Cancun [14]. Wastewater treatment plants in the hotel zone are on the island next to the lagoon, along with the rainwater drainage conducted to discharge over the lagoon. About 80% of the area of the island has been paved, which prevents the penetration of water from rain on the ground. Thus, when it drains, the same water carries heavy metals with it and other chemical compounds soluble or insoluble in the lagoon [15]. A great vulnerability of the Nichupte lagoon is the high residence time of the water and the fact that it only has two narrow inlets located as the only ways to communicate with the sea. This implies a restricted circulation pattern that allows the accumulation of organic matter, nutrients, and some other contaminants [11]. However, the lack of long-term monitoring programs in the

NLS makes it challenging to determine the resistance, vulnerability, and resilience of the area [13].

To assess how human activities are affecting the water quality in the NLS, baseline information is required. This research aims to confirm wastewater inputs (probably from hotels and urban settlements) by means of caffeine detection (anthropogenic tracer) and to determine water quality by measuring physicochemical parameters and nutrients and obtaining the TRIX index. Finally, the goal to capture the concentration variation related to either the number of tourists or/and the environmental conditions was also addressed. The results of this research will be relevant since the NLS lacks proper management and restoration programs and could transit from oligotrophic to eutrophic conditions, provoking the loss of biodiversity and functionality [11].

Thus, we analyze spatial and temporal variations in nutrients and caffeine concentrations using data from three continuous years and five zones of the lagoon. This information will enable better decision-making, creation, and modification of monitoring plans and actions for the management, rehabilitation, and conservation of the NLS.

2. Materials and Methods

2.1. Description of the Study Area

The Nichupte Lagoon System (NLS) is a coastal system in the state of Quintana Roo northeast of the Yucatan Peninsula (Figure 1); at lat. 21°02′ to 21°06′ N and long. 86°46′ to 86°50′ W [16].

The SLNB interacts with the Caribbean Sea through two openings: the Cancún Inlet located to the north of the complex and the inlet at Punta Nizuc in the south [17]. This system is a coastal lagoon complex consisting of five interconnected water bodies, with Laguna Nichupte being the largest, comprising approximately 46% of the area. Its four peripheral lagoons are Laguna de Bojorquez, located in the northwest of the system; Río Inglés is situated at the southwestern end and two smaller lagoons, Somosaya and La Caleta are found in the central–western and southern extremes, respectively [11].

The NLS is a low-energy system with little exchange of water with the open sea and a small (<16 cm) tidal range, with an estimated flushing time that takes from 1 to 3 years [11]. The NLS contains marine water, with salinity gradients of 24 to 30 PSU, as well as DO and pH values like the marine environment; sandy sediments covered by patches of grass and mangrove growths at the shores. The mangrove area that surrounds the Nichupte Lagoon has been declared a Natural Protected Area in terms of its flora and fauna. The climate of the region corresponds to subtype Aw1, warm subhumid, with an annual mean atmospheric temperature greater than 22 °C and a temperature of the coldest month greater than 18 °C. It experiences abundant rainfall in summer and scarce rainfall in winter, with the precipitation of the driest month being less than 60 mm. In the three-year follow-up sampling period in August 2018 (27th and 28th), 2019 (27th and 28th), and 2020 (25th and 26th) in rainy season, the mean water temperature went 31.9 °C in 2018, 31.5 °C in 2019, and 29.5 °C in 2020 and the monthly average rainfall for 2018 were 23.5 mm (23.4 to 23.6 mm), for 2019 were 54.1 mm (2.8 to 111 mm), and for 2020 19.8 mm (3.4 to 43.0 mm).

Based on the morphological characteristics of the NLS and with the aim of improving the design and distribution of the sampling stations, for this study, an 'a priori' zoning was carried out, considering criteria such as water exchange constriction and limitation between different areas. This zoning resulted in five zones distributed as follows: Bojorquez (ZI); North Zone (ZII); Central Zone (ZIII); South Zone (ZIV), and Río Inglés (ZV) (Figure 1).

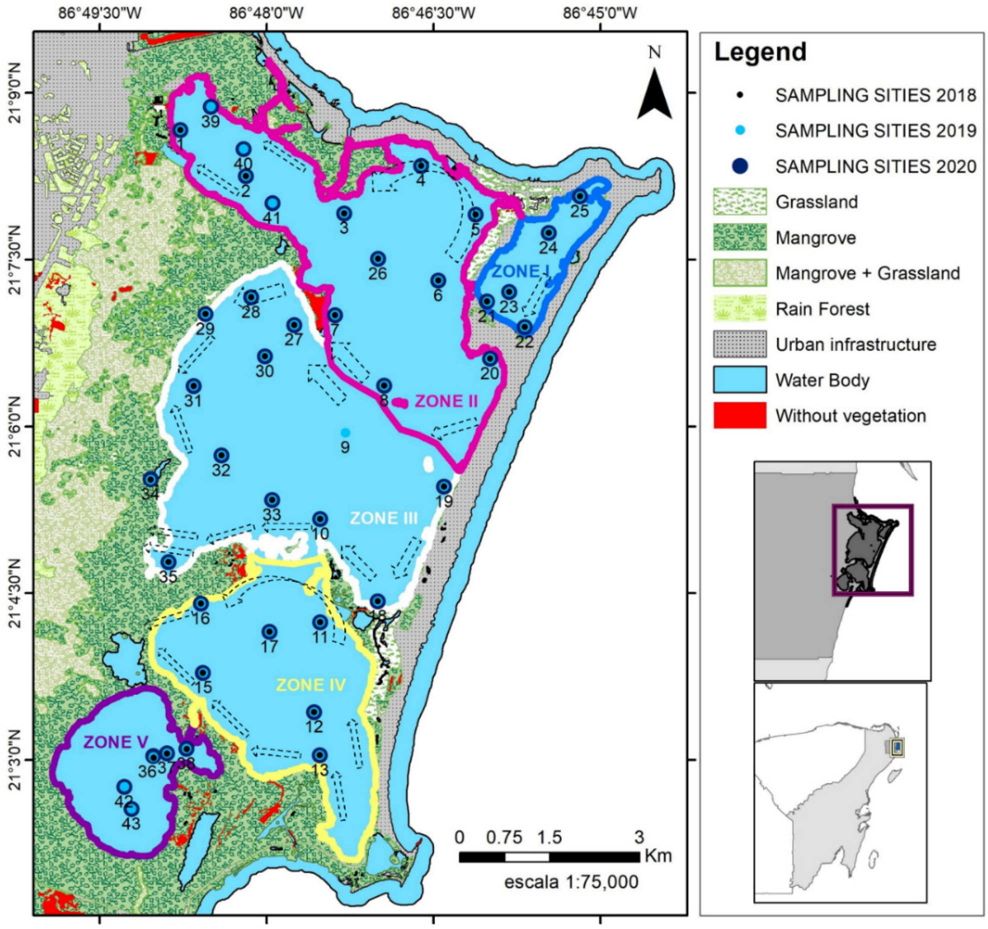


Figure 1. Location of the sampling stations along the five main zones of the Nichupte Lagoon System and the main current patterns in the lagoon (represented by the dashed arrows) adapted from the numerical model by [11]. Land use is a modification of the metadata obtained from the National Biodiversity Information System, SNIB for its initials in Spanish [18].

