Ocean
and Coastal
Research

ORIGINAL ARTICLE

http://doi.org/10.1590/2675-2824073.23175
ISSN 2675-2824

First determination of photosynthetic pigments in surface sediments from the continental shelf and slope of the northwestern Gulf of Mexico

Alejandro Estradas-Romero[1]*, Luis A. Soto[2], Lucía Álvarez-Castillo[1]

[1] Facultad de Ciencias – UNAM, Circuito Exterior s/n – Coyoacán – Ciudad Universitaria – Coyoacán – Ciudad de México – México. C. P. 04510
[2] Instituto de Ciencias del Mar y Limnología, UNAM (Retired), Ciudad Universitaria – Coyoacán – Ciudad de México – México.

* Corresponding author: estradas@ciencias.unam.mx

ABSTRACT

Marine pigments are more commonly used in food, pharmaceuticals, aquaculture and cosmetics industries. Marine pigments have a significant economic importance, constituting a multimillion-dollar industry that is still growing. Considering this, we decided to conduct a descriptive study of the photosynthetic pigments in surface sediments from the continental shelf and slope of 14 sites located in the northwestern Gulf of Mexico, obtained during October-November 2012. These pigments were analyzed using high-performance liquid chromatography. At least one pigment was detected in 10 of the samples examined, and a total of six pigments were identified, including three photosynthetic pigments and three chlorophyll-*a* degradation products: pheophorbide-*a*, pyrophaeophytin-*a* and phaeophytin-*a.* The pigments with the highest concentration were β-carotene and pheophorbide-*a*. Significant pigment concentrations were observed in inshore areas exposed to the influence of river discharge (Bravo and Soto La Marina) and Laguna Madre. The pigment composition and concentration were influenced by depth, temperature, salinity, and nickel concentration. Finally, a correlation between Ni, an indirect hydrocarbon contaminant marker, and pigment concentrations was observed. A deeper understanding of marine pigments certainly will fuel advances in biotechnology and bioengineering. We find it crucial to recognize the interactions between marine pigments and other ecosystem components. Despite pigment diversity, exploration in this field is still in its first stages, with many marine compounds awaiting further exploration.

Keywords: Photopigments, HPLC, Chlorophylls, Carotenoids, Sedimentary pigment

INTRODUCTION

Bacteria, cyanobacteria and actinobacteria (fungi) are a stable and large source of pigments in the marine environment (Ye et al., 2019). Photosynthetic pigments contained in marine sediments have been a research subject for several years (Palmer and Baker, 1978; Herblan, 1988; Jeffrey et al., 1999; Kowalewska, 2005). Presently, about 13 types of chlorophylls and 500 carotenoids have been described, many of them restricted to marine areas (Repeta and Simpson, 1991; Jeffrey et al., 1997). Pigments play an essential role in marine and terrestrial environments as light collectors in photosynthetic organisms and in photoautotrophic production (Herblan, 1988). The three main groups of marine pigments are chlorophyll, carotenoids

Submitted: 14-Nov-2023
Approved: 27-Dec-2024

Editor: Rubens Lopes

and phycobiliproteins. Currently, the most studied pigments include chlorophyll, fucoxanthin, lutein and phycocyanin.

Chlorophyll-*a*, as well as other pigments, are related to organic chemical compounds in marine systems and are also of interest in oceanography because they can be useful for evaluating phototrophic communities and possible environmental anomalies caused by hydrocarbon contaminants (Laneve et al., 2022; Othman et al., 2023). Hence, pigments can be used as biomarkers in marine and estuarine systems since they are produced by many organisms (macro and microorganisms) (Palmer and Baker, 1978; Kowalewska, 2005). Although chlorophyll-*a* does not have a specific classification and is commonly used to estimate phytoplankton biomass in aquatic systems, the wide range of degradation products that result from it can function as indicators of heterotrophic (Kowalewska, 2005) and other biological processes. For example, pheophytin-*a*, which occurs in seawater, is a marker of slightly decomposed phototrophic matter in sediments. In comparison, pheophorbides-*a* are relatively less stable derivatives and may indicate the presence of fresh material. Finally, pyropheophorbide-*a* is not only a marker of zooplankton and zoobenthos grazing but is also produced during the senescence of certain phytoplankton groups (Szymczak-Żyła et al., 2011). On the other hand, carotenes and their oxygen derivatives, xanthophylls, are effective indicators of different types of phytoplankton (Jeffrey et al., 1999).

Organisms capable of producing pigments, such as bacteria or microalgae, are ubiquitous and a major component in benthic ecosystems, representing an important portion of the sediment biomass (Megharaj et al., 2000). Pigment research efforts have focused on their production, degradation, and sedimentation both in the water column and on the seafloor in different environments (Guerrero et al., 1988; Nelson, 1993; Bianchi, 2000). Interestingly, Beyer et al. (2016) made a review of the environmental effects of the Deepwater Horizon (DWH) oil spill in the Gulf of Mexico. This study reveals that there are chlorophyll anomalies in the northern Gulf and studies regarding this topic have received scarce attention (Hu et al., 2011).

The qualification of pigments in marine sediments using the high-performance liquid chromatography (HPLC) technique has been successfully used by several authors (Kowalewska, 1994, 2005; Kowalewska et al., 1996; Kowalewska and Konat, 1997; Szymczak-Zyla and Kowalewska, 2007). These studies have revealed a link between pigments and physicochemical and biological factors. Thus, we hypothesized a relation between pigment concentration and environmental parameters measured in the area. Therefore, the aims of this study were firstly, to identify and quantify the pigments contained in surface sediments from the continental shelf and slope in the northwestern (NW) Gulf of Mexico (GoM), and secondly, to assess their relation with the environmental factors measured in the area, including heavy metals (Al, Co, Cr, Ni, V, Fe, Mg) and transboundary hydrocarbon contaminants possibly advected from the northern Gulf of Mexico where a massive oil spill occurred in April 2010.

METHODS

STUDY AREA

The study area (10,000 km^2) is in the northernmost corner of the Gulf of Mexico. It extends from the northern tip of the state of Tamaulipas near the mouth of the Rio Bravo (latitude 26°N) to northern Veracruz (latitude 22°N) (Figure 1). It involves the continental shelf and the upper slope, from 50 to 2,200 m deep, strongly influenced by the inflow of waters from the mainland, tropical, and subtropical marine waters (Delgado-Blas, 2001). This part of the Gulf is affected by the discharge of several rivers (Soto La Marina, Indios Morales, Tuxpan, San Fernando, Bravo, and Pánuco). Also, there are two large coastal lagoons: Laguna Madre is bordered in the North by the Río Bravo estuary, in the South, by the estuary of Soto la Marina River and the Laguna de Tamiahua, which is bordered in the North by the river of Pánuco. To the South is the Tuxpan River (Ayala-Castañares et al., 1969; Contreras, 1988).

