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The Hazards of Monitoring Ecosystem Ocean Health in the Gulf of Mexico: A Mexican Perspective

Luis A. Soto, Alejandro Estradas-Romero, Diana L. Salcedo, Alfonso V. Botello and Guadalupe Ponce-Vélez

Abstract

Ecological services provided by the Gulf of Mexico constitute vital assets for the socioeconomic development of the USA, Mexico, and Cuba. This ecosystem houses vast biodiversity and significant fossil fuel reserves. However, its ecological stability and resilience have been jeopardized by anthropogenic disturbances. Massive oil spills (Ixtoc-I, 1979; Deepwater Horizon, 2010) caused severe environmental injuries and unveiled the vulnerability of coastal and deep-sea habitats. Baseline and monitoring studies are actions implemented by the Gulf stakeholders to cope with such disturbances. The 3-year monitoring program implemented by Mexico in 2010 to assess the environmental damage caused by the Deepwater Horizon (DWH) event confirmed the void of knowledge on the complexity of physical and biological processes susceptible of being altered by oil spills. Between the pelagic and benthic compartments, the latter proved to be a better option in establishing the baseline concentration and trends of oil compounds. Surficial sediments exhibited an increasing concentration trend of PAH, AH, and trace metals throughout the 3-year monitoring. The macroinfauna and selected biomarkers experienced interannual variability attributed to critical hydrocarbon and trace metal thresholds. Sediment toxicity bioassays added support to the distribution and potential sources of oil contaminants dispersed from the northern gulf toward Mexican waters.

Keywords: Gulf of Mexico, oil spills, Deepwater Horizon, marine pollution, benthic ecology, macroinfauna

1. Introduction

Due to its geological origin, the Gulf of Mexico (GoM) represents an ideal semi-closed basin for the accumulation of fossil deposits of oil and gas [1]. This unique attribute has historically exposed the Gulf to natural seepage of oil and gas from the seabed. These natural emanations have been recorded in several sectors of the Gulf and represent a significant source of contamination [2, 3]. However, in recent times, the stability and resilience of this large marine ecosystem have been tested by severe anthropogenic disturbances. Massive spills of crude oil produced by the decontrol

of the Ixtoc well-I in the Campeche Sound in 1979 and, most recently, in the well Macondo caused by the collapse of the Deepwater Horizon (DWH) oil platform off the coast of Louisiana in 2010 are examples that have caused severe damage to the environmental health of the Gulf [4, 5].

In April 20, 2010, a severe accident occurred at the oil platform DWH about 50 nautical miles southeast of the Mississippi River Delta, in the north of the GoM. This unfortunate event caused the loss of 11 lives and caused a spill of 4.9 million barrels of crude oil from the Macondo's well at 1650 m of depth. Several authors already considered this environmental catastrophe as the greatest disaster in the oil industry of the United States [6, 7].

The British firm British Petroleum (BP), responsible for the operation of the DWH platform, implemented a series of immediate emergency actions to mitigate somewhat the damage to the marine ecosystem, caused by the leakage of roughly 12,000–19,000 barrels of oil per day. Such activities involved the direct recovery of liquid hydrocarbons, the selective burning of oil slicks in surface waters, and the use of 1.85 million gallons of chemical dispersants (Corexit®), both on the surface and in the seabed [8, 9]. The hydrographic conditions prevailing in the GoM during the summer of 2010, combined with the onset of hurricane Alex in July, helped to contain the black tide of crude oil near the Mississippi Canyon. The initial oil slick trajectories were toward the northeastern sector of the Gulf. The satellite images obtained by the National Oceanic and Atmospheric Agency (NOAA), later supplemented with the ocean circulation models generated by the Consortium of Universities of the Northern Gulf, confirmed those trajectories, with ensuing filaments flowing toward the Texas coast. Similarly, through the use of remote sensors, it was possible to identify traces of crude oil trapped by the Eddy Franklin Gyre, a critical component of the loop current; some of these images also revealed small traces of crude oil in the waters of Mexico's exclusive economic zone (EEZ), reaching the north of the Yucatan Peninsula [10].