2.2. Water Sampling and Analysis

For the NLS water quality analysis, 43 stations were selected based on previously defined spatial criteria and the hydrological influence (Figure 1). Measurements of water physicochemical parameters of dissolved oxygen (mg L^{-1}) and salinity (ups) were measured in situ with a multiparameter sonde (YSI Professional Plus), previously calibrated according to manufacturer guidelines. To determine the trophic state of the water, surface water samples were collected at each site using a 2L Van Dorn bottle. Then, 1L of the sample was stored in dark polyethylene and transported under refrigeration (4 °C) for subsequent processing in the laboratory. Subsequently, it was filtered in the laboratory through 0.45 mm pore Millipore membranes for the determination of chlorophyll-a according to the method of acetone (90%) extraction [19]. The remaining 500 mL were used for analyses of dissolved nutrients (nitrite NO_2^-; nitrate NO_3^-; ammonium, NH_4^+; soluble reactive phosphate, SRP; and soluble reactive silicate, SRSi) [20,21], using a spectrophotometer (Cary 60 Agilent Technologies-Agilent, Santa Clara CA, USA) equipped with UV/VIS.

Caffeine was quantified following the method described by [22]; quality control for this method includes a limit of detection (LD) of 12.1 ng L^{-1}. Caffeine was extracted by solid phase extraction (SPE) and determined by gas chromatography coupled to mass spectrometry (GC–MS). For SPE, 500 mg/6 mL Strata-X cartridges (Phenomenex, 8B-S100-HCH) were used and conditioned by eluting sequentially 10 mL of ethyl acetate, 10 mL of methanol, and 10 mL of Type I water. For extraction, 1 L of sample was passed through the cartridge with a flow of 10–15 mL min^{-1}. After sample loading, cartridges were washed with 10 mL of Type I water and dried under vacuum for approximately 120 min. Once extracted, the analyte was recovered, eluting 15 mL of ethyl acetate, and the extract was evaporated using a gentle nitrogen flow. Samples were then placed in 2 mL vials and caffeine was quantified by GC–MS operated in electron impact (EI) ionization mode and equipped with an automatic liquid sampler (Agilent Technologies 6850 Series II GC, 5975B VL MSD and 7683B ALS, respectively). Injections were carried out in splitless mode (0.5 min) at 280 °C. Chromatographic separation was performed using a Phenomenex Zebron ZB-5MSi capillary column (30 mm Å~0.25 mm with 0.25 µm of film thickness). The carrier gas was He (ultra-pure grade) with a flow rate of 0.8 mL/min; the initial oven temperature was 60 °C for 1 min, then increased from 10 °C/min to 300 °C (hold time 15 min). The transfer line temperature was 280 ÅãC. Mass spectra (*m*/*z* 50–550) were recorded at a rate of five scans per second at 70 eV. Mass spectrometric analysis for quantitative determination was performed by the selected ion monitoring (SIM Mode) of two characteristic fragment ions (*m*/*z*), 194 and 109. Analytical quality control included procedural blanks and calibration curves using the analytical standard Caffeine 99% (Fluka, Switzerland). All solvents were of chromatographic grade. The limit of detection (LOD) and limit of quantification (LOQ) were calculated based on the standard deviation of the response (Sy) of the curve and the slope of the calibration curve (S), LOD = 3.3(Sy/S) and LOQ = 10(Sy/S), which were, respectively, 12.1 ng L^{-1} and 36.7 ng L^{-1}. The identification of analytes in the samples was based on the retention time, presence of the qualifier ion, and the ratios between quantitation and qualifier ions according to those observed in calibration solutions.

2.3. Data Analyses

To determine the trophic state of the water, the Trophic State Index (TRIX) was used, which allowed the estimation of the degree of deterioration of the study area. The variables Dissolved Oxygen, Chl-*a*, NO_2^- + NO_3^-, NH_4^+, and FRS were used, which have been reported as the most important in identifying the trophic status of coastal ecosystems. The TRIX index is determined according to the equation proposed by [23].

$$TRIX = \frac{[\log(\mathrm{Chl} - \mathrm{a} * |\%\mathrm{DO}| * \mathrm{DIN} * \mathrm{P} * \mathrm{a}]}{b}$$

where Chl-*a* = Chlorophyll-*a* (µg L^{-1}), %DO = Absolute deviation of % dissolved oxygen saturation (100-DO%), DIN = dissolved inorganic nitrogen (µmol L^{-1}), and P = soluble reactive phosphorus (µmol L^{-1}). The parameters a = 1.5 and b = 1.2 are scale coefficients that were included to set the lower limit value of the index and the length of the related trophic scale from zero to ten; the meaning of the values is shown in Table 1.

Table 1. General ranking of TRIX assessment [23].

TRIX Value	Tropic Status	Water Quality	Condition
2–4	Oligotrophic	Very good	Low production, low trophic level
4–5	Mesotrophic	Good	Moderate production, medium trophic level
5–6	Eutrophic	Regular	Between moderate and high production, medium-high trophic level
6–8	Hypertrophic	Bad	High production, high trophic level

Land use in the map from Figure 1 is a modification of the metadata obtained from the National Biodiversity Information System, SNIB, for its initials in Spanish [18].

Interpolation maps for caffeine concentrations were created using simple kriging with a normal score transformation in ArcMap 10.5. The scale for interpolation was selected as follows: the minimum value corresponds to the lower value of the box and whisker plot for the three years (4.71 ng L^{-1}); the maximum value corresponds to the higher value (42.4 ng L^{-1}).

In this study, we measured the parameters and compared them during the three-year follow-up to identify changes over time and along the zones of the lagoon. The number of tourists was downloaded from the National Statistical Information System of the Tourism Sector of Mexico [24].

Prior to performing the statistical analysis on the dataset using Origin 2019 software (OriginLab Inc., Northampton, MA, USA), the Shapiro–Wilk test was applied to examine the normality. The Kruskal–Wallis test was implemented to determine whether there were statistically significant differences at the 95% confidence level.

To observe similarities by areas of the NSL, a cluster analysis was carried out with the Primer 6 program according to the method of [25]. To find out which variable had the greatest relationship with caffeine, a principal component analysis (PCA) was carried out; in this case, the car library of the R program was used.

3. Results and Discussion

Descriptive statistics of caffeine and nutrients in the Nichupte Lagoon System are detailed in Table 2.

The presence of caffeine was detected in all study zones of NLS, which show an increasing tendency in all sites in 2019 with peak concentrations of 2880 ng L^{-1} and 425 ng L^{-1} in Zone I (Bojorquez) and Zone II (North), respectively (Figure 2). But when caffeine (average value) is plotted against the number of tourists, it is appreciable that it does not fully account for what was found, since 2018 had tourists like 2019 who had a median caffeine value like the one in 2020 that had c.a. half of the tourist. This is an unexpected outcome, but it could be confirming what other [26,27] mention regarding the dependance between pollutants transport/dispersion and hydrological changes related with the anomalous precipitation events.