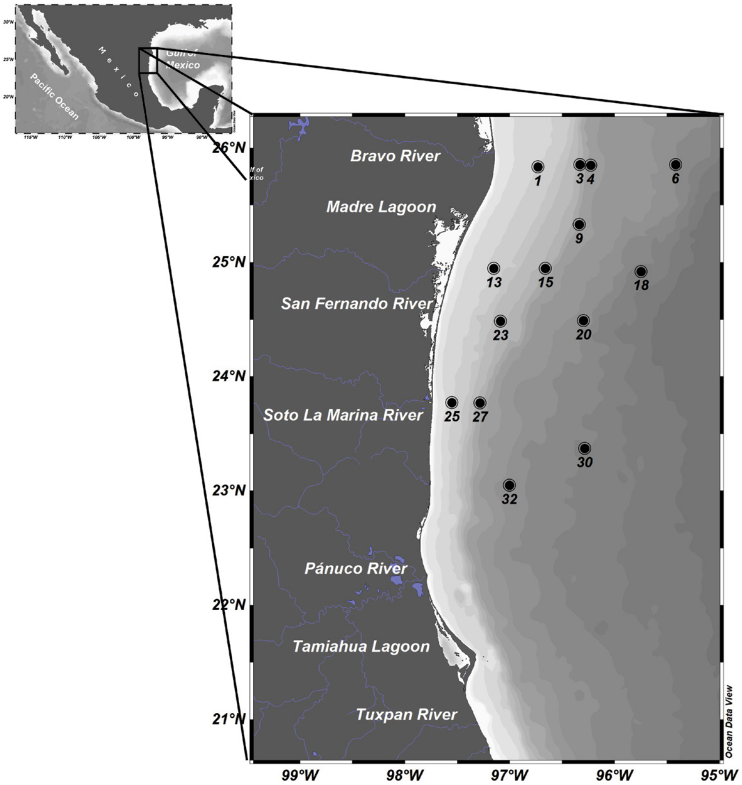

Figure 1. Study area in the northwest Gulf of Mexico during the MARZEE-III expedition onboard the R/V Justo Sierra in October-November 2012 (winter).

HYDROGRAPHIC SETTING

The circulation in the upper layer of the Gulf is primarily influenced by the Loop Current (LC), which carries warm, salty waters from the Yucatán Channel to the Strait of Florida. This current creates eddies that impact the thermohaline structure and environmental variables in the Gulf (Hamilton, 2009; Meza-Padilla et al., 2019). During fall and winter, circulation in the western inner shelf predominantly flows South, generating intense currents due to cold fronts, while high chlorophyll-*a* levels are observed. In the outer shelf and slope, circulation is influenced by cyclonic and anticyclonic eddies, with normal traffic directed North in their absence. In the summer, chlorophyll-*a* values are modified by a semi-permanent increase in circulation (Fernández-Eguiarte et al., 1998; Zavala-Hidalgo et al 2003, 2006).

SAMPLING

Fourteen sediment samples were collected during the MARZEE-III expedition on the R/V Justo Sierra in October–November 2012 in the northern Gulf of Mexico. Samples from the continental shelf and upper slope were obtained using a Smith McIntyre core, while deeper sediments (>200 m) were collected with a Reineck core. The sediments were stored at −70°C until processing, and pigment analysis was conducted using high-performance liquid chromatography (HPLC) based on a method by Vidussi et al. (1996).

CHROMATOGRAPHY

Surface sediments physicochemical parameters, including depth, temperature, salinity, dissolved oxygen (O_2), organic carbon (OC), organic matter (OM), heavy metals (Al, Ni), polycyclic aromatic hydrocarbons (PAHs) (15 priority polyaromatic hydrocarbons, USEPA, 2009), aliphatic hydrocarbons (C8 to C40) were obtained from study samples by Botello et al. (2015) (Table 1).

Table 1. Superficial sediment physicochemical parameters obtained from the continental shelf and slope in the NW Gulf of Mexico during the oceanographic cruise MARZEE-III in 2012 (derived from Botello et al., 2015). CS = Continental Shelf. OC = Organic Carbon. OM = Organic Matter. PAHs = Polycyclic Aromatic Hydrocarbons. AHs = Aliphatic Hydrocarbons. Al = Aluminum. Ni = Nickel (ERL 356.09, ERM 879.14). Only PAHs values exceeding the ERL are included.

	Station	Depth	ΣPAHs	ΣAHs	OC	OM	Salinity	Temp.	O_2	Al	Ni
		m	nmole/g	nmole/g	%	%	UPS	°C	mg/L	%	nmol/g
Inner CS	1	50	2.27	145.61	1.05	1.66	36.4	27.7	6.5	8.2	398.64
	13	52	1.82	108.75	1.40	2.26	36.4	27.3	6.6	5.9	583.22
	25	49	0.84	44.82	1.44	2.43	36.4	26.1	6.4	6	667.29
Outer CS	3	202	0.72	76.21	1.52	2.61	36.1	16	8	5.1	662.71
	15	197	0.84	46.44	1.07	2.38	36	15.5	7.9	8	697.29
	23	110	1.32	23.37	2.30	2.18	36.5	22.6	7	9.9	850.17
	27	205	1.63	56.89	1.60	2.33	35.9	14.7	8.1	6.6	741.86
Slope	4	492	0.51	99.1	1.74	2.14	35.1	9.3	9.2	5.9	720.34
	6	2173	0.99	26.4	0.30	1.92	35	4.3	10	2.1	903.56
	9	500	1.19	101.65	1.76	1.92	35.1	8.8	9.3	8.2	852.03
	18	2623	0.57	19.77	1.93	1.59	35	4.3	10	1.8	876.95
	20	1519	3.58	102.56	2.04	1.84	35	4.3	10	1.9	940.68
	32	1538	0.07	5.54	1.57	1.93	35	4.3	10	1.8	787.12
	30	2307	0.05	6.13	1.71	1.5	35	4.3	10	1.8	900.17

Pigment extraction

Five grams of surface sediment samples from each site were processed. Extractions were performed with 4 cm^3 of 100% HPLC acetone. Samples were stored in the dark for 24 hours at −20°C. They were then centrifuged at 4000 rpm for 15 min at 5°C. The extract was filtered through a 47 mm glass fiber membrane at 0.1%. Pore size is 45 µm. The volume was collected in 2 cm^3 Eppendorf bottles and stored at −20°C. 20 µL. Then the volume was injected into the high-performance liquid chromatograph (model 1100, Hewlett Packard).