Without a doubt, the volume of crude oil spilled, and the quantity of chemical dispersant employed, constituted a severe alteration to the ecological balance and the environmental health of the GoM. The precise calculation of the volume of spilled oil, the trajectory of the oil stains in subsurface and surface waters, as well as the degradation rates of crude oil and its derivative compounds remain controversial topics among specialists. This problem is magnified by the chemical complexity of the crude oil. Fossil hydrocarbons include up to 17,000 organic compounds [11], each with its solubility, volatility, and density properties, as well as its different degrees of toxicity in marine biota and humans.

According to the American agencies, NOAA and the Environmental Protection Agency (EPA), a significant percentage of crude oil was recovered, and the rest was burned or lost by evaporation. However, there was overwhelming evidence of the severe damage caused to the coastal areas in the northeastern GoM. Marshlands, swamps, and coastal lagoons, which represent vital breeding grounds for wildlife fauna, were severely affected by the invading black tide. In the face of this dramatic environmental setting, Mexico was also forced to implement emergency measures focused on the early detection of crude oil slicks or tar balls within its vast exclusive economic zone (EEZ) in the GoM. Given the prevailing surface water circulation and the high connectivity among the different sectors of the Gulf, there was potentially a risk of oil pollutants from Macondo's entering Mexican waters. It was then necessary as a government to maintain a monitoring plan of the general oceanographic conditions in Mexican waters.

1.1 Research guidelines and observational strategy

Mexico, as a neighboring country of the USA, and Cuba, shares a vast ocean space in the GoM, bounded by 200 miles known as the EEZ. Under the international Treaty Law of the Sea, coastal countries are held accountable for the preservation and study of biotic and natural resources such as minerals, contained in both its waters as in the marine seabed. Based on this precept, and by the seriousness that represented the spill of fossil hydrocarbons introduced to the marine ecosystem of the GoM, it was imperative to implement a program of systematized oceanographic observations. Such program would contribute to build a dependable database of environmental parameters and thus carry out an assessment of environmental damage in the short term and midterm. Under the rules of international law [12], Mexico is obliged to have reliable information on the sources and the kinds of contaminants to assess the physical damage to coastal and ocean ecosystems in the GoM.

This chapter presents to the reader a synthesis of the most outstanding features of a 3-year research program of oceanographic observations (MARZEE) on the continental and upper slope off the coasts of the states of Tamaulipas and Veracruz during the period of 2010–2012. Considering the early dispersion forecasts of crude oil leaks originating from the north of the GoM, there was a high risk that the coast of the above states would be impacted by crude oil, preferably in the winter. To anticipate this potential anthropic disturbance, a monitoring program was implemented whose observational strategy included the sampling of 35 abiotic and biotic variables. Water, sediment, and biota from the continental shelf (50–183 m) and upper slope (200–>2000 m) were obtained in the summer of 2010 (M-I), and the winter of 2011 (M-II), and 2012 (M-III).

1.2 Focus of the research

- Water column structure (thermohaline profile, density, oxygen concentration, and fluorometry)
- Concentration of polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons (AHs) in the water column and surficial sediments
- Identification of potential pelagic and benthic bioindicator species
- Concentration of trace metals derived from oil compounds in surficial sediments
- Biomass, abundance, and density of phytoplankton, zooplankton, and benthos (macroinfauna)
- Stable carbon isotope values in and surficial sediments
- Sediment toxicity
- Concentration of trace metals derived from oil compounds in tissues of demersal fauna

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2. Materials and variables of database

