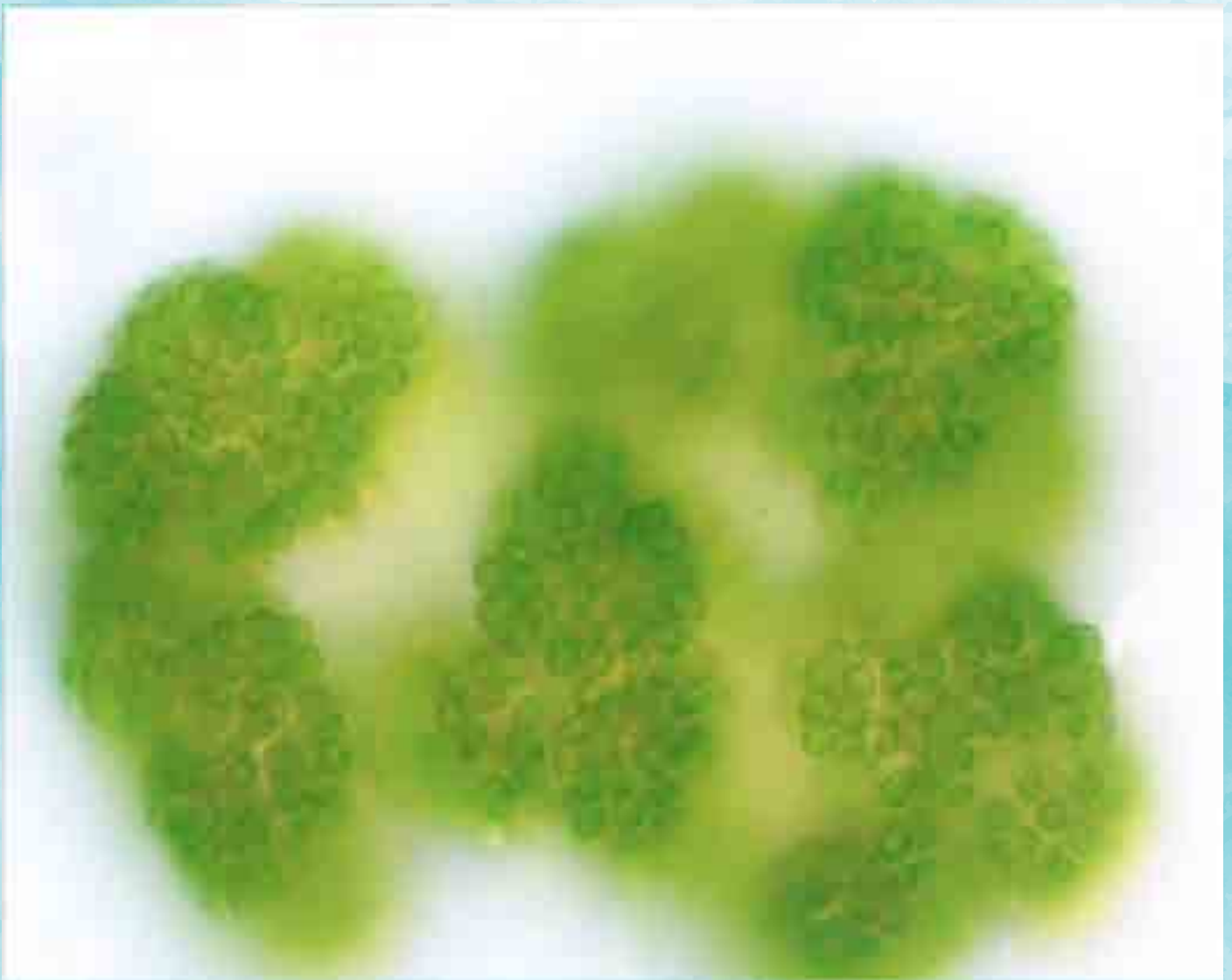


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Water quality assessment in the coastal zone of
Campeche, southeastern Gulf of Mexico



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Water quality assessment in the coastal zone of Campeche, southeastern Gulf of Mexico

Evaluación de la calidad del agua en la zona costera de Campeche, sureste del Golfo de México

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ABSTRACT

The purpose of this study was to assess the water quality at several sites with anthropogenic impact in the southeastern Gulf of Mexico. Eight sites at 3 coastal localities with different kinds of anthropogenic activity were monitored in September and November 2016. Water temperature, salinity, pH, dissolved oxygen, inorganic nutrients, heavy metals in sediments, fecal coliforms and phytoplankton abundance were determined. The pH values and the dissolved oxygen suggested a predominance of photosynthetic activity. Elevated nutrient contents were associated with sites of rainwater discharge with anthropogenic activities, as well as with biogeochemical processes. Inorganic nutrients, especially ammonium, nitrites and nitrates, heavy metals, and phytoplankton abundance showed influences of anthropogenic factors and can be considered indicators of water quality, although fecal coliforms (up to 900 Most Probable Number 100 mL⁻¹) were not a good indicator of fecal contamination. The

Nanoflagellates were the most abundant, followed by diatoms. The non-toxic diatom *Cylindrotheca closterium*, known to be a bloom-forming species, and the harmful cyanobacterium *Trichodesmium* sp. showed proliferations on the order of 10⁵ cells L⁻¹. These phytoplankton responses are indicative of the eutrophication due to fluctuations in environmental conditions because of the intensity and type of human activities that take place in the study area.

Keywords: eutrophication, Gulf of Mexico, heavy metals, phytoplankton, water quality

RESUMEN

El propósito de este estudio fue evaluar la calidad del agua en varios sitios con impacto antropogénico en el sureste del Golfo de México. En septiembre y noviembre de 2016 se monitorearon 8 sitios en 3 localidades costeras con diferentes tipos de actividad antropogénica. Se obtuvieron los datos de temperatura del agua, salinidad, pH, oxígeno disuelto, nutrientes inorgánicos, metales pesados en sedi-

mentos. También se determinaron coliformes fecales y abundancia de fitoplancton. Los valores de pH y el oxígeno disuelto sugirieron un predominio de la actividad fotosintética. Los contenidos elevados de nutrientes se asociaron con sitios de descarga de agua de lluvia con actividades antropogénicas, así como con procesos biogeoquímicos. Los nutrientes inorgánicos, especialmente amonio, nitritos y nitratos, metales pesados y abundancia de fitoplancton mostraron influencias de factores antropogénicos y pueden ser considerados indicadores de la calidad del agua, aunque los coliformes fecales (hasta 900 Número Más Probable 100 mL⁻¹) no fueron un buen indicador de contaminación fecal. Los nanoflagelados fueron los más abundantes, seguido de las diatomeas. La diatomea no tóxica *Cylindrotheca closterium*, una especie formadora de florecimientos y la cianobacteria nociva *Trichodesmium* sp. mostraron proliferaciones del orden de 10⁵ células L⁻¹. Estas respuestas del fitoplancton son indicativas de la eutrofización debido a las fluctuaciones en las condiciones ambientales propiciadas por la intensidad y tipo de actividades humanas que tienen lugar en el área de estudio.

Palabras clave: calidad del agua, eutrofización, fitoplancton, Golfo de México, metales pesados.

INTRODUCTION

In Mexico, in general, water quality criteria for the protection of aquatic life in estuarine and coastal environments have ignored the benefits of the coastal ecosystem health indicators used in other regions. The information published in Mexican regulations is very limited, and the standards are focused on the beaches. Since 2003, in Mexico, through the Integral Program of Clean Beaches, the monitoring of seawater quality has been carried out following the criteria described by the World Health Organization (WHO) for recreational sites within 17 coastal states of the country. Given the technical and economic difficulties in determining all the parameters related to the deterioration of water quality, the fecal enterococcal content was used as an indicator of the degree of contamination of seawater and the health risks resulting from its recreational use (SEMARNAT 2014).

For many decades, fecal coliform counts have been performed in Mexican coastal waters; thus, the value of the historical data is unquestionable. Fecal coliforms (FC) are widely recognized as bacteriological indicators because their presence in aquatic systems is evidence of fecal contamination. Under

current Mexican regulations, *Enterococcus* spp. are an indicator for establishing the microbiological quality of a beach for recreational use (SE 2016). However, the use of a single parameter can lead to erroneous results when characterizing a water body by only considering the potential danger of pathogens (Escobedo-Urías *et al.* 1999); therefore, a complex of variables is usually used.