HPLC pigment analysis

A mobile phase was created using two combined solutions: solution 1 consisting of HPLC grade methanol and 1 N aqueous ammonium acetate to form a 70:30 v/v mixture and solution 2, consisting of HPLC grade methanol. A 100 x 4.6-mm Hypersil MOS C8 column with 5 µm particle size was used for the separation (Vidussi et al., 1996). To identify the pigments, we first compared the maximum retention time of the sample with that of the pure standard and then assessed the absorption spectra against those of established library standards using chromatography with certified commercial standards (International Agency for ^{14}C determinations, Denmark). The pigments quantification was done running a calibration curve (R_2 = from 0.9107 to 1) that included the concentrations for each standard (20, 30, 40, 50, 60, and 100 ng). The detection limit was calculated following the method published by Küpper et al. (2007).

Statistics

The normality of all variables was confirmed with a Shapiro-Wilks test (Siegel, 1990).

The pigments, heavy metals, and hydrocarbons concentrations (derived from Botello et al., 2015) were converted from ng/g and µg/g (respectively) to nmole/g. Additionally, environmental parameters were initially transformed to $\log_{10}$. Furthermore, these were standardized, and matrices were prepared using Euclidean distances. For the statistical analysis of pigment concentrations, these were $\log_{10}$ (x+1) transformed, and a resemblance matrix was created using Bray Curtis similarities. To evaluate how the environmental parameters were distributed in the sampled area, a principal components analysis (PCA) was applied. For the rest of the statistical analyses, only depth, temperature, salinity, Al, and Ni were used as predictive variables, while pigment concentrations were considered response variables. Two one-way permutational multivariate analyses of variance (PERMANOVA) (Anderson, 2001) were conducted to test if the concentration of the pigments was a function of depth. A similarity percentage (SIMPER) analysis was conducted to identify pigments that caused significant differences in pigment concentration across stations. A spearman rank correlation test was performed to relate pigment concentrations per station with depth, temperature, salinity, dissolved oxygen, organic matter, organic carbon, heavy metals (Al, Co, Cr, Ni, V, Fe, Mg), and aliphatic hydrocarbons (∑PAHs and ∑AH) (Table 1). Analyses were run in the Past 4.03 software (Hammer et al., 2001). Multivariate analyses were performed using PRIMER v6.1.11 (Clarke and Warwick, 2001) with add-on PERMANOVA+software (Anderson et al., 2008).

RESULTS

Two principal components were identified explaining 99.71% of the total variance of the data using principal component analysis (PCA), which used environmental parameters. The first component of the model explained 74.65% of its content while the second component explained 25.003%, which was mainly determined by depth, followed by the concentration of V and Ni in component one and polycyclic aromatic hydrocarbons (∑AHs and ∑HAPs) in component two (Figure 2).

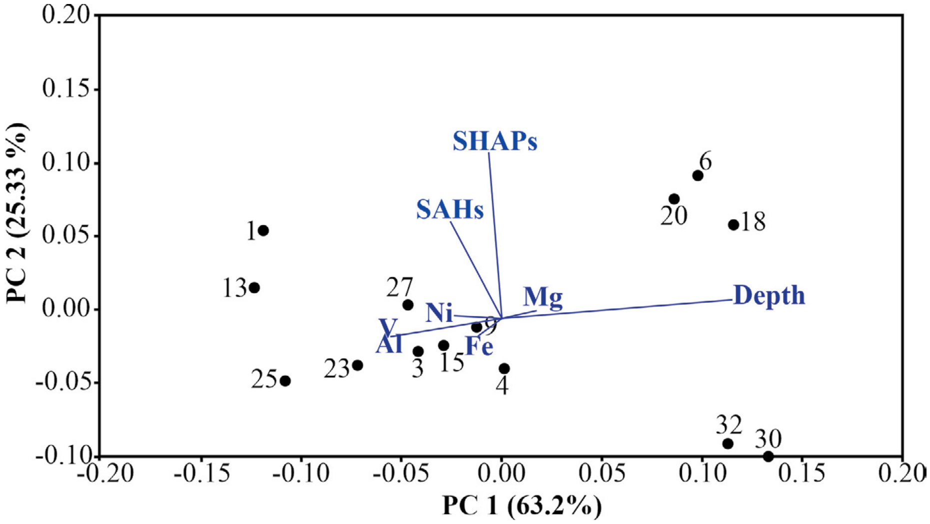

Figure 2. Two-dimensional PCA ordinations on the environmental variables (PC1 and PC2 accounted for 88.54 % of the total variation).

We identified seven photosynthetic pigments, which include chlorophyll-*a* along with its degradation products: pyrophaeophytin-*a*, phaeophytin-*a*, and pheophorbide-*a*. Additionally, β-carotene, and zeaxanthin are both oxygen derivatives of carotenes. Only six pigments had their concentrations calculated, which are listed in Table 2. Unidentified peaks were located at 4, 5, 7 min (Figure 3).

Table 2. Retention time (min) and pigment concentration (nmole/g) recorded in the sediment samples obtained during the oceanographic cruise MARZEE-III in 2012. Chromatogram registered at 440 nm. RT = Retention time. DL = Detection Limit (ng). A = Absent. CS = Continental Shelf.

Pigment Profile	RT	DL	Pigment Concentration Per Stations						
			Inner CS			Outer CS			
			1	13	25	3	15	23	27
Tetraterpenoid									
β-carotene	15	0.00019	0.29	0.31	0.41	0.09	0.04	0.12	0.04
Zeaxanthin	8	0.0007	0.23	0.14	0.35	0.02	A	0.04	A
Tetrapyrrole									
Chlorophyll-*a*	12	0.00022	0.23	0.15	0.41	A	A	A	0.01
Pyrophaeophytin-*a*	14	0.0022	0.08	A	0.15	0.03	0.03	0.04	0.03
Phaeophytin-*a*	13	0.0025	0.06	0.14	0.13	0.05	0.02	0.06	0.04
Pheophorbide-*a*	5	0.0024	0.34	0.12	0.64	A	A	A	0.05
			Slope						
			4	6	9	18	20	30	32
Tetraterpenoid									
β-carotene	15	0.00019	0.08	A	0.04	A	A	A	A
Zeaxanthin	8	0.0007	A	A	A	A	A	A	A
Tetrapyrrole									
Chlorophyll-*a*	12	0.00022	A	A	A	A	A	A	A
Pyrophaeophytin-*a*	14	0.0022	A	A	A	A	A	A	A
Phaeophytin-*a*	13	0.0025	A	A	A	A	0.02	A	A
Pheophorbide-a	5	0.0024	A	A	A	A	A	A	A