As a result of three oceanographic campaigns MARZEE-I (summer, 2010), MARZEE-II (winter, 2011), and MARZEE-III (winter, 2012), aboard the R/V “Justo Sierra,” a total of 93 oceanographic stations were sampled (35, 25, and 33, respectively) (**Figure 1**). At each station, water samples were collected at preselected depths (5, 10, 20, 30, 50, 75, 100, 150, and 200 m) in sites where high fluorescence (chlorophyll-*a*) was detected. A rosette device equipped with a conductivity, temperature, and depth sensors (CTD), 10 L Niskin bottles were deployed at each site. Zooplankton was sampled with a double bongo net, and benthos and sediments were obtained with either a Smith McIntyre grab or a Reineck box corer at depths ≤ 200 and >200 , at the points of intersection of the isobaths of 50, 100, 200, 500, and 1500 (>2000 m only for MARZEE-III).

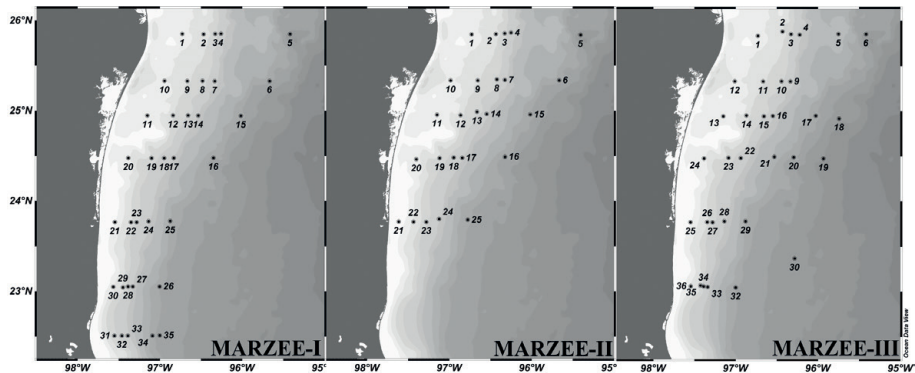


Figure 1. Sampling sites location corresponding to the three oceanographic campaigns: MARZEE-I (M-I), MARZEE-II (M-II), and MARZEE-III (M-III).

We analyzed a total of 35 variables, distributed in the following manner:

- Water column: depth (m), salinity (UPS), temperature (°C), dissolved oxygen (mL/L), Brunt-Väisälä frequency (cycles/s), chlorophyll-*a* (µg/L), nitrates (µM), nitrites (µM), ammonium (µM), phosphates (µM), silicates (µM), PAH (µg/g), and AH (µg/g)
- Sediments: depth (m), sediment texture, organic carbon (%), inorganic carbon (%), terrestrial carbon (%), organic matter (%), $\delta^{13}\text{C}_{\text{VDPB}}$ (‰), PAH (µg/g), AH (µg/g), cobalt (µg/g), chromium (µg/g), nickel (µg/g), and vanadium (µg/g)
- Biota: phytoplankton (cells/L) and zooplankton (mL/100 m³) abundance, zooplankton biomass (g/100 m³), mortality (%), macroinfauna biomass (g C/cm²), macroinfauna density (ind/10 cm²), and induction factor SOS (SOSIF)
- Other: longitude (W) and latitude (N)

2.1 Data processing

To test whether there were significant interannual differences among the three sampling periods, and spatial differences in the study area, the environmental and biotic parameters were assessed using an analysis of variance based on permutations PERMANOVA. No transformation was required on environmental data, while biotic data were log transformed. A principal component analysis (PCA) was performed on environmental data. A nonmetric multidimensional scaling (nMDS) was conducted to analyze biotic data. A nonparametric BIO-ENV analysis [13] was also conducted to determine the relationship among environmental variables and biotic components. All these analyses were performed using PRIMER v6 & PERMANOVA *add on* statistical package [14, 15].