Phytoplankton can be useful for the trophic classification of the aquatic environment as they reflect environmental conditions, respond quickly to changes that may occur through natural processes or human activities and modify the structure of their communities (De la Lanza-Espino & Gómez-Rojas 2005; Poot-Delgado *et al.* 2022). The dominant species, their relationships with environmental changes and their biomass increase can be used as indicators of the varying characteristics of coastal water quality as well as to predict the possible changes that could occur in the upper levels of trophic food webs (De la Lanza-Espino *et al.* 2000). In recent years, many environmental agencies around the world have used methods for assessing water quality based on biological communities (Ospina-Álvarez & Peña 2004). The regulatory framework of the European Directive that incorporates phytoplankton into the definition and classification of the ecological status of aquatic bodies, using metrics such as biomass (chlorophyll-*a*), changes in the community (species composition and abundance) and increased frequency and intensity of blooms is an example (Revilla *et al.* 2009). The standard Mexican NMX-AA-120-SCFI-2006 (SE 2016) does not consider the study of microalgal communities as one of the methodological lines to be followed for the characterization of different types of lakes, lagoons, reservoirs or coastal water bodies to obtain metrics for evaluation of their ecological state.

Sediments are also valuable indicators for monitoring pollutants in aquatic environments. They act as traps for various types of toxic substances, such as traces of accumulated heavy metals from direct or indirect discharges through effluents, runoff and leachates originating from numerous urban, industrial and agricultural activities, as well as from atmospheric deposition (Bejarano-Ramírez *et al.* 2017). It should be noted that there is no official Mexican standard for the maximum permissible limits of heavy metals in coastal sediments.

Since each ecosystem is unique, it is necessary to use effective tools for diagnosis and to identify the key parameters that indicate the degree of human impact or ecological status (Crooks & Turner 1999). To do this, the components of the medium that can be used as

indicators of ecological quality should be determined; these can be physicochemical (temperature, salinity, total suspended solids, dissolved oxygen (DO), nutrients), hydromorphological (tides, waves, depth, currents) or biological variables (phytoplankton, benthic flora and fauna) (Hermosilla-Gómez 2009).

For this purpose, partial information on the phytoplankton abundances and environmental variables (temperature, salinity, pH and DO) for September and November 2016 has been recovered from the data published in Poot-Delgado *et al.* (2022), where the authors concluded that the composition of the phytoplankton community, harmful and bloom-forming species may be subject to the increasing anthropogenic impact in the coastal zone of the State of Campeche. The purpose of the present study was to assess the water quality and to test the previous hypothesis with a greater number of variables (also considering inorganic nutrients, heavy metals in sediments and fecal coliforms).

MATERIAL AND METHODS

Field sampling. Sampling was carried out on September 10 and November 14, 2016, corresponding to the end of the rainy season (June to September) and the beginning of the windy season (October to January), respectively, at 3 coastal localities in the central zone of the State of Campeche (Table 1).

The average monthly rainfall in September was 202.8 mm; in November, it was 53.4 mm (CONAGUA 2016). In the study region the wind blows from the west almost throughout the year, causing a

persistent westward circulation (Zavala-Hidalgo *et al.* 2003; Kurczyn *et al.* 2020). From September to June, atmospheric cold fronts considerably change the regional wind flow and interrupt upwelling processes from the northeast (Kurczyn *et al.* 2021). Sampling stations (st.) were chosen at the points of rainwater discharge or near the sites with anthropogenic activities (Table 1, Fig. 1). Site depths were approximately 1 m at all the stations.

Surface seawater samples were collected with 1-liter plastic bottles; an aliquot of 100 mL was used for cell counting of phytoplankton taxa. Samples were immediately fixed with an alkaline iodine solution and subsequently preserved by adding 37% neutralized formalin to a final concentration of 4% (Thronsen 1978). Additionally, horizontal tows were taken for 5 min. with a conical hand net of 20 µm mesh size. The collected material for the study of phytoplankton was placed in glass vials and fixed using the same procedure as for cell counts. *In situ* temperature (°C), salinity, pH, and DO were measured using a HANNA Multiparameter probe, model HI9828, with a sensor model HI769828 (Hanna Instruments Inc., Woonsocket, RI, USA) and a HACH Multiparameter probe, model HQ40d (Hach Company, Loveland, CO, USA). For analysis of fecal coliforms (FC), water samples were collected in sterile Pyrex 250 mL flasks at each sampling site and were cold transported for later laboratory analysis.

To analyze the concentrations of the heavy metals aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg),

Table 1. Anthropogenic activities and their effects at sampling sites along the Campeche central coast, southeastern Gulf of Mexico.

Location	Stations	Anthropogenic activity	Impact
City of Campeche	S1	Beach restaurant businesses	Modification of coastal morphology and margins of aquatic systems, and anthropogenic contamination.
	S2	Rain discharge drainage	
	S3		
Seybaplaya	S4	Shrimp culture discharge drainage	Modification of neighboring zones, use of effluents and influents as supply and discharge, respectively.
	S5	Port operations	Contamination by fuels and noise.
Champotón	S6	Discharge of urban wastewater from the municipal market	Modification of morphology of margins of aquatic systems and alteration of native flora and fauna.
	S7	Port operations	Contamination by fuels and noise.
	S8	Tourism and recreation	Economic, social, and political conflicts in the zone.

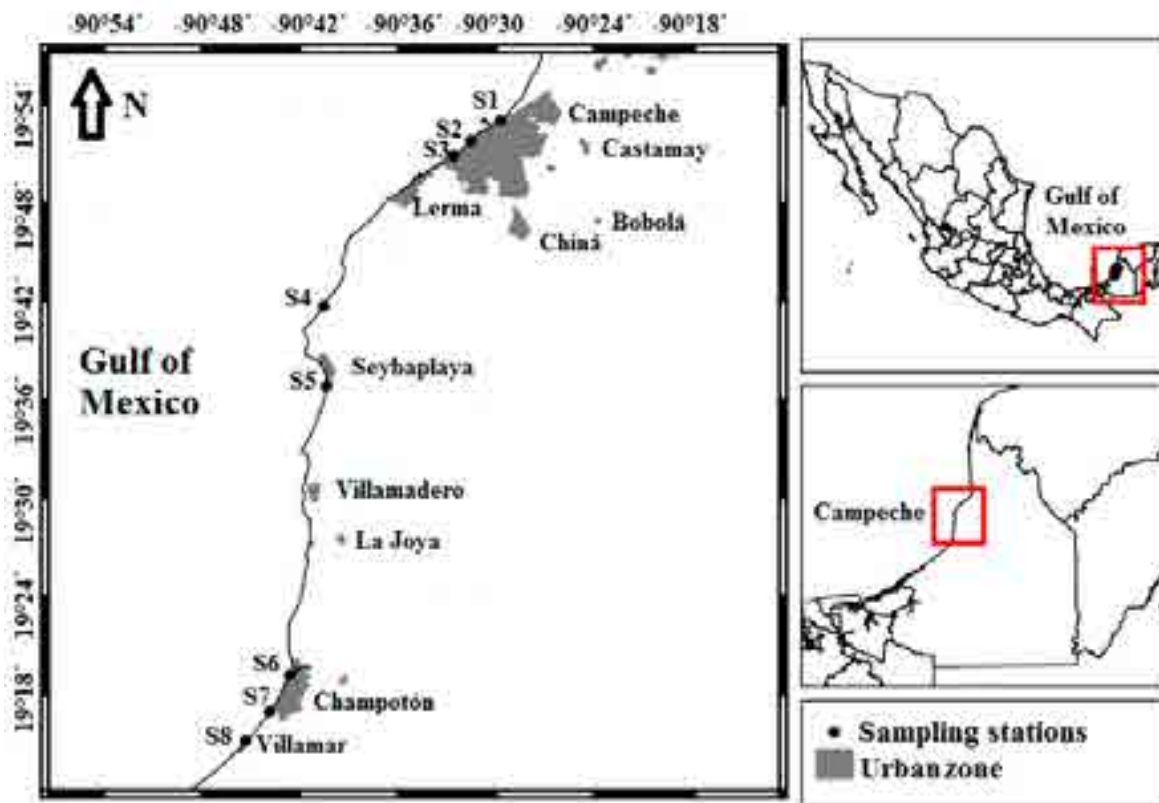


Figure 1. Study area (red boxes) and sampling sites in the coastal waters of the state of Campeche (modified from Poot-Delgado *et al.* 2022).

manganese (Mn), lead (Pb), vanadium (V) and zinc (Zn), sediment samples were collected from the muddy bottom (to a depth of 15 cm) in nursery bags and preserved in ice at 4 °C for further analysis. For processing the sediment matrix, the samples were dried in an oven at 35 °C for 48 h.

Laboratory analyses. Orthophosphate, ammonium, nitrite, nitrate and silicate analyses were performed in the laboratory following standard chemical methods for marine environmental monitoring (UNEP 1991). Phytoplankton cell counting was performed according to Utermöhl (1958), using 10-ml sedimentation cylinders and a Zeigen inverted microscope equipped with phase contrast 10x/0.25 Ph1 ADL and LD 25x/0.30 Ph1 objectives. Nanoflagellates (<20 µm), due to their small size, were not identified to species or higher level, nor were autotrophic and heterotrophic nanoflagellates distinguished. Abundance values were expressed as cells L⁻¹. Phytoplankton species were identified in fixed samples with a Carl Zeiss Axiostar Plus compound microscope (Oberkochen, Germany) equipped

with 5x/0.10, 10x/0.25, 20x/0.40, 40x/0.65, and 100x/1.25 planachromatic objectives. Specialized literature was consulted to identify phytoplankton species: Schiller (1931), Cupp (1943), Osorio-Tafall (1942), Dodge (1982), Komárek & Anagnostidis (1986a, b), Fukuyo *et al.* (1990).