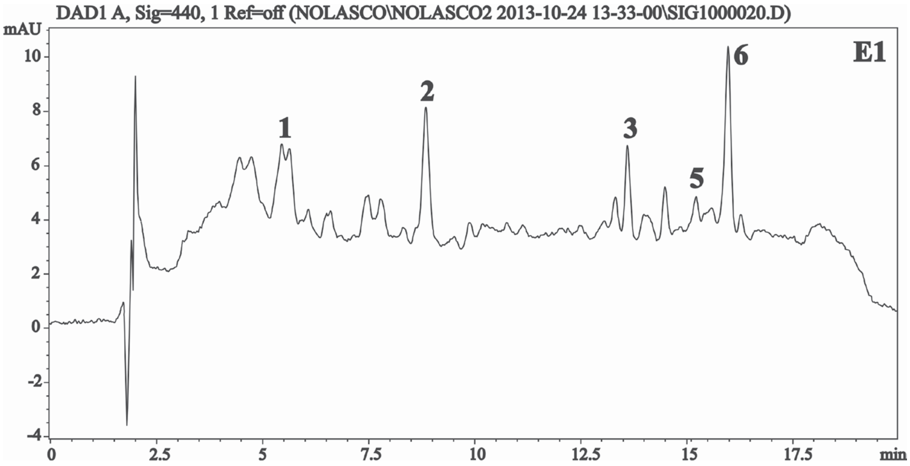

Figure 3. Chromatogram (440 nm) obtained from the sediment sample (Station 1). (1) Pheophorbide-*a*. (2) Zeaxanthin. (3) Chlorophyll-*a*. (4) Phaeophytin-*a*. (5) Pyropheophytin-*a*. (6) β-carotene.

In the 14 superficial sediment samples, the pigments that had a higher concentration were β-carotene (present in nine samples), representing 28.3% (1.42 nmole/g) of the total concentration of the pigments analyzed (5.01 nmole/g), followed by pheophorbide-*a* (in four samples) with 23.6% (1.15 nmole/g). The lowest concentrations corresponded to pyrophaeophytin-*a* (in six samples) with 7.2% (0.36 nmole/g). Station 25 showed the highest pigment concentrations (2.07 nmole/g, 41.3%) followed by stations 1 (1.23 nmole/g, 24.6%) and 13 (0.86 nmole/g, 17.2%), within the inner continental shelf (CS) (Table 2). Lower pigment concentrations were recorded at the stations located in the outer CS, 23 with 0.26 nmole/g (5.19%), 3 and 27 with 0.18 nmole/g (3.59%), and station 15 with 0.09 nmole/g (1.08%). The minimum pigment concentrations were recorded at the stations located on the slope (Table 2). In the deepest, stations 6, 18, 30 and 32 (> 1,500 m depth) no pigments were detected, except for a low concentration of phaeophytin-*a* in station 20.

The one-way PERMANOVA indicated significant differences in the concentration of tetrapyrrole pigments in different sites (Pseudo-F(2,7) = 4.87, p = 0.007). The post-hoc test showed that the inner CS was significantly different from the outer CS, while no significant differences between inner and outer CS and slope were detected. The same effect was recorded by a second one-way PERMANOVA, which indicated significant differences in the concentration of tetraterpenoid pigments in different sites (Pseudo-F = 8.26, p = 0.012). The post-hoc test demonstrated that the inner CS was significantly different from the outer CS, while no significant differences between inner and outer CS and slope were detected.

In the tetrapyrrole pigments SIMPER analysis, the inner CS and outer CS sites indicated presented an average dissimilarity of 78.82%. The pigment exhibiting the greater contribution to this dissimilarity was phaeophorbid-*a* (42.77%), followed by chlorophyl-*a* (36.08%). Inner CS and slope sites presented an average dissimilarity of 99.25%. The pigment that contributed most significantly to this dissimilarity was phaeophorbid-*a* (40.32%), followed by chlorophyl-*a* (33.45%). Outer CS and slope sites presented an average dissimilarity of 95.29%; again, the pigments correlated to this dissimilarity were phaeophytin-*a* (48.35%), followed by pyrophaeophytin-*a* (39.66%).

Additionally, the SIMPER analysis of the tetraterpenoid pigments, inner CS and outer CS sites indicated presented an average dissimilarity of 30.44%. The pigment exhibiting the greatest contribution to this dissimilarity was β-carotene (50%). Inner CS and slope sites presented an average dissimilarity of 83.44%. The pigment that contributed most significantly to this dissimilarity was β-carotene (56.82%). Outer CS and slope sites presented an average dissimilarity of 74.74%; again, the pigment correlated to this dissimilarity was β-carotene (86.70%).

Spearman's rank correlation test established a relation for all pigments ($p<0.05$) with depth, temperature, salinity, dissolved oxygen (O_2), and nickel (Ni). The results indicated a significant high negative correlation between the pigments concentration, and depth, dissolved oxygen (O_2) and Ni. Also, all pigment concentrations showed a significantly high positive correlation with temperature and salinity (Figure 4). Finally, pigments phaeophytin-*a,* β-carotene and zeaxanthin exhibited significant high positive correlations with Aluminum (Al).

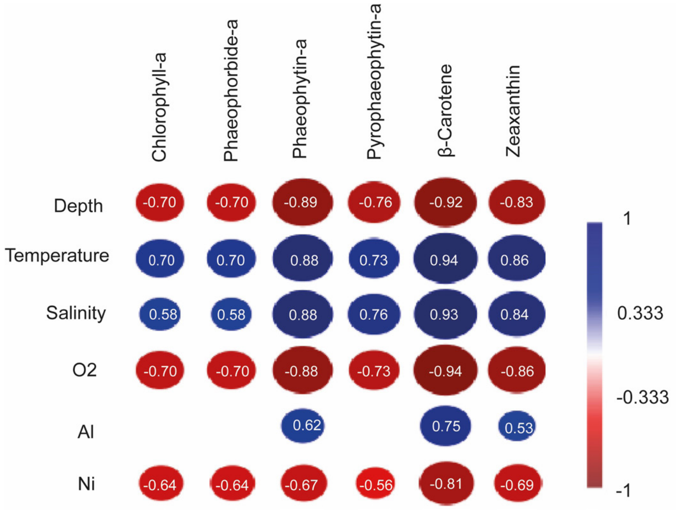

Figure 4. Spearman's rank correlation plot between the pigment's concentration and the environmental factors. Only significant correlations are considered ($p<0.05$).