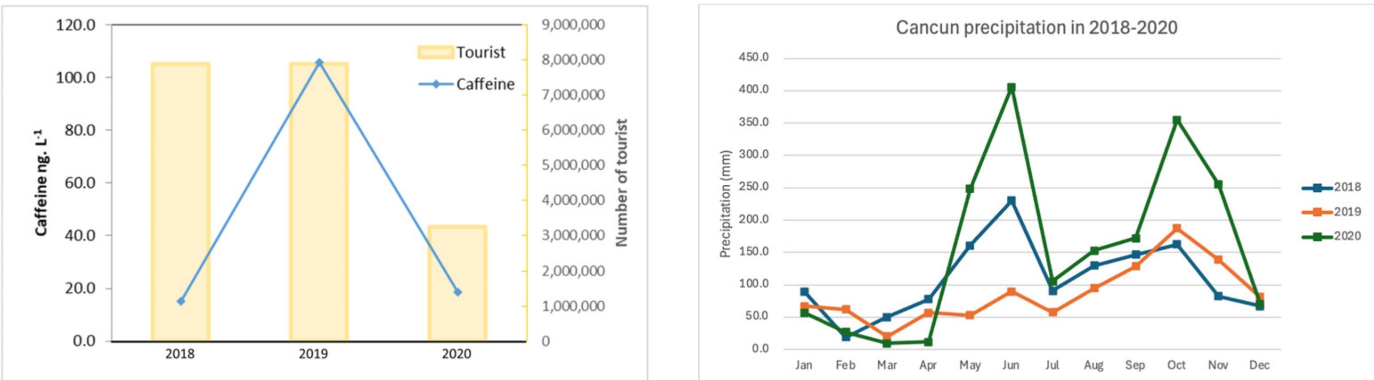


Figure 2. Average annual variation in the concentration of caffeine and number of tourists (**left** side) and monthly precipitation in Cancun 2018–2020 (**right** side).

Figure 2 also shows the precipitation in the area, and for 2020, according to CONAGUA, there was an anomalous precipitation (4× the common one of 100 mm) and high precipitation (2× the common one) in 2018 [28], both of which were prior to the sampling campaign (August); this could have promoted a higher hydraulic head that increased the dilution of caffeine in the groundwater system. For 2019, almost no rain was prior to the sampling; this diminished the hydraulic head, promoting less dilution and less transport, allowing a longer residence time of the wastewater and caffeine local inputs. Thus, when caffeine results are integrated to the hydrological process of the area, it could be seen that they are not only reflecting the presence of wastewater in the groundwater system, but also how it could be altered by the previous precipitation events.

Table 2. Descriptive statistics of the caffeine and nutrients values by zones of the Nichupte Lagoon System: three-year follow-up. Mean ± SD (min–max).

Year/Zone		Caffeine (ng L^{-1})	Salinity (PSU)	DO (mg L^{-1})	NO_3^- (µmol L^{-1})	NO_2^- (µmol L^{-1})	NH_4^+ (µmol L^{-1})	SRP (µmol L^{-1})	SRSi (µmol L^{-1})	Chl-*a* (µg L^{-1})	TRIX
2018	Bojorquez (ZI)	42.8 ± 10.1 (35.4–59.9)	31.9 ± 0.07 (31.9–32.0)	5.82 ± 0.33 (5.52–6.32)	14.1 ± 13.9 (3.10–36.5)	6.21 ± 1.10 (4.83–7.54)	31.0 ± 6.98 (24.0–38.7)	43.1 ± 35.2 (23.5–106)	1030 ± 339 (730–1510)	3.56 ± 1.59 (1.5–4.9)	3.8 ± 0.23 (3.5–4)
	North (ZII)	16.4 ± 11.2 (ND–29.2)	30.7 ± 2.17 (26.2–33.4)	5.48 ± 0.83 (3.73–6.60)	102 ± 92.7 (3.10–287)	4.85 ± 4.17 (1.52–15.5)	139 ± 266 (2.12–864)	3.71 ± 2.25 (2.85–9.98)	907 ± 652 (340–2690)	1.75 ± 0.6 (0.7–2.6)	3.11 ± 0.89 (1.7–4.8)
	Central (ZIII)l	ND (ND–21.1)	23.5 ± 3.89 (16.9–28.7)	5.45 ± 0.64 (4.41–6.32)	76.0 ± 85.0 (5.58–335)	8.49 ± 7.23 (1.89–29.7)	35.7 ± 16.3 (9.79–67.5)	24.9 ± 16.9 (2.85–30.2)	1381 ± 575 (623–2710)	1.07 ± 0.77 (0.3–2.2)	3.52 ± 0.34 (2.8–4.1)
	South (ZIV)	12.9 ± 13.7 (ND–38.6)	26.7 ± 1.03 (25.5–28.2)	5.54 ± 0.70 (4.58–6.34)	37.2 ± 25.0 (10.3–73.9)	3.81 ± 2.73 (0.46–8.33)	25.6 ± 15.1 (1.80–48.0)	3.80 ± 1.20 (2.85–5.70)	859 ± 258 (403–1080)	1.43 ± 0.42 (1.1–2.1)	2.77 ± 0.57 (1.8–3.3)
	Rio Ingles (ZV)	ND (ND–8.66)	20.9 ± 0.50 (20.5–21.5)	5.93 ± 0.49 (5.37–6.27)	162 ± 264 (3.10–467)	7.05 ± 6.70 (2.30–14.7)	41.9 ± 26.0 (14.0–65.5)	84.23 ± 94.9 (26.6–194)	1783 ± 1550 (0.00–2720)	0.57 ± 0.55 (0–1.1)	3 ± 2.23 (0.6–5)
2019	Bojorquez (ZI)	607 ± 1270 (ND–2880)	32.5 ± 1.11 (31.5–34.4)	8.12 ± 3.12 (5.93–13.6)	23.8 ± 14.4 (13.0–47.1)	16.7 ± 10.6 (5.06–29.0)	53.1 ± 61.6 (10.4–148)	27.5 ± 5.97 (19.0–35.2)	776 ± 114 (651–907)	8.46 ± 1.79 (5.4–9.8)	4.56 ± 0.57 (4.1–5.5)
	North (ZII)	47.2 ± 114 (ND–425)	29.1 ± 2.41 (24.9–31.8)	6.12 ± 0.57 (5.27–7.04)	159 ± 113 (5.58–342)	8.00 ± 5.26 (1.38–16.6)	332 ± 564 (1.38–16.6)	50.8 ± 54.2 (20.9–173)	1140 ± 475 (538–1980)	4.49 ± 1.18 (3.1–6.8)	4.42 ± 0.8 (3.5–6.4)
	Central (ZIII)	22.5 ± 12.6 (ND–41.7)	24.9 ± 6.28 (10.2–31.8)	5.42 ± 1.44 (0.73–6.27)	171 ± 146 (29.8–486)	21.9 ± 16.5 (1.84–49.7)	28.3 ± 44.8 (1.08–167)	61.5 ± 52.9 (18.1–176)	1350 ± 452 (677–2160)	4.17 ± 1.37 (0.8–6.2)	4.42 ± 0.42 (3.6–5)
	South (ZIV)	35.1 ± 16.7 (ND–50.9)	31.2 ± 1.15 (29.4–32.3)	5.12 ± 0.52 (4.22–5.61)	92.9 ± 82.4 (32.9–240)	8.89 ± 7.18 (1.38–20.2)	15.2 ± 10.5 (4.14–33.5)	31.5 ± 10.5 (20.0–44.7)	452 ± 348 (77.3–942)	1.98 ± 0.37 (1.7–2.7)	4.02 ± 0.4 (3.5–4.6)
	Rio Ingles (ZV)	58.3 ± 25.5 (24.1–89.5)	26.3 ± 3.42 (23.2–31.9)	5.90 ± 1.23 (4.96–8.03)	246 ± 171 (68.8–524)	9.3 ± 75.3 (4.60–183)	63.0 ± 34.3 (29.8–116)	63.3 ± 65.6 (29.5–180)	2860 ± 1280 (1210–4420)	0.96 ± 0.51 (0.6–1.8)	4.38 ± 0.38 (3.8–4.8)
2020	Bojorquez (ZI)	31.3 ± 4.36 (27.5–37.9)	28.0 ± 0.04 (27.9–28.1)	5.90 ± 0.32 (5.55–6.37)	0.9 ± 0.43 (0.44–1.6)	0.04 ± 0.01 (0.02–0.05)	0.16 ± 0.17 (0.02–0.42)	0.29 ±0.14 (0.15–0.45)	24.01 ± 0.9 (22.9–25.28)	7.86 ± 2.11 (4.4–9.7)	4.06 ± 0.39 (3.7–4.7)
	North (ZII)	12.4 ± 5.33 (ND–22.3)	26.5 ± 1.43 (22.0–27.6)	5.67 ± 0.61 (4.28–6.88)	2.06 ± 1.58 (0.38–5.23)	0.21 ±0.5 (0–1.75)	15.02 ± 36.67 (0.1–128)	0.29 ±0.11 (0.05–0.43)	13.55 ± 7.02 (8.68–35)	7.49 ± 8.22 (2.8–30.9)	4.65 ± 0.54 (4–5.8)
	Central (ZII)	12.7 ± 7.18 (ND–25.2)	24.3 ± 1.58 (20.6–26.3)	5.47 ± 0.54 (4.55–6.41)	1.05 ± 0.78 (0–3.08)	0.03 ± 0.03 (0–0.09)	0.83 ± 0.81 (0–2.88)	0.23 ± 0.15 (0–0.4)	14.45 ± 5.34 (0–19.48)	4.95 ± 1.71 (2.9–8.5)	4.17 ± 0.5 (3.2–4.8)
	South (ZIV)	24.4 ± 13.3 (ND–42.3)	27.2 ± 1.16 (25.8–28.7)	4.94 ± 0.55 (4.12–5.75)	0.96 ± 0.62 (0.26–1.77)	0.01 ± 0.01 (0.01–0.03)	1.62 ± 0.43 (1.14–2.18)	0.26 ± 0.12 (0.13–0.41)	9.65 ± 3.34 (5.4–13.55)	1.83 ± 0.25 (1.5–2.2)	4.1 ± 0.24 (3.8–4.4)
	Rio Ingles (ZV)	27.7 ± 12.6 (18.3–48.9)	18.5 ± 1.84 (17.2–21.7)	5.64 ± 1.25 (3.49–6.78)	0.55 ± 0.64 (0.06–1.27)	0.03 ± 0.03 (0.01–0.06)	1.26 ± 0.47 (0.73–1.61)	0.16 ± 0.12 (0.03–0.26)	16.72 ± 2.58 (13.84–18.82)	2.3 ± 1.58 (1.1–5)	3.63 ± 0.84 (3.1–4.6)