The determination of FC was in accordance with the standard NOM-112-SSA1-1994 (SSA 1994) that consists of a presumptive and confirmatory test; 0.1, 1 and 10 mL of each sample were inoculated in triplicate in 25 mL tubes with 10 mL of lactose broth with Durham tubes inverted inside and were incubated at 36 °C for 24 h. From the tubes that were positive for gas production, aliquots were taken and inoculated into tubes with 2% brilliant green bile broth containing inverted Durham tubes and incubated at 36 °C for 24 h for quantifying FC. The microbial density is expressed as a most probable number (MPN) per 100 mL.

Metal contents in sediment were determined by differential pulse anodic stripping voltammetry (DPASV) following the procedure proposed by

Praveen-Kumar *et al.* (2005): 0.5 g of sediment was transferred to a Teflon reaction vessel with 10 mL of distilled water and an acid mixture of 5 ml of 65% HNO₃, 4 ml of HF at 38-40%, and 1 mL of 37% HCl. The digestion was carried out in a microwave digestion system MARS Xpress 5 (CEM Corporation) (USEPA 1996). The digested sample was completed to a volume of 250 mL, and the pH was adjusted to 2.2 with 0.1 M NaOH. Voltammetric measurements of heavy metals were performed with a 797 VA Computrace (Metrohm AG) electrochemical system and computer-controlled by VA Computrace Metrodata software (Metrohm AG). The techniques for determination of the heavy metals were performed according to the USEPA (1996). Validation and quality control according to Metrohm standard application procedures were used in each metal determination. Similarly, the calibration curves of each of the metals analyzed were performed with certified standards.

Statistical analyses. To observe changes in physicochemical variables, the normality of the recorded data was assessed with the Kolmogorov-Smirnov test and homoscedasticity with the Bartlett's test (Garson 2012). The hypotheses of differences between seasons were tested by analysis of variance (ANOVA), and Tukey TSD (truly significant difference) was applied with a significance level of 0.05 (Daniel 1993). Calculation routine was performed with Statgraphics Centurion XV program (version 18.2.06). SigmaPlot (version 10.0) was used to obtain graphics of phytoplankton and physicochemical variables (Statgraphics Technologies, Inc., The Plains, VA, USA). The effect of physicochemical variables on FC and abundances of a major group of phytoplankton was tested using canonical correspondence analysis (CCA). It was performed using a matrix of environmental factors and abundances of a major group of phytoplankton (Ter Braak 1986). Data were transformed to Log 10 (data + 1) before the analysis because (1) data did not follow a normal distribution, and (2) a significant difference in magnitude between the values of biological and physicochemical data occurred. The significance of the axes of the CCA was tested using a Monte Carlo analysis with 199 permutations (Ter Braak 1986). Calculation routine was performed using the CANOCO program (version 201.4.56).

RESULTS

The results obtained from both physicochemical and bacteriological characteristics were compared with the water quality criteria of the maximum permissible limits established for estuaries and coastal marine waters in monthly averages under Mexican laws (SEMARNAT 1996; CNA 2016). The variability

of physicochemical characteristics is shown in Figures 2 and 3 and in Table 2.

Temperature. The eight stations sampled in September showed an average of 31.5 °C, a minimum of 30 °C at st. 1 and a maximum of 32.8 °C at st. 7. In November, the eight stations showed an average of 30.1 °C with a variability range of ±3.52 °C, a maximum of 38.6 °C at st. 8 and a minimum of 27.5 °C at st. 1. However, there were no significant differences between months ($F=0.001$; $p>0.05$).

Salinity. The salinity in September showed an average of 38.25 with a variability range of ±0.21, a minimum of 28.2 at st. 6 and a maximum of 41.5 at st. 4. In November the eight stations showed an average of 26 with a variability range of ±7.96, a minimum of 17 at st. 2 and a maximum of 39 at st. 4 (Fig. 2). There were no significant differences between months ($F=0.11$; $p>0.05$).

pH. The pH values at the eight stations in September showed an average of 9.2 and a standard deviation of 0.17, with a variability range of ±0.5. In November, the pH values fluctuated ± 2.5 with an average of 7.2 and a standard deviation (SD) of 0.79, with a maximum of 9.0 at st. 7 and a minimum of 6.5 at st. 3 (Fig. 2). Significant differences occurred between months ($F=0.0005$; $p<0.05$).

Dissolved oxygen. The values of DO at the eight stations in September showed an average of 7.1 mg L⁻¹ with a variability range of ±0.55. In November, the minimum value was 4.1 mg L⁻¹ at st. 7, the maximum value was 7.5 mg L⁻¹ at st. 5 and the average value was 6.1 mg L⁻¹ with a variability range of ±1.37 (Fig. 2). DO showed no significant differences between months ($F=0.02$; $p>0.05$).

Nitrogen-containing nutrients. In September, at all stations nitrites were above the maximum limit established for marine waters (Table 2). As in November, the maximum value of 0.045 μmol L⁻¹ was determined at st. 2 (Fig. 3). There were no significant differences observed between months ($F=0.27$; $p>0.05$). In September and November, nitrates were above the maximum limit established for marine waters. There were significant differences between months ($F=0.006$; $p<0.05$). In September, at st. 1, 2, 4 and 8 ammonium was above the maximum limit established for marine waters. In November, only st. 1, 2, 3 and 4 showed values above the maximum limits established for marine waters. Significant differences occurred between months ($F=0.074$; $p<0.05$).

Orthophosphates. In both September and November, orthophosphates were well below the maximum limit established for marine waters (Table 2). No significant differences were observed between months ($F=1$; $p>0.05$).

Table 2. Summarized statistics of environmental variables and nutrients from eight sampling sites along the central coast of Campeche, southeastern Gulf of Mexico, in September and November 2016 (range and mean \pm SD). **Water quality criteria for the protection of aquatic life (CNA 2016).

Month	Environmental variables						Nutrients ($\mu\text{mol L}^{-1}$)				
	t°C	Salinity	pH	DO (mg L ⁻¹)	Nitrites	Nitrates	Ammonium	Orthophosphates	Silicates		
September	30-32.8	28.2-41.5	9-9.6	6.2-7.9	0.006-0.06	0.07-0.27	0.07-0.27	0.01-0.08	0.8-19.8		
	31.5 \pm 0.84	38.2 \pm 4.21	9.2 \pm 0.17	7.1 \pm 0.55	0.02 \pm 0.01	0.16 \pm 0.07	0.14 \pm 0.07	0.04 \pm 0.02	5.76 \pm 6.6		
November	27.5-38.6	17-39	6.5-9	4.1-7.5	0.006-0.045	0.19-0.84	0.04-0.23	0.01-0.08	0.7-12.2		
	30.1 \pm 3.52	26 \pm 7.96	7.2 \pm 0.79	6.1 \pm 1.37	0.02 \pm 0.01	0.46 \pm 0.24	0.10 \pm 0.06	0.04 \pm 0.02	4.83 \pm 4.2		
SD \div month	2.582	8.825	1.188	1.142	0.015	0.237	0.069	0.021	5.366		
Limit of detection	0.01	0.00-70	\pm 0.02	0.00-50	0.01-2.5	0.05-45	0.1-10	0.03-5	0.1-140		
**Upper limits established for marine coastal waters	\pm 1.5 of natural conditions reported previously	-	>5 to >10	>5	0.002	0.04	0.01	5	-		