DISCUSSION

The environmental parameters (PAHs, AH, OC, OM, salinity, temperature, and Al) describing the study area are congruent with those reported concerning areas of the Gulf of Mexico (Table 1) (Botello, 2005; Camilli et al., 2010; Dierks et al., 2010; Roux and Flores-Torres, 2015). However, the Ni concentration reported globally for uncontaminated locations (442.98 nmole/g) was exceeded in all stations (Macías-Zamora et al., 1999) (Table 1).

In this study, pigment distribution was normal, but pigment concentration was low. This is consistent with what was reported by several authors. For instance, Biggs (1992) concluded, after quantifying chlorophylls, nitrates, phosphates, and primary productivity, that the GoM is an oligotrophic and biologically impoverished ecosystem, particularly at depths greater than 100 m. Salas-Perez et al. (2016) found, in a tropical coastal lagoon (Laguna de Tamiahua) located in the NW Gulf of Mexico, oligotrophic conditions throughout the year (chlorophyll-*a* >5 mg m^{-3}) with maximum values in the summer. Photosynthetic pigments (chlorophyll-*a* and carotenoids) are rapidly assimilated and their concentration in neritic waters far from the inner continental shelf reveals a negative exponential trend to the depth gradient as indicated in our results. The assimilation process in shallow waters generates oligotrophic conditions in oceanic waters as shown by Biggs (1992). In the study area, chlorophyll-*a* showed significantly impoverished concentrations (< 0.41 nmole/g) at three sites within the inner CS (stations 1, 13, 25) and one in the outer CS (station 27). These results confirmed an active deposition process of photosynthetic pigments on the inner CS and a passive deposition on the outer CS and slope. Beyer et al. (2016) mentioned that presumably, areas exposed to ecosystem-level injuries, like the Deepwater Horizon (DWH) accidental oil spill, are liable to display chlorophyll anomalies like those found in this contribution and those documented by Hu et al. (2011). Szymczak-Zyla and Kowalewska (2007) discussed that chlorophyll-*a* has been frequently used as a research subject due to its abundance and function as a biomarker in different processes occurring in the marine environment, like eutrophication or the presence of phytoplankton. These authors also mention that chlorophyll-*a* is a marker of fresh plant material from the coast influenced by river discharge, which is usually enriched with nutrients and has better light penetration and oxygen conditions. Oil derivatives, including Ni, can affect phytoplankton production and exacerbate oligotrophic conditions in the area studied herein, particularly in offshore waters (> 200 m).

The applied Spearman's rank correlation test showed that depth, O_2, and Ni were the only variables that present a high negative significant statistical difference ($p \leq 0.05$) to the concentration of the pigments (Figure 4). The sites near the coast with low O_2 and Ni concentrations exhibited more pigments, unlike the deeper sites on the slope. The spatial distribution registered in the pigments is consistent with that reported by other authors like Yentsch (1965), Kowalewska (2005), and Szymczak-Zyla and Kowalewska (2007), who indicated that pigment concentration declines with increased depths. Furthermore, several authors agree that in sediments distant from the coast, the concentration of pigments may decrease as a result of environmental (temperature, light, and oxygen) and biotic (microorganisms or heterotrophic organisms) factors, influencing the deposition process and degradation (Yentsch, 1965; Schwartz and Von Elbe, 1983; Herblan, 1988; Heaton et al., 1996; Jeffrey et al., 1997; Szymczak-Zyla and Kowalewska, 2007). Our findings coincided with the estimated percentages of pigment concentrations for coastal (81%) and deep environments (27%) offered by Yentsch (1965).

In reference to the presence of heavy metals in our sediment samples, the increasing trend of Ni concentration from 2010 to 2012 is highly relevant, 374.83 to 698.55 nmole/g; 306.34 to 856.14 nmole/g; and 398.64 -900.17 nmole/g, respectively reported by Botello et al. (2015). One may argue that the main Ni source in the study area can be linked to the sedimentary transport processes typical of the north of the Gulf; another possibility is the presence of subsurface hydrocarbon and gas plumes detected after the Deepwater Horizon oil spill that occurred during the spring and summer of 2010 (Spier et al., 2013) since Ni is another of the trace metals whose concentration increases with oil degradation (Liu et al., 2011). Such a concentration trend indicates critical contamination conditions caused by this metal, particularly in the deep sediments of the study area. Nickel is one of the heavy metals related to petrogenic sources that provide more evidence about the type of dominant source of hydrocarbons and the metals present (Botello et al., 2015). On the other hand, Gerendás et al. (1999) and Gajewaska et al. (2006) considered Ni as an essential micronutrient since it acts as a cofactor for enzymes and is favorable for both plants and animals. Nevertheless, in high concentrations, it causes toxic effects on plant growth, reducing metabolic rate activities, and decreasing the absorption of water and nutrients. The results of Ni concentrations herein suggest a possibly harmful effect on the benthic community (Table 1). This, to a certain extent, may explain the negative correlation of Ni with all pigments analyzed (Figure 4).

Finally, contrary to Ni, Zeaxanthin, Phaeophytin-*a* and β-carotene pigments also showed a significant positive correlation with aluminum (Al) (r = 0.53, r = 0.62, r = 0.75, respectively). According to Pilon-Smits et al. (2009) and Liu et al. (2019), there are beneficial effects to marine organisms, especially in marine phytoplankton growth, of low doses of heavy metals such as Al, Co, Na, and Se. These same studies mention that all these elements promote growth for various taxa under certain environmental conditions, however, the function and concentration are specific for each element and species. The Al concentrations analyzed in this contribution promote organisms with Zeaxanthin, β-carotene pigments, and chlorophyll-*a* since phaeophytin-*a* is a Chl-*a* subproduct. In the work of Buchaca and Catalan (2007), they mention that the zeaxanthin pigment has taxonomic affinities with taxa such as cyanobacteria and chlorophytes. Furthermore, β-carotene and chlorophyll-*a* are associated with cyanobacteria, other algae, and vascular plants. Meanwhile, phaeophytin-*a*, a Chl-*a* degradation product, indicates old sediments (senescence). As with many other topics in science, these studies have received little attention compared to those of the toxic effects that typically occur at higher concentrations. A better understanding of the effects of these beneficial elements (Al), typical environmental parameters (depth, temperature, salinity, and contaminants (Ni) are important to estimate and draw better conclusions regarding how photopigment concentrations could potentially help us describe marine sedimentary environments.