3. Study area

The GoM is one of the most diverse and productive world marine ecosystems. In this semi-closed basin, one can distinguish temperate, subtropical, and tropical habitats [16]. Its surface area is of approximately 1,768,000 km with a maximum depth of 4000 m in the central region [17, 18]. Mexico's EEZ in the Gulf has an extension of nearly 900,000 km², which represents 55% of its total surface area [19]. The area of study considered for this project is situated within Mexico's EEZ, on the northwestern corner of GoM. It spans from the northern end of the State of Tamaulipas, near the mouth of the Rio Bravo (approximately 26°N latitude), to the north of the State of Veracruz (22°N latitude) (**Figure 2**).

The study area has a surface area of 10,000 km², and its hydrographic conditions are highly influenced by the input of epicontinental, tropical, and subtropical marine waters [20]. The coastal zone of this part of the Gulf receives the runoff of several rivers (Bravo, Tuxpan, Pánuco, Indios Morales, Soto La Marina, and San Fernando or Carbonera). There are also two coastal lagoons systems: (a) the Laguna Madre, bounded on the north by the Rio Bravo's delta and on the south by the mouth of the Rio Soto la Marina and (b) the Laguna de Tamiahua, bounded on the north by the Pánuco River and on the south by the River Tuxpan [21, 22].

Its continental shelf lacks topographic irregularities. Its contour displays a gradual depth gradient ranging from 36 to 360 m. However, the floor of the

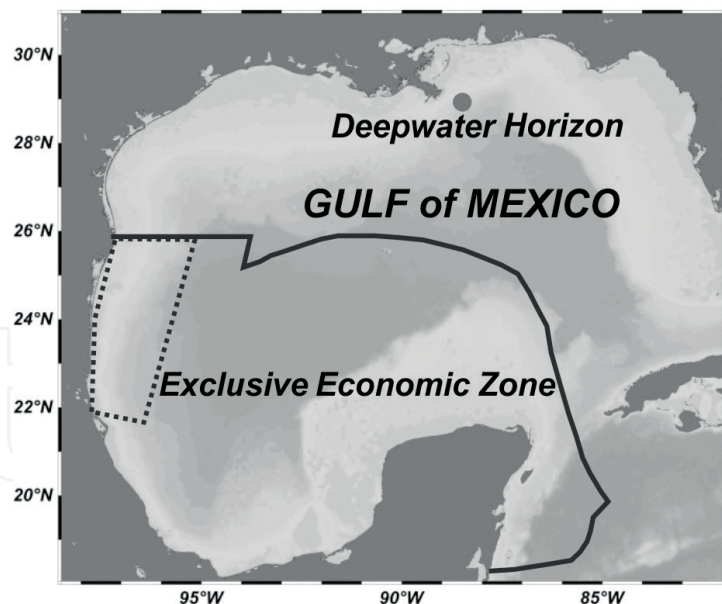


Figure 2.
Study area (dotted square). Exclusive economic zone (EEZ) (continuous line).

continental slope is rather abrupt, reaching depths between 540 and 1260 m. The continental shelf has a variable length—off the Rio Bravo reaches about 72–80 km, but toward the 23°N is close to 33–37 km—and further south just off Los Tuxtlas, Veracruz becomes narrower (between 6 and 16 km) [23].

The sea floor in the area of study is covered by muddy terrigenous sediments [24, 25] whose primary source is the sediment load discharged by the rivers mentioned above. The river runoff contributes to the formation of a strip of silty-sandy sediments running along the inner shelf. In the Tamaulipas coastal zone, sandy sediments prevail, while silts and clays are common far from the coast [17].

4. Hydrographic setting

The surface circulation of the GoM is dominated by the warm and saline waters that flow in through the Strait of Yucatan, forming the Loop Current (LC), and then exit at the Florida Strait [26]. In its passage through the Gulf Basin, anticyclonic gyres are formed from the LC, that later collide with the upper slope of the north-western Gulf [27]. The speed of these vortexes ($\sim 6 \text{ km day}^{-1}$) and their residence time ($\sim 9\text{--}12$ months) determine the distribution of physicochemical properties of the water masses, the circulation field, and the transport that controls the exchange of water masses between the continental shelf and the oceanic region [28, 29].