Furthermore, rainfall and the connectivity of the submarine springs to the nearshore coastal environment contribute to the transfer of caffeine from the inland zones to the NLS. These discharges of groundwater at the Mexican Caribbean range from 48 m^3 d^{-1} m^{-1} in the northeast region to 568 m^3 d^{-1} m^{-1} in the southeast areas [12]. Moreover, the NLS dynamics is also influenced by processes such as tides, waves, winds, and the geometry and bathymetry of the system [17], provoking restricted circulation patterns (see Figure 1) that allow the accumulation of caffeine under dry or low precipitation conditions. This could explain why the highest concentrations of caffeine in 2019 were in Z1 Bojorquez (2880 ng L^{-1}), Z1 North (425 ng L^{-1}), and Z5 Río Inglés (85 ng L^{-1}), as is seen in Figure 3.

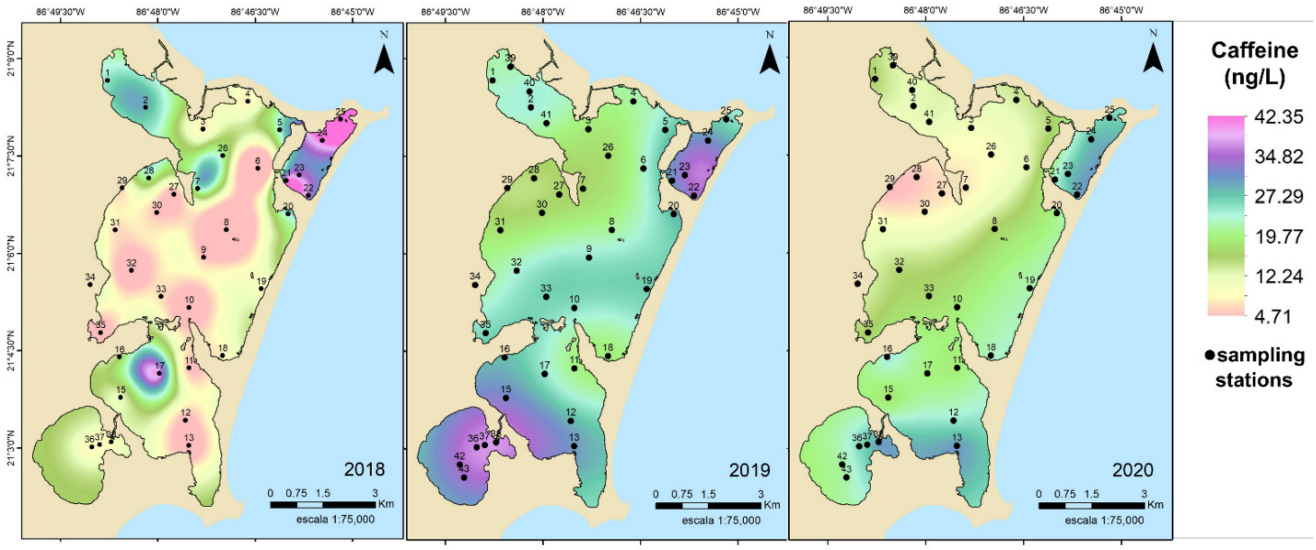


Figure 3. Distribution of caffeine throughout the zones of the NLS in the three-year follow-up.

Most of the caffeine values detected in this study are within or above the concentrations ranged from non-detected to 2390 ng L^{-1}, reported by [22], a study also conducted in coastal lagoons near urban and touristic settlements in the Yucatan Peninsula. Moreover, the seasonal increase in population due to tourism in the coastal areas has been correlated with a significant increase in caffeine concentrations in coastal waters [29].

In the Cancun area alone, the tourism rate is measured through hotel occupancy and the number of tourists per year, and an average occupancy of 75% was reported during 2018 and 2019 with more than 7 million visitors per year [24], compared to the drastic decrease in these numbers and consequently, in caffeine concentrations in 2020 during the COVID-19 pandemic; as shown before, the hydrological conditions effect on the groundwater system also play an important role in the caffeine concentrations. Since the Nichupte lagoon is surrounded by three main urban areas, the hotel area on Cancun Island, the first phase of the City of Cancun, and the area where the international airport is located, there is, therefore, a consequent unplanned urban expansion that takes place where the treatment of water sewage is inadequate [30]. Therefore, the spatial and temporal distribution of caffeine in the NLS (Figure 3) clearly shows that touristic activity and the inefficiency of treatment promote the presence of wastewater, but the concentration and dispersion will be altered by the hydrological conditions related with anomalous precipitation events.

In terms of nutrients in 2019 (see Table 2 and Figure 4a–e), compared with data from the previous year, there is also an increasing tendency in nitrate and nitrite concentrations and variability in the quantification of ammonia, phosphate, and silicate. However, from 2019 to 2020, there was a decrease in nutrients, while the chlorophyll concentration increased (Figure 4f). This could be the result of the infiltration of rainwater because of the Cristobal storm that lasted 9 days in the Yucatan Peninsula [28]. This could have favored the dilution of nutrients in the lagoon and the suspension of particles that increased the concentration of chlorophyll-a. Also, the previously discussed effect of the anomalous rain/higher groundwater input in the area is observed for salinity levels in 2018 and 2020, as can be seen in Figure 4h where values as low as 23.8 ppt were detected.