CONCLUSION

As expected, an exponential reduction in pigment concentration occurred with the distance from the shoreline and the increasing depth gradient in the studied area. The maximum pigment concentrations were obtained at shallow sites in the inner continental shelf directly exposed to the organic matter load exported by the Bravo and Soto La Marina rivers, in addition to active sediment discharge processes. The low pigment concentration recorded in this study confirms the oligotrophic conditions prevailing in the northwestern Gulf of Mexico. The oil derivatives detected in the deep sediments analyzed probably contributed to exacerbating such conditions given the increasing trend of Ni concentrations detected from 2010 to 2012, which eventually could result in producing negative effects on the benthic inhabitants and therefore expressing low concentrations of sediment pigments. A better understanding of marine pigments and their interaction with several environmental factors certainly will drive studies regarding the biotechnology and bioengineering of pigments. Marine pigments are more and more commonly used in food, pharmaceutical, aquaculture, and cosmetic industries. They hold tremendous economic importance as a multi-billion-dollar industry that is still growing. We find it crucial to recognize the interactions between marine pigments and other ecosystem components. Despite the fact that pigment diversity exploration on this field is still in its first stages, with many marine compounds awaiting further exploration.

Data availability statement

The data that support the findings of this study are available from the corresponding author.

Supplementary material

There is no supplementary material.

ACKNOWLEDGMENTS

The authors express gratitude to C. Illescas-Monterroso and the Benthic Ecology Laboratory for their assistance with sampling, and to Francisco S. Hernández-Sandoval for pigment processing. They acknowledge the crew of the R/V JUSTO SIERRA for their invaluable support during the MARZEE-III oceanographic campaign, which is part of a monitoring program in the Gulf of Mexico. Anonymous reviewers provided valuable feedback that improved the content of the manuscript.

FUNDING

The project received funding from the Instituto Nacional de Ecología y Cambio Climático (INECC), with additional support from the Instituto de Ciencias del Mar y Limnología (ICMyL, UNAM).

AUTHOR CONTRIBUTIONS

A.E.R.: Conceptualization, Investigation, Writing - Original Draft, Writing - Review & Editing, Visualization.

L.A.S.: Conceptualization, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

L.A.C.: Formal analysis, Methodology, Writing - Review & Editing.

CONFLICTS OF INTEREST

The authors declare there is no conflict of interest and no competing financial interests.

REFERENCES

Anderson, M. J., Gorley, R. N. & Clarke, K. R. 2008. *PERMANOVA for PRIMER: Guide to Software and Statistical Methods*. PRIMER-E Ltd, Plymouth, U.K. (214 pp).

Anderson, M. J. 2001. A new method for non-parametric multivariate analysis of variance. *Austral Ecology*, 26(1), 32–46. DOI: http://dx.doi.org/10.1111/j.1442-993.2001.01070.pp.x

Ayala-Castañares, A., Cruz, R., García-Cubas, A. & Segura, L. R. 1996. Síntesis de los conocimientos sobre la Geología Marina de la Laguna de Tamiahua, Veracruz, México. In: AYALA-CASTAÑARES, A. & PHLEGER, F. B. (Ed). *Lagunas Costeras, un Simposio. Memorias del Simposio Internacional sobre Lagunas Costeras: Origen, Dinámica y Productividad* (pp. 39-48). Ciudad de México, DF: UNAM-UNESCO.

Beyer, J., Trannum, H. C., Bakke, T., Hodson, P. V. & Collier, T. K. 2016. Environmental effects of the Deepwater Horizon oil spill: A review. *Marine Pollution Bulletin*, 110(1), 28–51. DOI: https://doi.org/10.1016/j.marpolbul.2016.06.027

Bianchi, T. S., Johansson, B. & Elmgren, R. 2000. Breakdown of phytoplankton pigments in Baltic sediments: effects of anoxia and loss of deposit-feeding macrofauna. *Journal of Experimental Marine Biology and Ecology*, 251(2), 161–183. DOI: https://doi.org/10.1016/S0022-0981(00)00212-4

Biggs, D. C. 1992. Nutrients, plankton, and productivity in a warm-core ring in the western Gulf of Mexico. *Journal of Geophysical Research*, 97(C2), 2143. DOI: https://doi.org/10.1029/90JC02020

Botello, A. V. (Ed.). 2005. *Golfo de México: contaminación e impacto ambiental: diagnóstico y tendencias*. Universidad Juárez Autónoma de Tabasco.

Botello, A. V., Soto, L. A., Ponce-Vélez, G. & Villanueva F., S. 2015. Baseline for PAHs and metals in NW Gulf of Mexico related to the Deepwater Horizon oil spill. *Estuarine, Coastal and Shelf Science*, 156, 124–133. DOI: https://doi.org/10.1016/j.ecss.2014.11.010

Buchaca, T. & Catalan, J. 2007. Factors influencing the variability of pigments in surface sediments of mountain lakes. *Freshwater Biology*, 52, 1365–1379. DOI: https://doi.org/10.1111/j.1365-2427.2007.01774.x

Camilli, R., Reddy, C. M., Yoerger, D. R., Van Mooy, B. A. S., Jakuba, M. V., Kinsey, J. C., Mcintyre, C. P., Sylva, S. P. & MALONEY, J. V. 2010. Tracking Hydrocarbon Plume Transport and Biodegradation at Deepwater Horizon. *Science*, 330(6001), 201–204. DOI: https://doi.org/10.1126/science.1195223

Clarke, K. R. & Warwick, R. M. 2001. *Change in Marine Communities: An Approach to Statistical Analysis and Interpretation*. Plymouth: Plymouth Marine Laboratory.

Contreras, E. F. 1988. *Las Lagunas Costeras Mexicanas*. Ciudad de México: Secretaria de Pesca.

Delgado-Blas, V. H. 2001. Distribución espacial y temporal de poliquetos (Polychaeta) bénticos de la plataforma continental de Tamaulipas, Golfo de México. *Revista Biología Tropical*, 49, 141–147. Available at: https://www.scielo.sa.cr/scielo.php?pid=S0034-77442001000100013&script=sci_abstract&tlng=es. Access date: 2022 Sep. 20.

Diercks, A. R., Highsmith, R. C., Asper, V. L., Joung, D., Zhou, Z., Guo, L., Shiller, A. M., Joye, S. B., Teske, A. P., Guinasso, N., Wade, T. L. & Lohrenz, S. E. 2010. Characterization of subsurface polycyclic aromatic hydrocarbons at the Deepwater Horizon site: Subsurface Pah At Deepwater Horizon Site. *Geophysical Research Letters*, 37(20). DOI: https://doi.org/10.1029/2010GL045046

Dubranna, J., Pérez-Brunius, P., López, M. & Candela, J. 2011. Circulation over the continental shelf of the western and southwestern Gulf of Mexico. *Journal of Geophysical Research*, 116(C8), C08009. DOI: https://doi.org/10.1029/2011JC007007

Fabiano, M. & Danovaro, R. 1994. Composition of organic matter in sediments facing a river estuary (Tyrrhenian Sea): relationships with bacteria and microphytobenthic biomass. *Hydrobiologia*, 277, 71–84. DOI: https://doi.org/10.1007/BF00016755

Fernández-Eguiarte, A., Zavala, J. & Romero, R. 1998. Circulación de invierno en la Plataforma de Tamaulipas y áreas adyacentes. *IX Reunión Nacional SELPER-México*. Available at: https://www.scienceopen.

com/document?vid=b7d5d818-e55f-4012-a51b-2f529ac22dec. Access date: 2022 Sep 20.