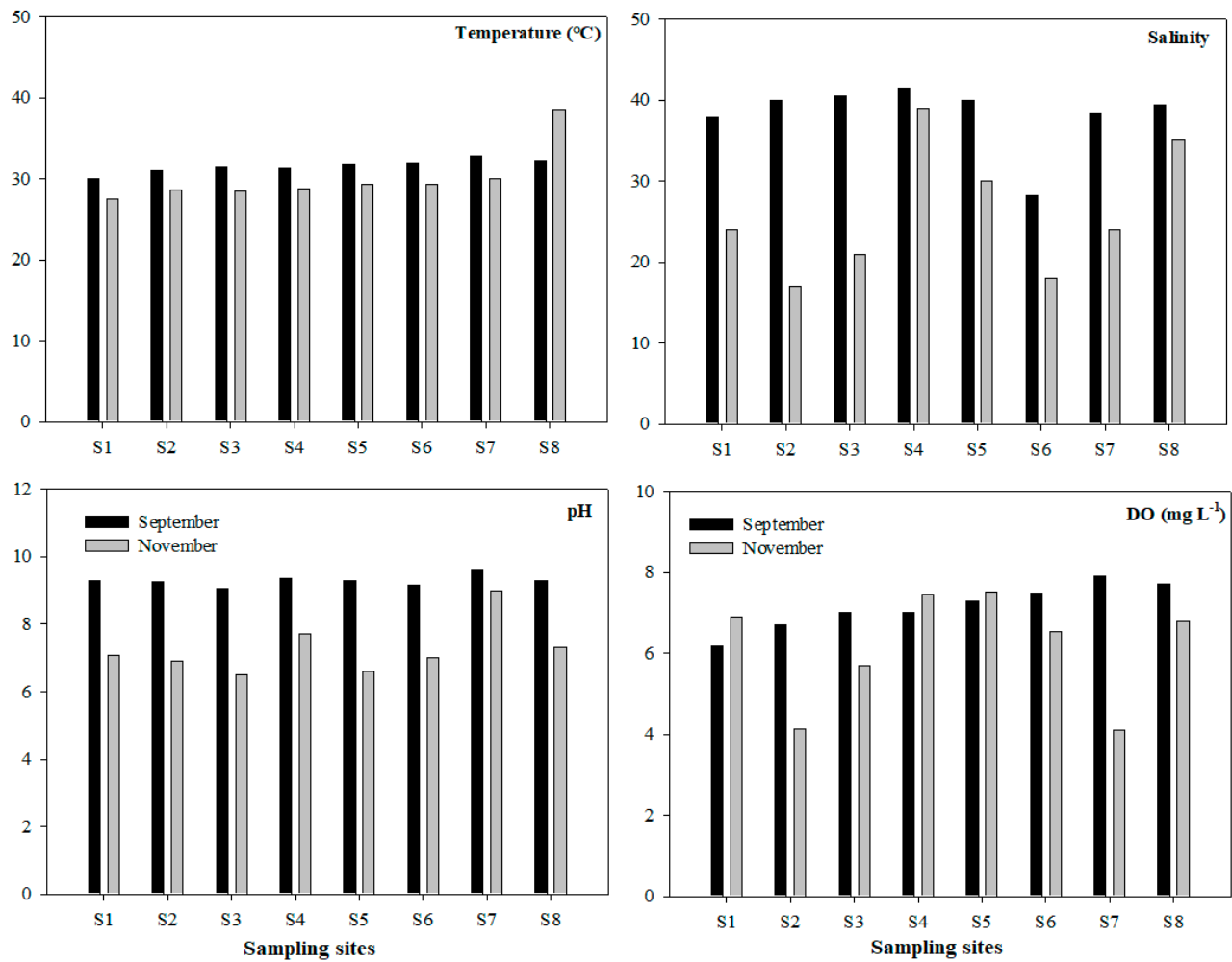


Figure 2. Temporal variation of some physicochemical characteristics at eight stations (S1-S8) along the Campeche central coast, southeastern Gulf of Mexico.

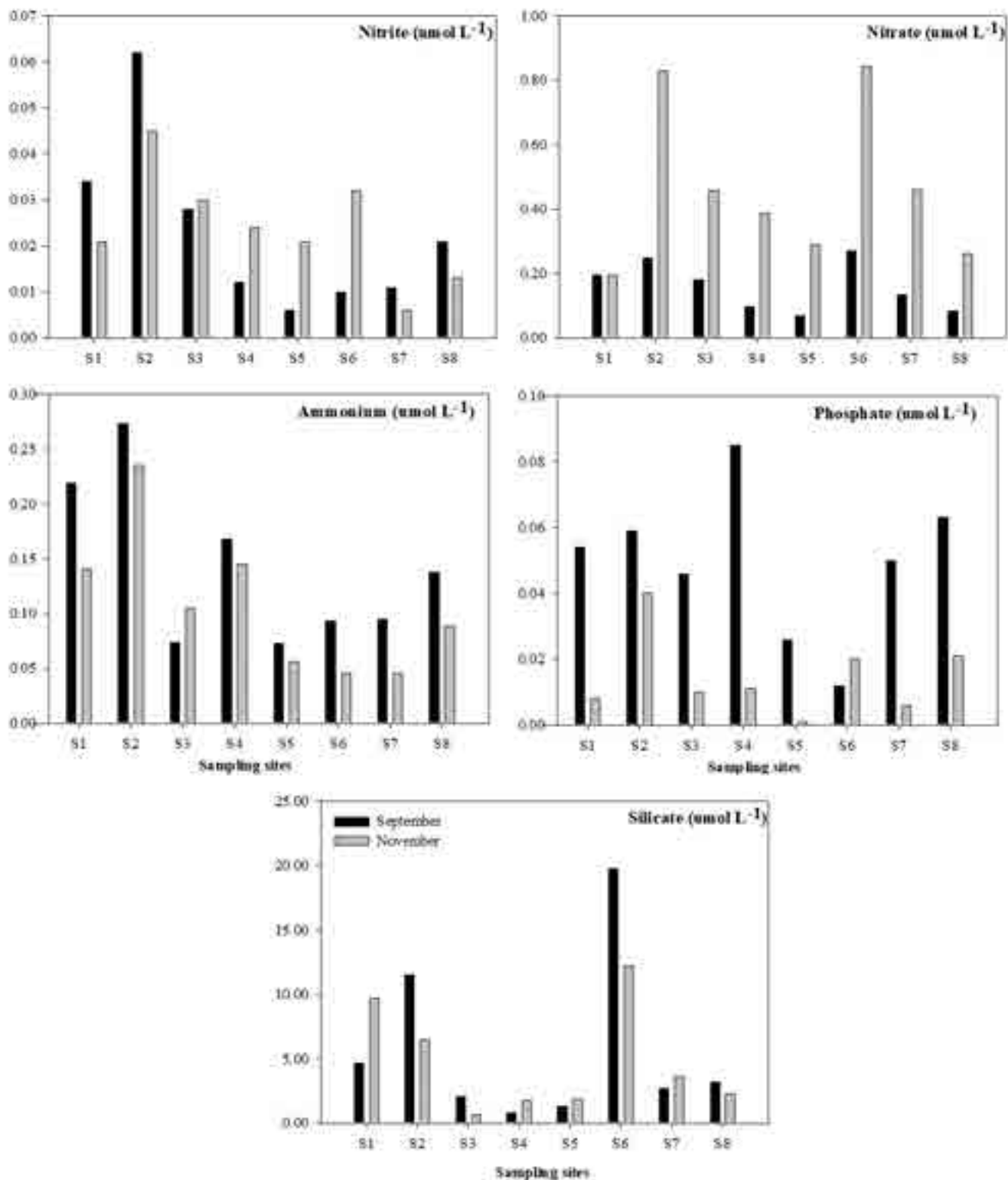


Figure 3. Temporal variation of nutrients at eight stations (S1-S8) along the Campeche central coast, southeastern Gulf of Mexico.

Silicates. In September, silicates did not differ significantly between months ($F=0.25$; $p>0.05$). It should be noted that silicates are not included in the current Mexican regulations (Table 2).

Total heavy metals. The total concentration of total heavy metals (Table 3) varied widely between months. Only Zn showed significant differences between months ($F=0.044$; $p<0.05$). Cu, Fe and Hg showed the highest values in September, and Zn, Pb, Mn and Cr in November. Al and V showed maximum and minimum values in September. Mn was the highest in September at st. 1. Cd was present in September at st. 1 and 8, and As was present at st. 4 in November.

Phytoplankton in general. In total, 43 microalgal species were identified, of which 18 (41%) were diatoms, 17 (39%) dinoflagellates, 4 (10%) cyanobacteria, 3 (7%) nanoflagellates and 1 (3%) silicoflagellate (Table 4). The average abundance of marine phytoplankton during the study period was 4.8×10^5 cells L^{-1} , ranging from 1.1×10^5 to 1.5×10^6 cells L^{-1} (Fig. 4a, b). In September, the minimum value of 6.0×10^3 cells L^{-1} and the maximum value of 1.3×10^6 cells L^{-1} between stations (with a mean of 1.53×10^5 cells L^{-1} and a SD of 4.8×10^5 cells L^{-1}) were recorded; unidentified nanoflagellates were the most abundant at st. 5. At all the other stations dinoflagellates were the most abundant, followed by diatoms. Cyanobacteria showed their maximum abundance at st. 7 (Fig. 4a). In November, a minimum value of 1.1×10^5 cells L^{-1} and a maximum value of 1.2×10^6 cells L^{-1} (with an average of 3.7×10^5 cells L^{-1} and a SD of 3.5×10^5 cells L^{-1}) were observed; diatoms were the dominant taxonomic group (Fig. 4b). In September and November the minimum total phytoplankton abundance occurred at st. 3 and the maximum at st. 5. There were no significant differences between months ($F=0.42$; $p>0.05$).