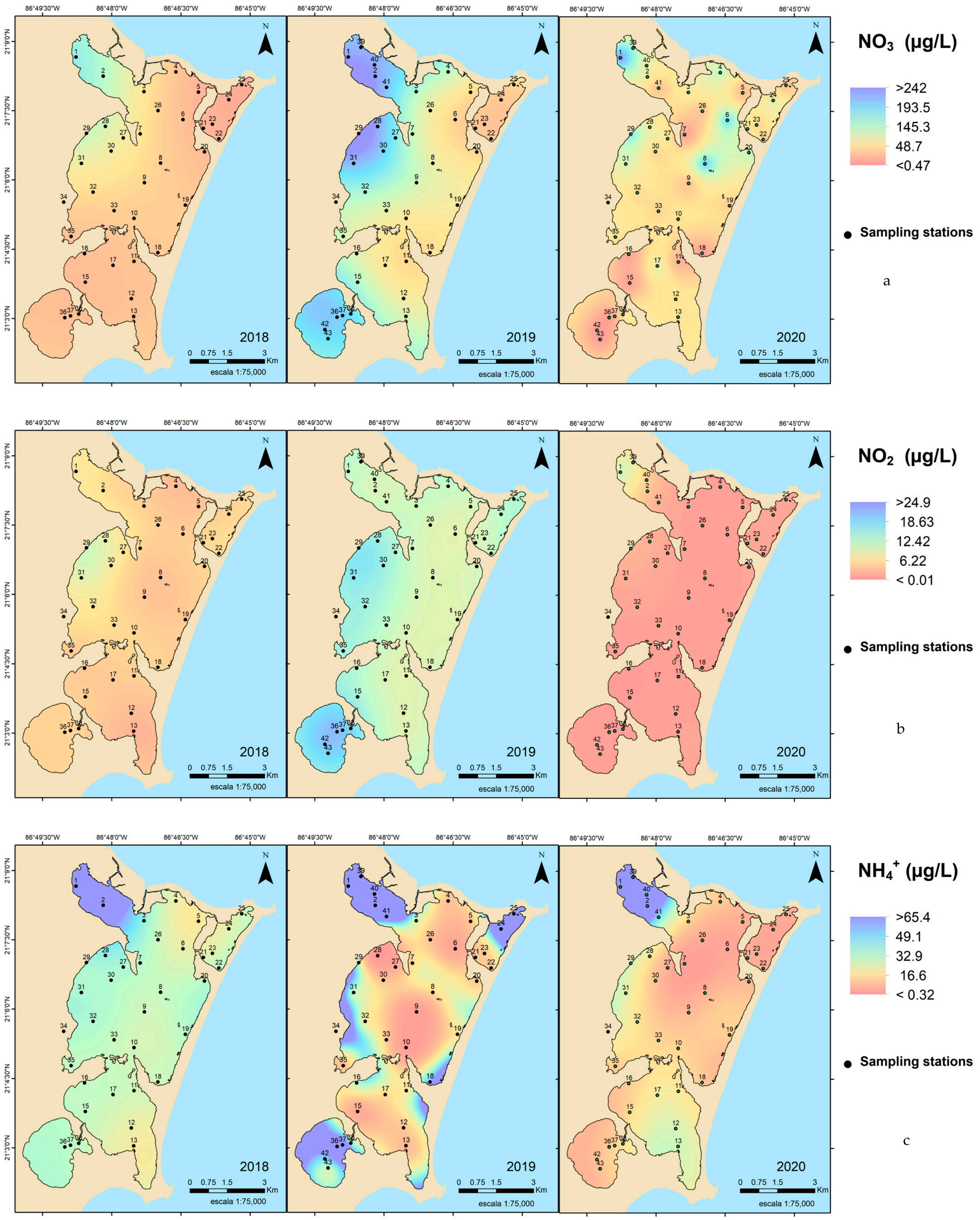
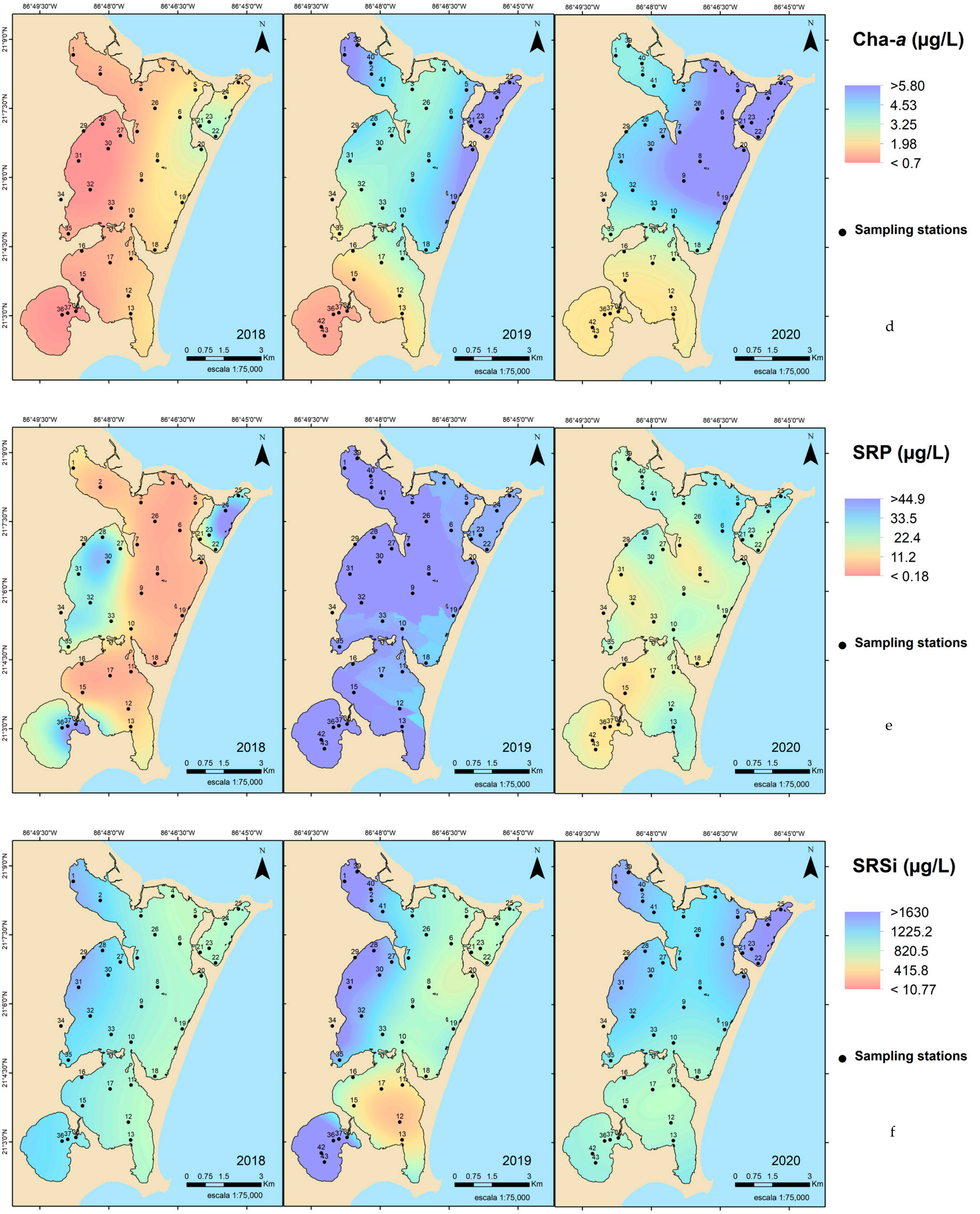