Gajewska, E., Skłodowska, M., Słaba, M. & Mazur, J. 2006. Effect of nickel on antioxidative enzyme activities, proline, and chlorophyll contents in wheat shoots. *Biologia Plantarum*, 50(4), 653–659. DOI: https://doi.org/10.1007/s10535-006-0102-5

Gerendás, J., Polacco, J. C., Freyermuth, S. K. & Sattelmacher, B. 1999. Significance of nickel for plant growth and metabolism. *Journal of Plant Nutrition and Soil Science*, 162(3), 241–256. DOI: https://doi.org/10.1002/(SICI)1522-2624(199906)162:3<241:AID-JPLN241>3.0.CO;2-Q

Guerrero, F., Rodríguez, V., Bautista, B. & Jiménez-Gómez, F. 1988. Procesos de formación y pérdida de feopigmentos en sistemas pelágicos: evaluación en condiciones de laboratorio. *Investigación Pesquera*, 52, 437–449.

Hamilton, P., Fargion, G. S. & Biggs, D. C. 1999. Loop Current Eddy paths in the Western Gulf of Mexico. *Journal of Physical Oceanography*, 29, 1180–1207. DOI: https://doi.org/10.1175/1520-0485(1999)029<1180:LCEPIT>2.0.CO;2

Hamilton, P. 2009. Topographic Rossby waves in the Gulf of Mexico. *Progress in Oceanography*, 82(1), 1–31. DOI: https://doi.org/10.1016/j.pocean.2009.04.019

Hamilton, P., Berger, T. J. & Johnson, W. 2002. On the structure and motions of cyclones in the northern Gulf of Mexico: Cyclones in the Northern Gulf of Mexico. *Journal of Geophysical Research*: Oceans, 107(C12), 1–18. DOI: https://doi.org/10.1029/1999JC000270

Hammer, Ø., Harper, D. A. T. & Ryan, P. D. 2001. PAST: Paleontological Statistics Software Package for Education and Data Analysis. *Palaeontologia Electronica*, 4(1), 1–9.

Heaton, J. W. & Marangoni, A. G. 1996. Chlorophyll degradation in processed foods and senescent plant tissues. *Trends in Food Science & Technology*, 7(1), 8–15. DOI: https://doi.org/10.1016/0924-2244(96)81352-5

Herbland, A. 1988. The Deep Phaeopigments Maximum in the Ocean: Reality or Illusion? *In*: ROTHSCHILD, B. J. (Ed.). *Toward a Theory on Biological-Physical Interactions in the World Ocean* (pp. 157–172). Dordrecht: Springer.

Hu, C., Weisberg, R. H., Liu, Y., Zheng, L., Daly, K. L., English, D. C., Zhao, J. & Vargo, G. A. 2011. Did the northeastern Gulf of Mexico become greener after the Deepwater Horizon oil spill? *Geophysical Research Letters*, 38(9), 2011GL047184. DOI: https://doi.org/10.1029/2011GL047184

Jeffrey, S. W. & Vest, M. 1997. Introduction to marine phytoplankton and their pigment signatures. In*:* Jeffrey, S. W., Mantoura, R. F. C. & Wright, S. W. (Ed.). *Phytoplankton Pigments in Oceanography* (pp. 37–84). Paris: Unesco.

Jeffrey, S. W., Wright, S. W. & Zapata, M. 1999. Recent advances in HPLC pigment analysis of phytoplankton. *Marine and Freshwater Research*, 50, 879–896. DOI: https://doi.org/10.1071/MF99109.

Kowalewska, G. & Konat, J. 1997. Distribution of polynuclear aromatic hydrocarbons (PAHs) in sediments of the southern Baltic Sea. *Oceanologia*, 39(1), 83–104.

Kowalewska, G. 1994. Steryl chlorin esters in sediments of the southern Baltic Sea. Netherlands *Journal of Aquatic Ecology*, 28(2), 149–156. DOI: https://doi.org/10.1007/BF02333985

Kowalewska, G. 2005. Algal pigments in sediments as a measure of eutrophication in the Baltic environment. *Quaternary International*, 130(1), 141–151. DOI: https://doi.org/10.1016/j.quaint.2004.04.037

Kowalewska. G., Witkowski, A. & Toma, B. 1996. Chlorophylls c in bottom sediments as markers of diatom biomass in the southern Baltic Sea. *Oceanologia*, 38(2), 227–249.

Küpper, H., Seibert, S. & Parameswaran, A. (2007). Fast, sensitive, and inexpensive alternative to analytical pigment HPLC: quantification of chlorophylls and carotenoids in crude extracts by fitting with Gauss peak spectra. *Analytical Chemistry*, 79(20), 7611–7627.

Laneve, G., Bruno, M., Mukherjee, A., Messineo, V., Giuseppetti, R., De Pace, R. & D'ugo, E. 2021. Remote sensing detection of algal blooms in a lake impacted by petroleum hydrocarbons. *Remote Sensing*, 14(1), 121. DOI: https://doi.org/10.3390/rs14010121

Liu, Q., Zhou, L., Liu, F., Fortin, C., Tan, Y., Huang, L. & Campbell, P. G. 2019. Uptake and subcellular distribution of aluminum in a marine diatom. *Ecotoxicology and Environmental Safety*, 169, 85–92. https://doi.org/10.1016/j.ecoenv.2018.10.095

Liu, Y., Weisberg, R. H., Hu, C. & Zheng, L. 2011. Tracking the Deepwater Horizon Oil Spill: A Modeling Perspective. *EOS, Transactions American Geophysical Union*, 92(6), 45–46. DOI: https://doi.org/10.1029/2011EO060001

Macías-Zamora, J. V., Villaescusa-Celaya, J. A., Muñoz-Barbosa, A. & Gold-Bouchot, G. 1999. Trace metals in sediment cores from the Campeche shelf, Gulf of Mexico. *Environmental Pollution*, 104(1), 69–77. DOI: https://doi.org/10.1016/S0269-7491(98)00153-5