Nanoflagellates. In September, the highest nanoflagellate abundance was observed at st. 5 (1.31×10^6 cells L^{-1}) and the minimum value at st. 7 (6.0×10^3 cells L^{-1}), with a mean of 2.1×10^5 cells L^{-1} and a SD of 4.4×10^5 cells L^{-1} (Fig. 4a). In November, the total abundance, in general, was lower; it decreased markedly to 3.3×10^4 cells L^{-1} at st. 1, and a maximum value of 9.7×10^4 cells L^{-1} occurred at st. 6, with a mean of 6.2×10^4 cells L^{-1} and a SD of 2.2×10^4 cells L^{-1} (Fig. 4b). There were no significant differences between months ($F=3.85$; $p>0.05$).

Diatoms. In September, the average diatom abundance was 1.1×10^5 cells L^{-1} with a SD of 7.8×10^4 cells L^{-1} . The minimum value (1.8×10^4 cells L^{-1}) was recorded at st. 3 and the maximum (2.3×10^5 cells L^{-1}) at st. 7 (Fig. 4a). In November, the maximum value (8.7×10^5 cells L^{-1}) was recorded at st. 5 and the mini-

um value (4.5×10^4 cells L^{-1}) at st. 1, with a mean of 2×10^5 cells L^{-1} and a SD of 2.7×10^5 cells L^{-1} (Fig. 4b). However, no significant differences were observed between months ($F=0.003$; $p>0.05$). *Cylindrotheca closterium* was the most abundant diatom with a maximum value of 1.4×10^5 cells L^{-1} . Its maximum abundance was observed in September at st. 3.

Naked dinoflagellates >20 μm . In September, the average naked dinoflagellate >20 μm abundance was 950 cells L^{-1} with a SD of 1.2×10^3 cells L^{-1} . A minimum value (400 cells L^{-1}) was recorded at st. 6 and a maximum (3.0×10^3 cells L^{-1}) at st. 2 (Fig. 4a). In November, the maximum value (1.3×10^3 cells L^{-1}) was recorded at st. 8 and a minimum value (400 cells L^{-1}) at st. 7, with a mean of 475 cells L^{-1} and a SD of 582 cells L^{-1} (Fig. 4b). However, no significant differences were observed between months ($F=1.01$; $p>0.05$).

Thecate dinoflagellates >20 μm . In September, the highest thecate dinoflagellate >20 μm abundance was observed at st. 2 (8.1×10^5 cells L^{-1}) and the minimum at st. 6 (500 cells L^{-1}), with a mean of 2.5×10^4 cells L^{-1} and a SD of 2.9×10^4 cells L^{-1} (Fig. 4a). In November, the total abundance, in general, was lower; it decreased markedly to 100 cells L^{-1} at st. 7, and a maximum value of 5×10^3 cells L^{-1} occurred at st. 8, with a mean of 1.5×10^3 cells L^{-1} and a SD of 1.7×10^3 cells L^{-1} (Fig. 4b). Significant differences were observed between months ($F=5.29$; $p<0.05$).

Dinoflagellates <20 μm . In September, the minimum value (1.3×10^3 cells L^{-1}) was recorded at st. 4 and the maximum value (2.1×10^4 cells L^{-1}) at st. 1, with a mean of 9.3×10^3 cells L^{-1} and a SD of 5.9×10^3 cells L^{-1} (Fig. 4a). In November, the abundances were lower. The minimum value (1.0×10^3 cells L^{-1}) was recorded at st. 2 and the maximum value (2.1×10^4 cells L^{-1}) at st. 1, with a mean of 7.0×10^3 cells L^{-1} and a SD of 7.2×10^3 cells L^{-1} (Fig. 4b). No significant differences were observed between months ($F=0.52$; $p>0.05$). The non-toxic benthic-planktonic brackish-marine thecate dinoflagellate *Blixaea quinquecornis* (T.H. Abé) Gottschling (= *Peridinium quadridentatum* T.H. Abé, *Peridinium quadridentatum* (F. Stein) G. Hansen) was found in September with a maximum abundance of 6.5×10^3 cells L^{-1} at st. 3.

Cyanobacteria. Cyanobacteria ranged from none observed in September at st. 5 to a maximum value of 5.2×10^5 cells L^{-1} at st. 7, with a mean of 9.8×10^4 cells L^{-1} and a SD of 1.7×10^5 cells L^{-1} (Fig. 4a). In November, the minimum value (1.1×10^4 cells L^{-1}) occurred at st. 4 and the maximum value (1.7×10^5 cells L^{-1}) at st. 5, with a mean of 5.0×10^4 cells L^{-1} and a SD of 4.2×10^4 cells L^{-1} (Fig. 4b). There were no significant differences between months ($F=0.001$;

Table 3. The concentration of total heavy metals (mg Kg⁻¹) in sediments at eight stations along the central coast of Campeche, southeastern Gulf of Mexico (SD: standard deviation). *Months when heavy metals were determined. **Threshold effect sediment quality guidelines for metals (Burton 2002). ***Limit of detection (LOD) and limit of quantification (LOQ) for all total heavy metals determined by differential pulse anodic stripping voltammetry in sediments.

Station	Zn		Pb		Cu		Mn		Al		Fe		V		Cr		*Cd	*As	*Hg
	Sep	Nov	Sep	Nov	Sep	Nov	Sep	Nov	Sep	Nov	Sep	Nov	Sep	Nov	Sep	Nov	Sep	Nov	Sep
S1	32.9	18.6	7.5	0.3	8.2	1.2	907.3	240.4	399.6	32.1	685.0	66.1	10.6	11.4	0.4	24.1	2.7	0	144.6
S2	33.7	40.1	4.2	4.4	7.9	3.7	398.1	248.0	55.1	4.7	506.0	254.6	64.2	16.2	4.8	11.4	0	0	57.9
S3	28.0	62.8	9.7	5.6	6.5	4.7	508.7	433.1	20.8	49.2	401.8	261.0	35.7	10.0	1.8	5.6	0	0	34.3
S4	28.3	77.0	1.9	3.7	4.7	7.3	346.9	464.6	8.0	57.8	185.2	145.1	90.9	19.1	3.6	13.5	0	4.85	22.7
S5	22.3	53.9	0.8	2.7	3.9	2.0	431.6	540.2	13.9	55.6	225.8	142.7	1.0	33.0	5.8	14.2	0	0	34.8
S6	18.6	61.4	0.7	5.1	3.9	5.9	352.3	469.6	11.3	39.8	254.6	182.9	6.7	24.0	0.6	13.0	0	0	22.5
S7	25.0	97.9	6.7	12.7	7.5	5.5	493.1	607.7	51.6	46.0	411.7	459.7	1.2	4.6	3.4	18.9	0	0	26.5
S8	25.9	73.1	4.5	6.2	5.5	2.5	464.9	526.5	68.8	52.9	158.5	99.4	86.9	17.1	0.3	14.3	2.7	0	14.1
SD ÷ station	5.08	24.06	3.3	3.58	1.75	2.11	179.8	133	131.7	17.4	181.7	124.6	38.41	8.83	2.11	5.4	0.04		42.44
**	123		35		-		-		-		-		-		37.5		0.6	59	0.17
LOD µg g ⁻¹	0.50		0.30		0.50		1.00		0.50		2.00		0.25		0.05		0.50	0.20	0.20
LOQ µg g ⁻¹	5.0		2.3		2.5		7.0		6.0		5.5		5.0		4.5		4.5	5.0	4.0

Table 4. Abundances of representative species recorded from eight sampling sites along the central coast of Campeche, southeastern Gulf of Mexico, in September and November 2016.