Figure 4. *Cont.*



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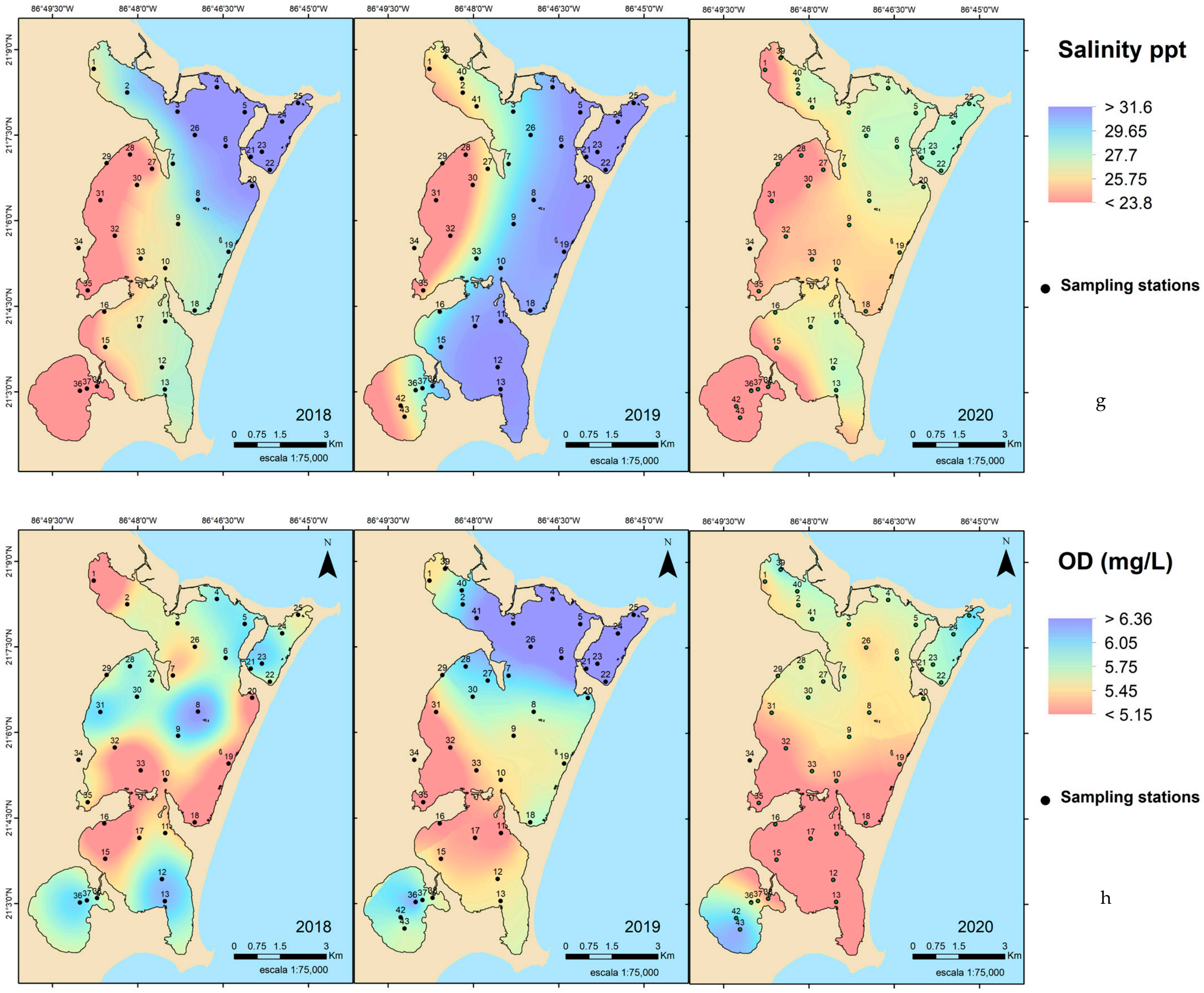

Figure 4. Spatial and temporal variations in the NLS of (**a**) NO_3^-, (**b**) NO_2^-, (**c**) NH_4^+, (**d**) SRP, (**e**) SRSi, (**f**) Cha-a, (**g**) salinity, and (**h**) DO.

Also, groundwater inputs to the NLS in the same years promote a decrease in oxygen levels as seen in Figure 4g [10], although oxic values prevail.

Our results are comparable with the values presented in Table 3 for similar systems during rainy seasons: coastal lagoons also in the Yucatan. Moreover, this information is essential to assess the anthropogenic contamination in the area.

Table 3. Overview of nutrient comparison data from coastal zones in the Yucatan Peninsula.

Salinity (PSU)	DO (mg L^{-1})	NO_3^- (µg L^{-1})	NO_2^- (µg L^{-1})	NH_4^+ (µg L^{-1})	PO_4^{3-} (µg L^{-1})	SiO_4^{4-} (µg L^{-1})	Study Area	Reference
25.8		180	381	173			Dzilam Lagoon	[31]
33.2	3.2	471	93.0	657			Chelem Lagoon	[32]
33.3	3.99	236	52.1	225	41.54	8476	Celestun Lagoon	[33]
28.4	4.07	691	54.7	195	1410	4680	Nichupté mangroves	[3]

Results from the Kruskal–Wallis test are shown in Table 4; this nonparametric test was carried out after the results of non-normally distributed data were given by the Shapiro–

Wilk test. Significant differences were observed between the salinity ($p < 0.05$). Most of the zones remained classified as polyhaline (18–30 PSU) throughout the three years of the study. The distinguishing aspect of the NLS is the interaction with groundwater flows and the pressure gradient oriented from the mainland to the lagoon system; thus, the salinity values suggest that near the coast, there is a process of mixing due to the known limestone and cavernous structure of the subsoil between the fresh water and seawater [17]. Zone I (Bojorquez) presents a direct influence of the water of the Caribbean Sea and long residence times; therefore, in this zone, the salinity was above 30 PSU. For dissolved oxygen, no significant differences were observed over the years ($p = 0.109$) but the range of variation in dissolved oxygen indicates intense metabolic activity in the water column [34]. Finally, for caffeine and nutrients, it shows significant differences ($p < 0.05$). The fact that these parameters, both present in anthropogenic wastewater and both useful as human contamination, significantly change shows that the distribution and concentration will result not only from wastewater inputs, but as previously discussed, the hydrological changes could determine the distribution and concentration. The increasing discharge of nutrients could cause eutrophication, so it is necessary to reduce the load of nutrients toward these key ecosystems for the permanence of the coastal landscape and, therefore, of tourist activities.

Table 4. The Kruskal–Wallis test. * = significant differences.