Martínez-López, B. & Zavala-Hidalgo, J. 2009. Seasonal and interannual variability of cross-shelf transports of chlorophyll in the Gulf of Mexico. *Journal of Marine Systems*, 77, 1–20. DOI: https://doi.org/10.1016/j.jmarsys.2008.10.002

Megharaj, M., Singleton, I., Mcclure, N. C. & Naidu, R. 2000. Influence of Petroleum Hydrocarbon Contamination on Microalgae and Microbial Activities in a Long-Term Contaminated Soil. *Archives of Environmental Contamination and Toxicology*, 38(4), 439–445. DOI: https://doi.org/10.1007/s002449910058

Meza-Padilla, R., Enriquez, C., Liu, Y. & Appendini, C. M. 2019. Ocean circulation in the western Gulf of Mexico using self-organizing maps. *Journal of Geophysical Research Oceans*, 124, 4152–4167. DOI: https://doi.org/10.1029/2018JC014377

Nelson, J. R. 1993. Rates and possible mechanism of light-dependent degradation of pigments in detritus derived from phytoplankton. *Journal of Marine Research*, 51(1), 155–179. DOI: https://doi.org/10.1357/0022240933223837

Othman, H. B., Pick, F. R., Hlaili, A. S. & Leboulanger, C. (2023). Effects of polycyclic aromatic hydrocarbons on marine and freshwater microalgae–A review. Journal of Hazardous Materials, 441, 129869.

Palmer, S. E. & Baker, E. W. 1978. Copper Porphyrins in Deep-Sea Sediments: A Possible Indicator of Oxidized Terrestrial Organic Matter. *Science*, 201(4350), 49–51. DOI: https://doi.org/10.1126/science.201.4350.49

Pérez-Brunis, P., Furey, H., Bower, A., Hamilton, P., Candela, J. & García-Carrillo, P. 2018. Dominant Circulation Patterns of the Deep Gulf of Mexico. *Journal of Physical Oceanography*, 48, 511–529. DOI: https://doi.org/10.1175/JPO-D-17-0140.1

Pilon-Smits, E. A., Quinn, C. F., Tapken, W., Malagoli, M. & Schiavon, M. 2009. Physiological functions of beneficial elements. *Current Opinion in Plant Biology*, 12(3), 267–274. https://doi.org/10.1016/j.pbi.2009.04.009

Repeta, D. J. & Simpson, D. J. 1991. The distribution and recycling of chlorophyll, bacteriochlorophyll and carotenoids in the Black Sea. *Deep Sea Research Part A. Oceanographic Research Papers*, 38, S969–S984. DOI: https://doi.org/10.1016/S0198-0149(10)80019-6

Roux, R. & Flores Torres, O. 2015. Los Hidrocarburos en el noreste de México. Available at: http://www.coltam.edu.mx/wp-content/uploads/2016/09/2015-HIDROCARBUROS-EN-EL-NORESTE-DE-MEXICO-.pdf. Access date: 2022 Aug.

Salas-Pérez, J. De J. & González-Gándara, C. 2016. Temporal and spatial fluctuations of sea surface temperature and chlorophyll a levels due to atmospheric forcing in a tropical coastal lagoon. *Ciencias Marinas*, 42(1), 49–65. DOI: https://doi.org/10.7773/cm.v42i1.2551

Schwartz, S. & Von-Elbe, J. H. 1983. Kinetics Of Chlorophyll Degradation to Pyropheophytin in Vegetables. *Journal of Food Science*, 48, 1303–1306. DOI: https://doi.org/10.1111/j.1365-2621.1983.tb09216.x

Siegel, S. 1990. *Estadística no paramétrica: aplicada a las ciencias de la conducta*. Editorial México: Trillas.

Spier, C., Stringfellow, W. T., Hazen, T. C. & Conrad, M. 2013. Distribution of hydrocarbons released during the 2010 MC252 oil spill in deep offshore waters. *Environmental Pollution*, 173, 224–230. DOI: https://doi.org/10.1016/j.envpol.2012.10.019

Szymczak-Żyła, M. & Kowalewska, G. 2007. Chloropigments a in the Gulf of Gdańsk (Baltic Sea) as markers of the state of this environment. *Marine Pollution Bulletin*, 55(10–12), 512–528. DOI: https://doi.org/10.1016/j.marpolbul.2007.09.013

USEPA (United States Environmental Protection Agency). 2009. *Ecological Toxicity Information*. Available at: www.epa.gov/region5/superfund/ecology/html/toxprofiles.htm. Access date: 2022 Jun. 1.

Vidal, V. M. & Vidal, F. V. 1997. La importancia de los estudios regionales de circulación oceánica en el Golfo de México. *Revista de la Sociedad Mexicana de Historia Natural*, 47: 191–200.

Vidussi, F., Claustre, H., Bustillos-Guzmán, J., Cailliau, C. & Marty, J. C. 1996. Determination of chlorophylls and carotenoids of marine phytoplankton: separation of chlorophyll-*a* from divinylchlorophyll-*a* and zeaxanthin from lutein. *Journal of Plankton Research*, 18(12), 2377–2382. DOI: https://doi.org/10.1093/plankt/18.12.2377

Xue, Z., He, R., Fennel, K., Cai, W. J., Lohrenz, S. & Hopkinson, C. 2013. Modeling ocean circulation and biogeochemical variability in the Gulf of Mexico. *Biogeosciences*, 10(11), 7219–7234. DOI: https://doi.org/10.5194/bg-10-7219-2013

Ye, K.-X., Fan, T.-T., Keen, L. J. & Han, B.-N. 2019. A Review of pigments derived from marine natural products. *Israel Journal of Chemistry*, 59, 327–338. DOI: https://doi.org/10.1002/ijch.201800154

Yentsch, C. S. 1965. Distribution of chlorophyll and phaeophytin in the open ocean. *Deep Sea Research and Oceanographic Abstracts*, 12(5), 653–666. DOI: https://doi.org/10.1016/0011-7471(65)91864-4

Zavala-Hidalgo, J., Gallegos-García, A., Martínez-López, B., Morey, S. L. & O'brien, J. J. 2006. Seasonal upwelling on the Western and Southern Shelves of the Gulf of Mexico. *Ocean Dynamics*, 56(3–4), 333–338. DOI: https://doi.org/10.1007/s10236-006-0072-3

Zavala-Hidalgo, J., Morey, S. L. & O'brien, J. J. 2003. Seasonal circulation on the western shelf of the Gulf of Mexico using a high-resolution numerical model. *Journal of Geophysical Research*, 108(C12), 3389. DOI: https://doi.org/10.1029/2003JC001879