Species composition	Abundance (cells L ⁻¹)	
	September	November
Diatoms		
<i>Bacteriastrum</i> sp.	-	200
<i>Chaetoceros</i> spp.	2700	3900
<i>Cyclotella</i> sp.	13500	1300
<i>Cylindrotheca closterium</i> (Ehrenberg) Reimann et J.C. Lewin	143300	16100
<i>Guinardia striata</i> (Stolterfoth) Hasle	500	-
<i>Melosira nummuloides</i> C. Agardh	1700	32500
<i>Odontella</i> sp.	200	-
<i>Paralia fenestrata</i> Sawai et Nagumo	-	49000
<i>Pseudo-nitzschia</i> sp.	400	3800
<i>Skeletonema</i> sp.	300	1200
Unidentified centric diatoms	126300	76900
Unidentified pennate diatoms	77700	165200
Dinoflagellates		
<i>Akashiwo sanguineum</i> (Hirasaka) G. Hansen et Ø. Moestrup	2500	400
<i>Alexandrium</i> sp.	600	700
<i>Blixaea quinquecornis</i> (T.H. Abé) Gottschling	22900	8300
<i>Ceratium furca</i> (Ehrenberg) Claparède et Lachmann	1400	200
<i>Cochlodinium polykrikoides</i> Margalef	-	1000
<i>Dinophysis caudata</i> Saville-Kent	-	400
<i>Gymnodinium catenatum</i> H.W. Graham	3500	1600
<i>Karenia brevis</i> (C.C. Davis) G. Hansen et Ø. Moestrup	800	300
<i>Prorocentrum compressum</i> (Bailey) T.H. Abé ex J.D. Dodge	1900	2000
<i>P. micans</i> Ehrenberg	-	1,000
<i>P. minimum</i> (Pavillard) J. Schiller	200	-
<i>P. rathymum</i> A.R. Loeblich III, Sherley et R.J. Schmidt	4700	3300
<i>Protoperidinium</i> spp.	32600	35400
<i>Pyrodinium bahamense</i> Plate	4000	1500
Naked dinoflagellates >20 µm	6600	4000
Thecate dinoflagellates >20 µm	204400	12800
Cyanobacteria		
<i>Anabaena</i> sp.	15300	2000
<i>Trichodesmium</i> sp.	100900	154400
<i>Merismopedia</i> sp.	900	3400
Nanoflagellates		
	1708099	499000

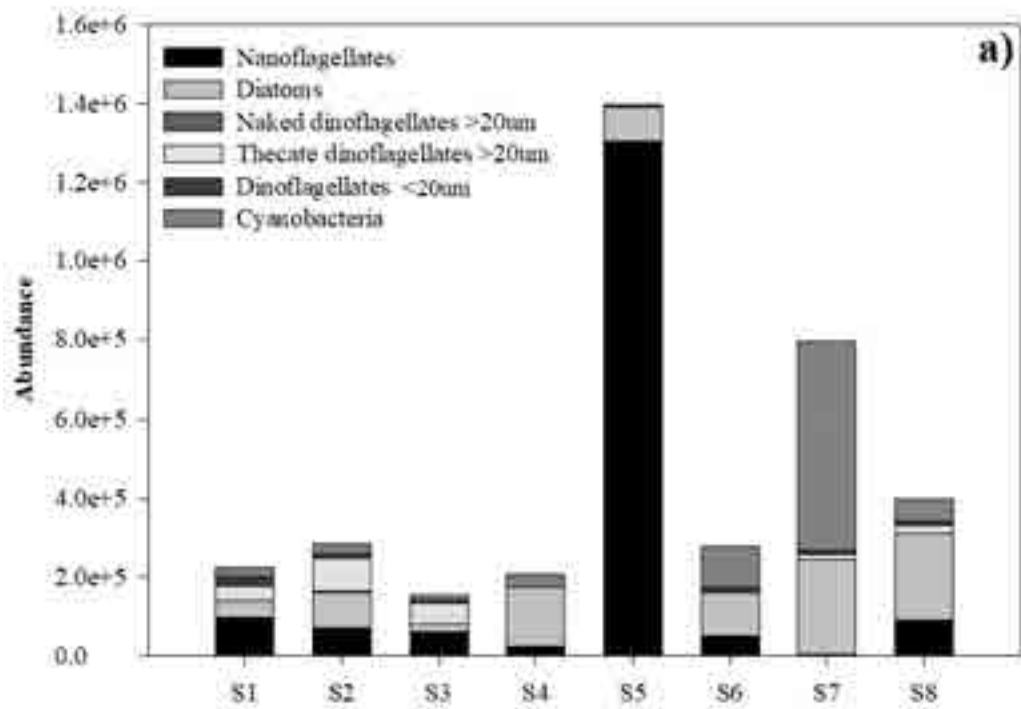


Figure 4a. Spatio-temporal variation in abundances of major phytoplankton groups in September 2016 along the Campeche central coast, southeastern Gulf of Mexico.

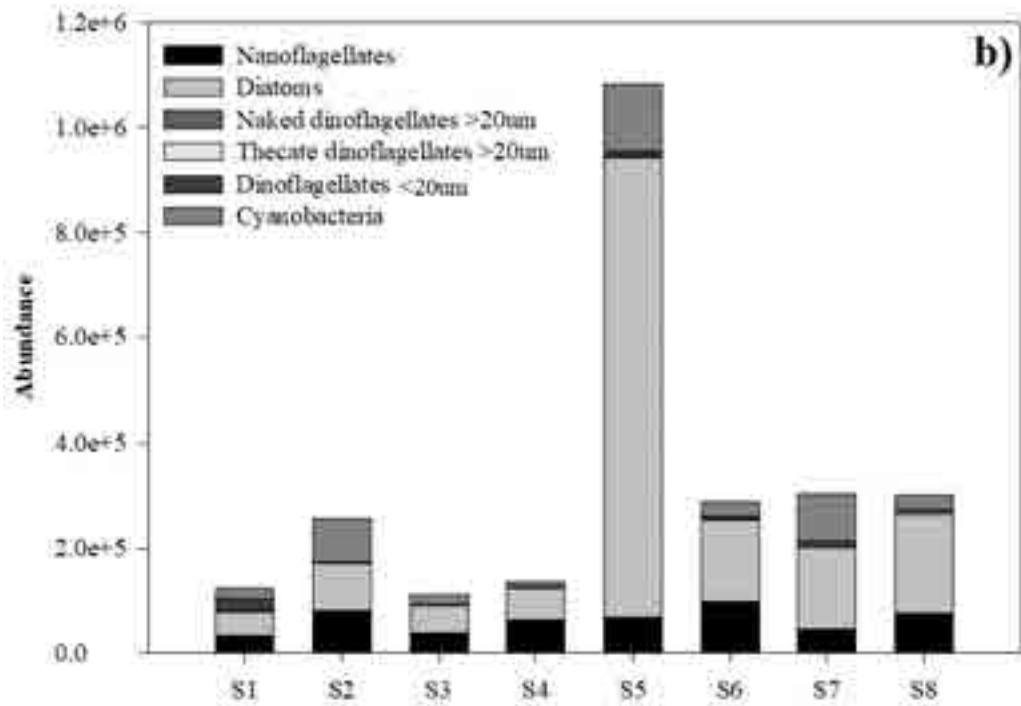


Figure 4b. Spatio-temporal variation in abundances of major phytoplankton groups in November 2016 along the Campeche central coast, southeastern Gulf of Mexico.

$p > 0.05$). The genus *Trichodesmium* Ehrenb. ex Gomont was present in both months and at all stations with values on the order of 10^5 cells L^{-1} .

Fecal coliform bacteria. The highest concentrations of FC in September (>200 MPN per 100 mL) were observed at st. 5, 7 and 8, exceeding 900 ± 344 MPN/100 mL at st. 3 (Fig. 5). This value exceeds that allowed for water quality according to the aquatic life protection ecological criteria (CNA 2016). Significant differences were observed between stations ($p < 0.05$). In November, low levels of FC were found (Fig. 5) except at st. 2, 4, and 6 where values of >200 MPN 100 mL^{-1} were recorded. Significant differences were observed between stations ($p < 0.05$). In both months, st. 1 showed a minimum value of <30 MPN 100 mL^{-1} . However, no significant differences were observed between months ($F = 3.03$; $p > 0.05$).

Relationships between bacteria, phytoplankton, and physicochemical characteristics. The response of the major phytoplankton groups to physicochemical variables is primarily explained by the first two axes (axis 1: 57.5%, axis 2: 34%, total

91.5%). The correlation between FC, major phytoplankton groups and physicochemical variables was high ($r \approx 0.8$), indicating a significant correlation between FC and phytoplankton species composition used in the analysis. All canonical axes were not statistically significant ($p > 0.05$, Monte Carlo). However, the CCA graphs showed that the first axis (positive values) separates the samples of FC, nanoflagellates, diatoms, dinoflagellates $<20\ \mu\text{m}$ and cyanobacteria with high values of nitrites, ammonium, and orthophosphates from the samples with naked and thecates dinoflagellates $>20\ \mu\text{m}$. Regarding the second axis FC, nanoflagellates and diatoms were abundant in positive coordinates when the nitrate concentration was higher. Cyanobacteria were abundant in negative coordinates, coinciding with the samples with high values of nitrites, ammonium, orthophosphates, and other physicochemical variables. However, the naked and thecated dinoflagellates $>20\ \mu\text{m}$ did not show an affinity for the measured physicochemical parameters (Fig. 6).