Year	Parameter	Caffeine	Salinity	DO	NO_3^-	NO_2^-	NH_4^+	SRP	SRSi	Chl-*a*	TRIX
	χ^2	14.5	13.5	4.43	89.5	90.7	86.3	92.5	83.5	36.62	43.49
	df	2	2	2	2	2	2	2	2	2	2
	$p < 0.05$	<0.001 *	0.001 *	0.109	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *
2018	Min	0.05	16.9	3.73	3.1	0.46	1.80	2.85	0	0.001	0.6
	Q1	4.73	23.8	5.15	17.4	2.81	19.3	2.85	725	0.7	2.9
	Median	8.33	27.1	5.63	40.7	7.73	30.9	7.6	967	1.45	3.5
	Q3	24.6	31.6	6.11	83.9	7.73	47.7	29.3	1330	2	3.7
	Max	59.9	33.4	6.60	466.9	29.7	864	194	2720	4.9	5
2019	Min	2.32	10.2	0.73	44.2	1.38	1.08	18.1	77.3	0.6	3.5
	Q1	12.8	24.9	5.37	44.1	4.95	9.63	24.7	776	2	4.1
	Median	23.3	30.3	5.81	87.4	24.9	17.0	31.8	1000	3.9	4.3
	Q3	42.4	31.5	6.36	242	24.9	65.4	44.9	1630	5.4	4.7
	Max	2880	34.4	13.6	524	183	1530	181	4420	9.8	6.4
2020	Min	1.04	17.2	3.49	0.05	0.05	0.01	0.03	0.004	1.1	3.1
	Q1	9.54	24.3	5.17	0.47	0.01	0.32	0.18	10.77	2.8	4
	Median	17.0	26.3	5.62	0.93	0.03	0.68	0.26	13.96	3.8	4.2
	Q3	23.2	27.3	6.00	1.6	0.05	1.51	0.4	18.79	5.8	4.7
	Max	48.9	28.7	6.88	5.23	1.75	128	0.45	35	30.9	5.8

As nutrients are not toxic to aquatic organisms and humans at low concentrations, nutrient criteria are ecological (not toxicological) and cannot be derived by simple dose-response relationships [35], we calculated the water quality TRIX index to identify the trophic state of the NLS. The results of Table 5 and Figure 5 show how there was an increase in the TRIX values in 2019, with a hypertrophic state. In 2020, because of water dilution due to the Cristobal storm, the trophic state improved, becoming mesotrophic. As mentioned by [36], the problems that affect the environmental condition of the NLS stand out: the sanitary drainage pipes and septic tanks at the hotel zone and surrounding urban settlements are in inadequate conditions, causing water leaks due to insufficient infrastructure to treat sewage seeping into aquifers interconnected with the lagoon system, the lack of regulation for tourist activities on the lagoon bank, the lack of monitoring and sanitation programs, and finally, the unawareness of the population about the level of contamination and environmental deterioration.

Table 5. Ranking for the TRIX assessment for each zone of the NLS.

Year	TRIX Value by Zone/Trophic Status (Condition)				
	I	II	III	IV	V
2018	3.78 Oligotrophic (High)	3.10 Oligotrophic (High)	3.52 Oligotrophic (High)	2.78 Oligotrophic (High)	3.94 Oligotrophic (High)
2019	7.06 Hypereutrophic (Poor)	6.92 Hypereutrophic (Poor)	6.92 Hypereutrophic (Poor)	6.53 Hypereutrophic (Poor)	6.87 Hypereutrophic (Poor)
2020	4.06 Mesotrophic (Good)	4.65 Mesotrophic (Good)	4.17 Mesotrophic (Good)	4.1 Mesotrophic (Good)	3.63 Oligotrophic (High)

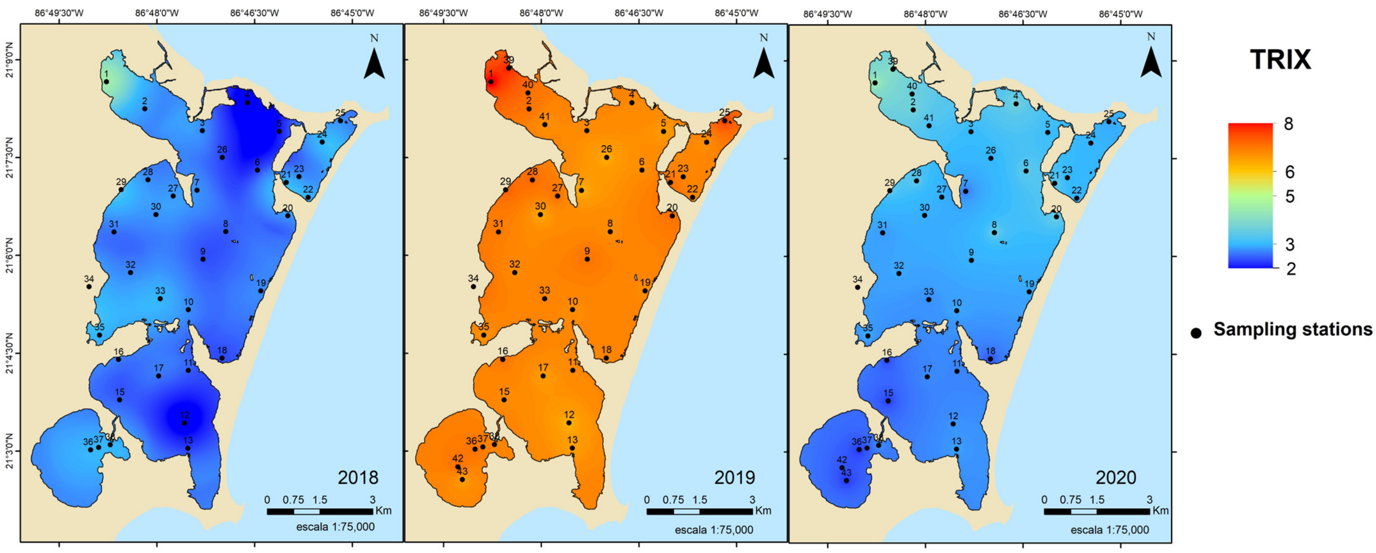

Figure 5. Overall water quality health status of the NLS in 2018, 2019, and 2020.

The cluster analysis (Figure 6) showed that the areas with the greatest similarity were the ZII and ZIV (>80%), while the least similar areas were the ZI (70%) and ZV (56%). These last two zones have characteristics since the water has a longer residence time due to its geomorphology. In the case of the ZI, it is the most restricted and least connected with the rest of the NLS, while in the ZV, there are freshwater springs that give it other characteristics [17].

Principal component analysis (Figure 7) indicated that the variables that had the greatest positive relationship with caffeine were OD and Chl-*a*. One of the characteristics of wastewater (traced by caffeine) is to contain nutrients that promote algal growth, which seems to be the case in NLS. The primary producer bloom (higher Chl-*a*) will promote the production of oxygen in the area [37–40]; this could be seen as a positive outcome, nevertheless, it could lead to a eutrophic state or a toxic algal bloom, as has been reported for the area [4,41]. Also, it is noteworthy that nutrients are not totally related to caffeine; this could be the result that for the area, the source of caffeine is solely groundwater or direct inputs from the surroundings; nutrient marine inputs [42,43], besides their release from sediments resuspension [44–46], are also relevant, thus, PCA shows this.