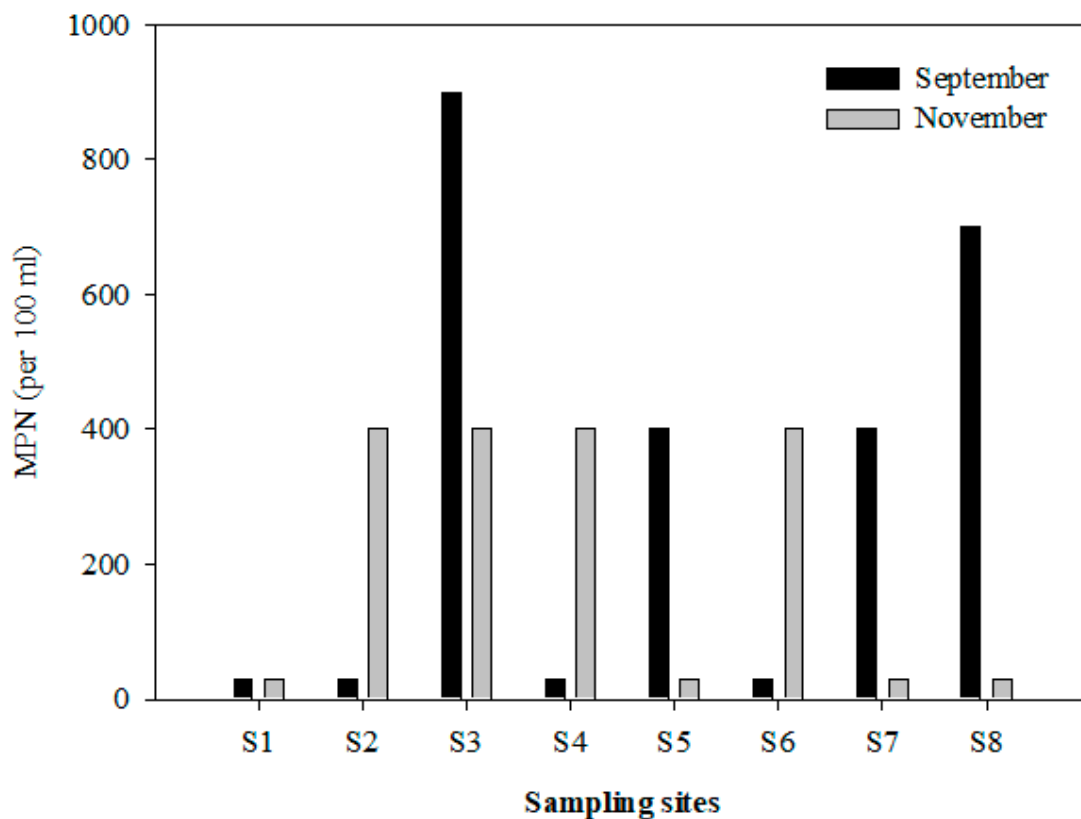


Figure 5. The concentration of fecal coliform bacteria in water along the Campeche central coast, southeastern Gulf of Mexico, in 2016.

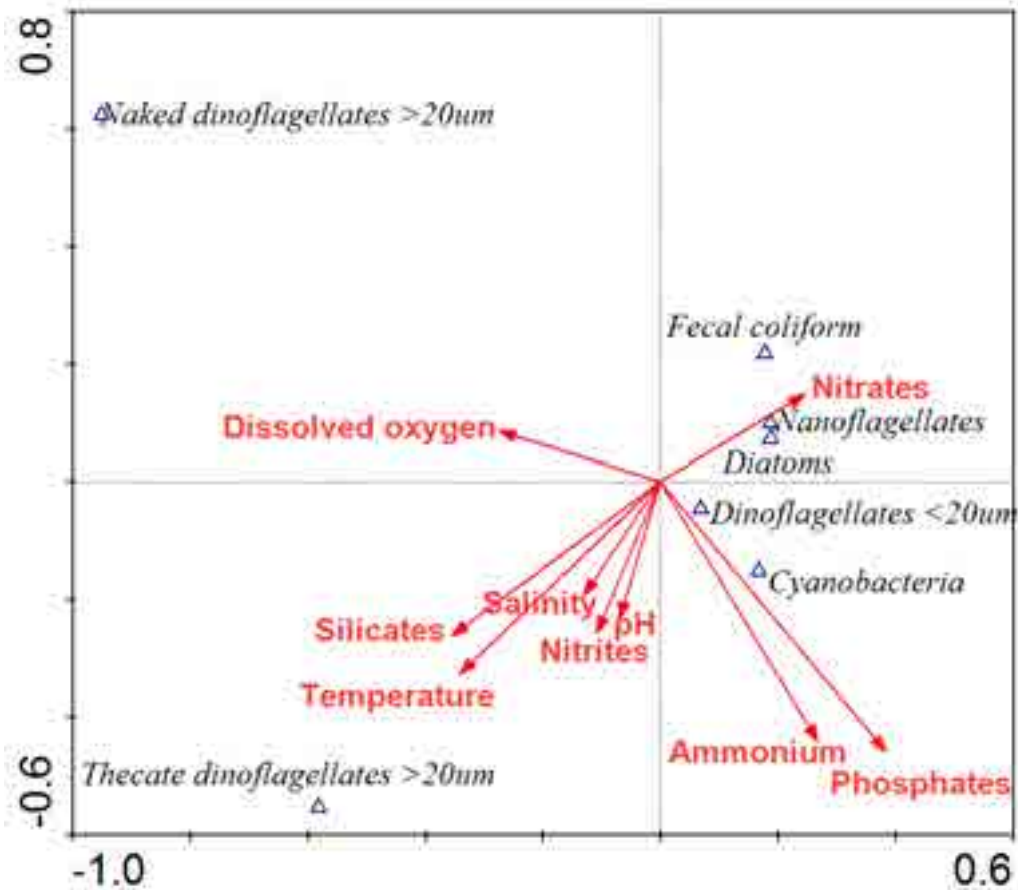


Figure 6. Canonical correspondence analysis applied to relationships between fecal coliforms, major phytoplankton groups, and physicochemical variables along the Campeche central coast, southeastern Gulf of Mexico.

DISCUSSION

Physicochemical variables. The temperature and salinity at the sampled sites were shown to be favorable with respect to the presence and abundance of the major taxonomic phytoplankton groups. This is supported by the CCA analysis that showed a high correlation ($r \approx 0.8$). The ranges of the measured parameters varied depending on the climatic season caused by local hydrography and the shallowness of the study area (Poot-Delgado *et al.* 2014, 2022; Kurczyn *et al.* 2021). The pH values and oxygen saturation suggest high activity of the primary producers in the water column, leading to changes in water quality (especially in pH and DO) that could be related to the phytoplankton proliferations that occur in the area (Gómez-Figueroa 2020; Poot-Delgado *et al.* 2022).

Nitrogen compounds (nitrites, nitrates, and ammonium) were above the maximum limit established

for marine waters, coinciding with those reported by Alpuche-Gual (2014), Varona-Cordero *et al.* (2014) and Gómez-Figueroa (2020). This is due to the effect of water discharges in the rainy season and to a lesser extent to the effect of sediment resuspension in the windy season (Monreal-Gómez *et al.* 1992, 2004; Varona-Cordero *et al.* 2014). The foregoing may suggest problems due to nutrient enrichment in the coastal waters of the Campeche central zone. For example, the presence of urban wastewater generates lower levels of DO due to bacterial degradation of organic matter, creating high negative redox potential values resulting in low levels of nitrites and high ammonium values (Masters & Ela 2008). Silicates are not regulated within the water quality criteria for the protection of aquatic life; however, their values reported in this study are similar to those by Gómez-Figueroa (2020) who found the lowest concentrations at coastal sites compared to

freshwater ones, which may be due to the abundance of silicates in the Earth's crust that come from the weathering and metamorphism of rocks (Cervantes-Sandoval *et al.* 2014).

The orthophosphate values well below the maximum limit established for marine waters, contrary to those reported by Alpuche-Gual (2014) and Gómez-Figueroa (2020), may be due to the differences in the systems of phosphate acquisition and storage capacities between phyto- and bacterioplankton, which affect their response to phosphorus increase (Talarmin *et al.* 2015; Barcelos e Ramos *et al.* 2017).

Phytoplankton and physicochemical characteristics. A rather quick response of the phytoplankton community (in terms of the abundance and changes in the species composition) to eutrophication should be considered an ecological process, characterized by the complexity and peculiarities of each system (Barcelos e Ramos *et al.* 2017). In addition, each nutrient has a limiting potential that depends on many factors, such as the nutrient absorption rates in different major phytoplankton groups and interactions between the factors (Saito *et al.* 2008). Although this study represents a temporal section with its corresponding limitations (especially temporal), the results obtained can be considered as a photograph of the moment of the interaction of the abiotic and biotic variables of the water column to assess the water quality. The phytoplankton acts as a natural indicator of the effects of eutrophication, due to his rapid response to fluctuations of environmental conditions (Livingston 2001) because of the intensity and type of human activities (Kelly-Gerreyn *et al.* 2004; Álvarez-Góngora & Herrera-Silveira 2006).

In the study area, these conditions may contribute to changes in species composition and abundance of phytoplankton in general and nanoflagellates, diatoms, dinoflagellates <20 µm and cyanobacteria in particular. The latter two are likely to benefit from high temperatures (up to 30.1 °C) and the relatively low salinity (26) related to the continental runoff during the rainy season (Yáñez-Arancibia & Day 2005), which could be combined with the chemical compounds linked to urban residuals from adjacent settlements.