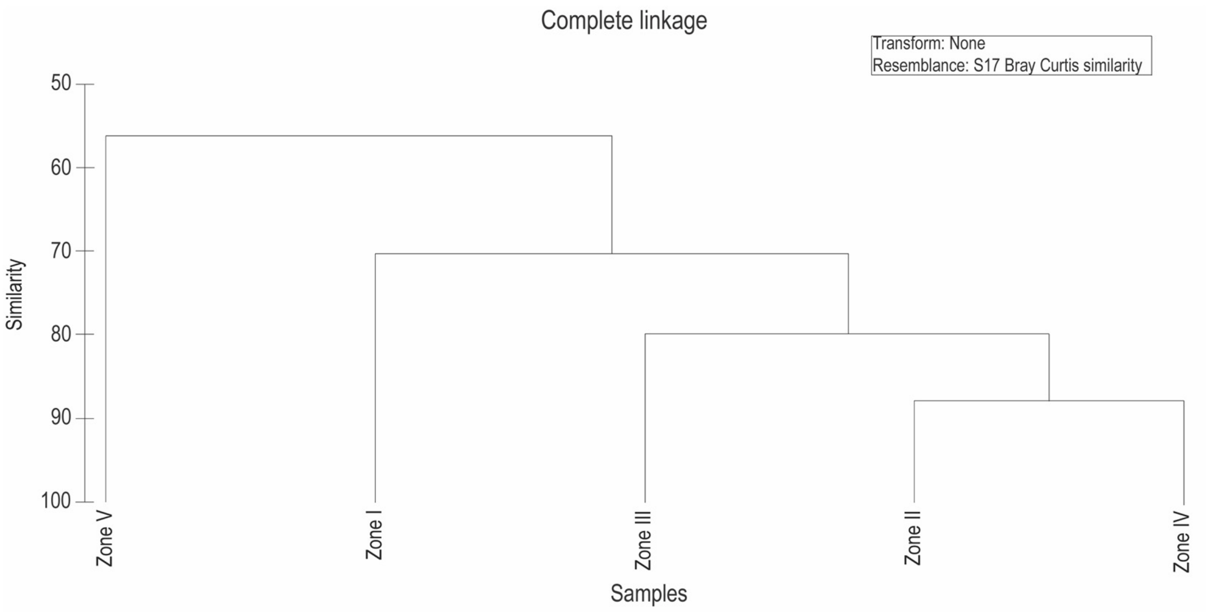

Figure 6. Cluster analysis by NLS area.

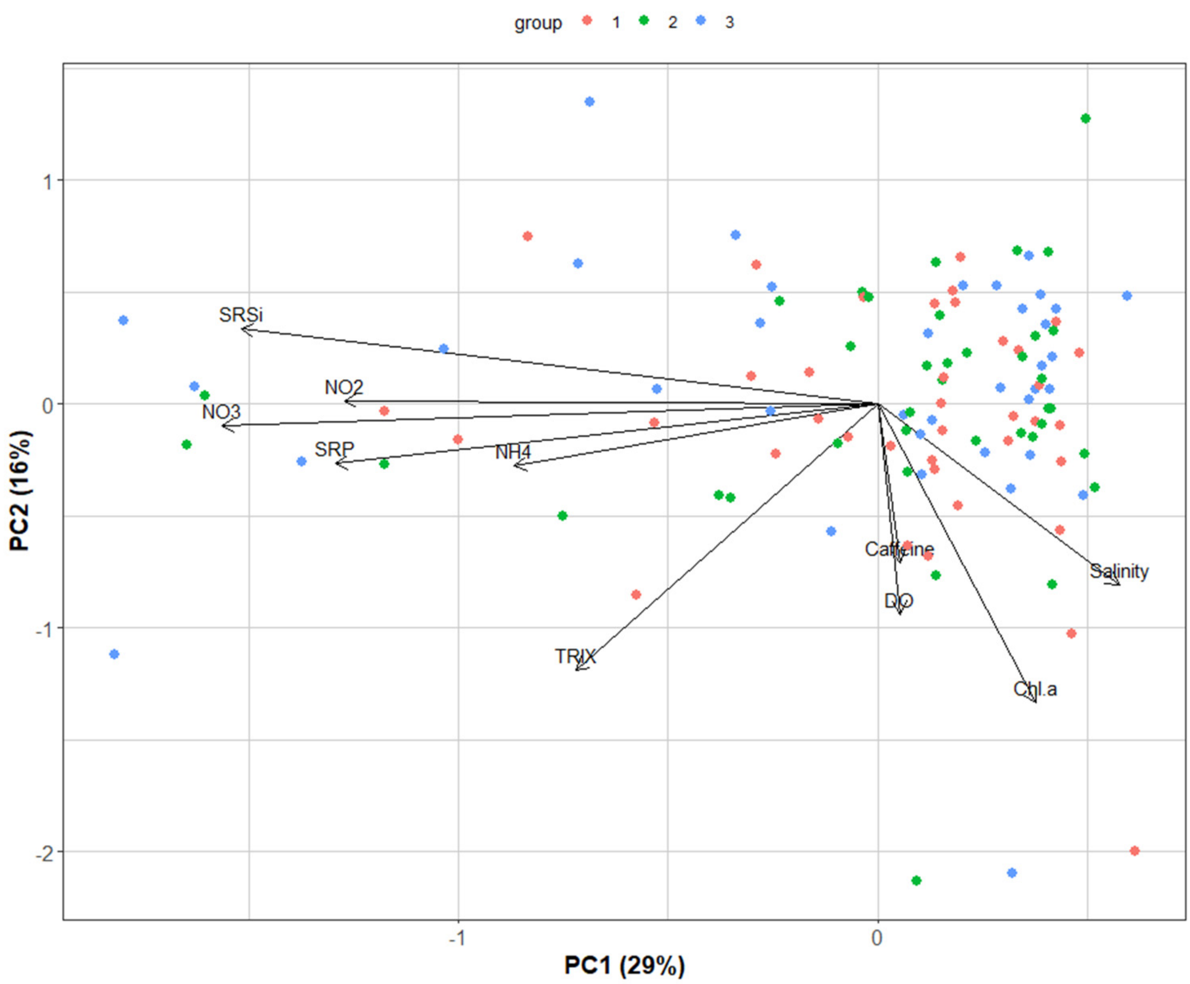

Figure 7. Principal component analysis of the measured variables in the NSL.

Unfortunately, the promotion of the tourism sector in the Cancun area was not accompanied by a strengthening of environmental regulations; in the case of the Nichupté Lagoon, it is threatened by human activities such as urbanization, infrastructure development, exploitation of agricultural land, and tourism activities, where new urban development projects continue to be generated, namely vertical housing projects and irregular urban settlements, with negative effects that are serious for the contamination and deterioration of the SLN ecosystem [3,15,17]. These activities have damaged the lagoon ecosystem, deteriorating the functions of ecological activities carried out by the wetland of this Lagoon, which is key to maintaining the ecological dynamics of the reefs.

4. Conclusions

The results of this study provide an updated reference of the status of the various zones within the lagoon system, impacted by anthropogenic activities and seasonal variations, particularly related to tourism and hydrometeorological events. Although a decrease in nutrient and caffeine concentrations was recorded in 2020 (possibly influenced by reduced tourism activities due to the pandemic and dilution from Tropical Storm Cristóbal), the increases observed in 2019 reflect a eutrophication process related to anthropogenic wastewater input. This phenomenon, driven by wastewater discharges and contaminant transport through underground connectivity and water flows, suggests that the system's resilience capacity is being exceeded by the load of nutrients and other contaminants, thereby compromising its functionality and biodiversity [47,48].

The findings in this work provide a reference for the current contamination state of the different areas within the lagoon system and demonstrate the presence of anthropogenic wastewater by means of the caffeine tracer, showing that the spatial and temporal variations in the lagoon could result from normal precipitation vs. anomalous precipitations hydrological changes, coupled with the number of tourists in the area.

Considering this, there is an urgent need to implement wastewater treatment programs and continuous monitoring of key indicators (nutrients, dissolved oxygen, chlorophyll-a, and caffeine) during at least two climatic seasons throughout the system to determine whether the conditions observed in this study are permanent or variable over time. Additionally, daytime monitoring of dissolved oxygen using continuous meters is recommended in each zone as an early warning measure to address the worsening of potential negative effects on the ecosystem and the implications for human health.

The results of this study showed the relevance of year-by-year monitoring of vulnerable systems such as the NLS, to fully understand the dynamics of human contamination and the changes derived from the hydrological or geological context, which are highly relevant in karstic areas worldwide.

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