Phytoplankton cell size is important because smaller sized cells have an increased surface/volume ratio that provides a competitive advantage when nutrients are limiting (Chisholm 1992). Therefore, the nanophytoplankton and thecate dinoflagellate >20 µm abundance was high in September. No nitrogen limiting conditions can explain the predominance of small-sized species (cells >20 µm) whose

growth would be supported by reduced forms of nitrogen such as ammonium. This is reinforced by the presence of the cyanobacterial genus *Trichodesmium* in both months throughout the study period, with abundances on the order of 10⁵ cells L⁻¹ due to the physiology of *Trichodesmium* spp., although they are non-heterocystous nitrogen-fixing species that contribute nitrogen in both oligotrophic (Holl *et al.* 2007) and eutrophic waters (White *et al.* 2007). It is well accepted that human activities, especially nutrient pollution, have contributed to the global expansion of harmful algal blooms in terms of increasing abundance, frequency and geographic extent, and that new records of known species are being documented in new areas (Glibert & Burford 2017; Glibert 2020).

The benthic-planktonic pennate diatom *Cylindrotheca closterium* has been reported as a bloom-forming species in the southeastern Gulf of Mexico (Poot-Delgado 2016). In the coastal waters of northern Yucatan, *C. closterium* showed a high abundance throughout the year, so its seasonality remains unclear, although the highest abundances were found from mid-May to mid-October (Merino-Virgilio *et al.* 2019), coinciding with those observed during the study period.

In coastal brackish-water lagoons, the relative contribution of cyanobacteria to the total phytoplankton biomass can be used as an indicator of eutrophication (Poot-Delgado *et al.* 2018). It is known that an increase in temperature (>20 °C), favoring cyanobacteria blooms in marine ecosystems, is closely associated with eutrophication (Anderson *et al.* 2002). *Trichodesmium* spp. showed values on the order of 10⁵ cells L⁻¹ in both months, resulting in an alert for the occurrence of blooms of *Trichodesmium* in the coastal zone. Some marine *Trichodesmium* spp., such as *T. thiebautii* Gomont *ex* Gomont, can be toxic to smaller crustaceans, and *Trichodesmium* blooms may have indirect effects on molluscan and public health due to significant changes in water quality (Gárate-Lizárraga & Muciño-Márquez 2012). There is also evidence of a highly potent neurotoxic compound isolated from a mixed *T. thiebautii* – *T. erythraeum* bloom that occurred in the east Caribbean (for references, see Landsberg 2002). The blooms of *Trichodesmium* are followed by blooms of the toxic dinoflagellate *Karenia brevis* (C.C. Davis) G. Hansen & Ø. Moestrup; this was reported by Lenne *et al.* (2001) for the coasts of Florida. However, this species was absent at almost all the stations in Campeche, with very low abundances at some stations during the study period. *Karenia* spp. have been reported in variable abundances along the lit-

toral of the Gulf of Mexico from Veracruz to Yucatán (Aké-Castillo 2011; Merino-Virgilio *et al.* 2013; Muciño-Álvarez *et al.* 2015; Poot-Delgado *et al.* 2018).

Finally, in trying to understand the life strategies of individual species, it must be recognized that phytoplankton populations in general are partly determined by the amplitude and frequency of fluctuations in the dynamics of their limiting resources. HAB constitute only part of the more difficult tasks of controlling and managing water quality in aquaculture, freshwater, brackish and marine environments (Poot-Delgado & Okolodkov 2016).

Fecal coliform bacteria. Marine pollution along the central coast of Campeche comes from discharges of wastewater from various anthropogenic activities (Table 1) aggravated by the absence or inefficiency of water treatment plants in the large cities of the region (Gracia *et al.* 2014), as was verified by the presence of FC found in concentrations above the current Mexican regulations for coastal waters and estuaries (240 MPN 100 mL⁻¹ FC). However, the abundance of FC is mainly regulated by the synergistic effect among sunlight, temperature, salinity, and pH (Figueroa-Zavala 2007), which was not statistically observed in the present study (all the canonical axes were not statistically significant). Surprisingly, at st. 3, an unexpected value of 900 MPN 100 mL⁻¹ was found, well below values reported by Rendón-von Osten & Lara-Flores (2015) for the same study area (Campeche and Champotón; Fig. 1). Those authors reported values higher than 2400 MPN 100 mL⁻¹ during the rainy season (May to September), which reflects the high population density adjacent to the discharge zone as well as the lack of treatment of the city's waste (Rendón-von Osten & Lara-Flores 2015). Both recorded values coincide with the rainy season when they are closely linked to the rainwater discharges.

In this study, different anthropogenic activities (urban waste, port operations, tourism and recreation, beach restaurant businesses, rain discharge drainage and shrimp culture discharge drainage) affected the sampling stations, and the FC concentrations also varied. FC were not a good indicator of fecal contamination because they disappeared quickly. However, FC are known to be highly abundant in the coastal area, and their persistence indicates a constant effluent of sewage that contributes large amounts of organic matter to the system (Arcos-Pulido *et al.* 2005).

Total heavy metals. The analyzed total heavy metals were selected because they have been previously reported for the study area. Furthermore, most of them are toxic to aquatic organisms

(Villanueva & Botello 1998; Botello *et al.* 2004). In aquatic environments heavy metals occur in higher concentrations in sediments, and their presence in the coastal zone is due to the anthropogenic activities and certain point sources (Vázquez-Gutiérrez *et al.* 1988). For most heavy metals, runoff water is the dominant source for the marine environment, except for some elements such as Hg and Pb, whose atmospheric input is important, particularly in the coastal zone (Páez-Osuna 2005). In the present study, metals considered to be of terrigenous origin were present in both September and November. This is supported by Carranza-Edwards *et al.* (2015), who found sediments of recent terrigenous origin on the beaches of the southern Gulf of Mexico, suggesting that there may be a greater influence of anthropogenic factors in recent sediments.

The same situation occurred in the sediments of the mangrove ecosystem influenced by Laguna de Términos, where the contaminating elements were mainly of anthropogenic origin (De la Cruz-Landero *et al.* 2013). Although in the present study the measurements of heavy metals were obtained only in sediments, it can be stated that their accumulated concentrations were very high, which likely affected the phytoplankton species by inhibiting their growth and reducing their chlorophyll concentration, photosynthesis and cell respiration. This type of response has been observed in trials with aqueous solutions of dissolved Cd, Cu, and Hg in monospecific cultures of the marine planktonic green microalga *Tetraselmis chuii* Butcher (Cordero *et al.* 2005). The total heavy metals are retained in sediments most of the time, and a detailed understanding of the direct relationship between sediment and surrounding water and bioavailability of heavy metals to phytoplankton is still lacking (Kottuparambil *et al.* 2019).

CONCLUSIONS

Nutrient enrichment, high abundance of FC (up to 900 MPN/100 mL at st. 3), high phytoplankton abundances (on the order of 10⁶ L⁻¹ cells), the presence of potentially harmful (including toxic) microalgal species, the presence of cyanobacteria (mainly *Trichodesmium* sp.) and temporal changes in the phytoplankton community were considered for evaluation of the water quality. The non-toxic benthic-planktonic brackish-marine pennate diatom *Cylindrotheca closterium*, previously reported as a bloom-forming species in the southern Gulf of Mexico, reached an abundance of 1.4×10⁵ cells L⁻¹ in September 2016. At the end of the rainy season (September), at st. 3 that was directly affected by

rainwater discharge, the physicochemical conditions favored the proliferation (6.5×10^3 cells L^{-1}) of the non-toxic dinoflagellate *Blixaea quinquecornis*, known to be associated with eutrophic environments. The determination of phytoplankton abundance and the presence of the bloom-forming species were the most useful tools for evaluating anthropogenic effects on the studied marine coastal ecosystem.

Some inorganic nutrients (especially ammonium, nitrites, and nitrates) showed an association with the rainwater discharge sites or with those near anthropogenic activities. At present, there is no official Mexican standard for the maximum permissible limits of heavy metals in coastal sediments. Therefore, the choice of ecological indicators for water quality studies should be the result of careful consideration and an understanding of the natural mechanisms that cause stress in aquatic environments. In the case of eutrophication, nutrient enrichment must be considered to cause changes in biodiversity, taking as a response changes in the species composition of the phytoplankton community. However, due to the complexity and variability of phytoplankton, changes in the composition and structure of the phytoplankton community are not axiomatic. To understand their dynamics and to obtain knowledge of the factors underlying these changes, more detailed autecological and annual phytoplankton community studies are necessary. Coastal zones are subjected to wide ranges of physicochemical and biological variables. The present study may serve as a baseline monitoring to distinguish between natural conditions and anthropogenically impacted environment in the near future.

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