On the inner continental shelf on the west coast, in the province called “continental shelf and slope of the NW Gulf of Mexico” that goes from the south of Veracruz to the north of the Rio Bravo [30], the circulation is primarily toward the south from September to March and to the north from May to August. This circulation pattern produces temperature and salinity changes and coastal upwellings [31–33]. During the autumn and winter, cold fronts generated intense flows to the south that are alternated with periods of relative calm and flows to the north that coincide with high chlorophyll-*a* values at the surface. The summer-autumn conditions are less variable but are strongly affected by the passage of eddies and meteorological disturbances (tropical storm or hurricane); under these conditions, the lowest chlorophyll-*a* concentrations are recorded at the surface [26, 34]. Few are the studies on the dynamic conditions on the Tamaulipas coastline. The water masses on the platform are different from those on the slope or in the deep-sea. The

circulation in the outer shelf and on the slope is often affected by the presence of cyclonic and anticyclonic eddies. When these are absent or weak, the circulation is toward the north. During the summer there is a semipermanent upwelling in the area, and during the winter there is advection of cold water and low salinity different to that of offshore waters [31, 32, 35]. On the slope, there is a strong influence of cyclonic and anticyclonic eddies generated in the east by the LC. These events do not have a seasonal periodicity or occur in the slope region. During the winter, the strong winds from the north (northerlies) maintain a homogenized water column, while in the summer the water column is stratified [26].

5. Oceanographic conditions

During M-I, toward the end of June, the studied area endured in its surface waters the effects of Hurricane Alex. The instability caused by this meteorological phenomenon produced strong turbulence in the water column along the coastal zone. Also, due to the unusual discharge from the Rio Bravo, salinity values were diluted in neritic waters, the concentrations of nutrients were high, and the zooplankton biomass exhibited a shift toward the north. There were abnormal values of oxygen and Chl-*a*. The interpretation of the hydrographic conditions and concentrations of nutrients indicated ascending conditions of the subsurface water in the northern sector and a sinking process of water in the southern sector. The upward motion of subsurface water took place mainly on the edge of the continental shelf, causing processes of fertilization in the euphotic zone.

During M-II, hydrographic conditions presented greater instability in the surface water, with a significant injection of water coming from the continental shelf of Louisiana to Texas. The structure of the water masses in the oceanic area was similar to the one described during M-I. The water column did not present a marked stratification in neritic waters, and the mixed layer was slightly deeper. On this occasion, no processes of upwelling of deep water were recognized nor intrusion of oceanic waters on the continental shelf.

The processes of convection of water masses that govern the concentrations of oxygen, Chl-*a*, and nutrients in the water column helped to maintain values of these variables within the normal ranges for neritic and oceanic waters of the GoM.

The concentrations of dissolved oxygen reported for the Gulf of Mexico vary from 2.4 to 5.4 mL/L [36, 37]. In this study, the oxygen remained relatively constant during the three oceanographic cruises, registering an average of 4.3 ± 0.8 mL/L. The highest values were recorded at the surface (<4.0 mL/L) and the lowest between 200 and 500 m (<3.0 mL/L). This layer corresponds to the Tropical Atlantic Central Water (TACW) located between 250 and 400 m. The minimum oxygen (2.6–2.9 mL/L) in M-II and M-III was recorded between 100 and 600 m depth.

In the case of the nutrients, the values showed a slight impoverishment (nitrates, 29.3–37.9 μ M; silicate, 3.5–8.2 μ M; phosphates, 1.9–3.4 μ M). This fact emphasized the prevailing oligotrophic conditions (Chl-*a* $< 0.25 \pm 0.14$ μ g/L) reflected in the plankton components.

In M-III, the analysis of the density and the flotation frequency data, particularly at the isobaths of 500, 1500, and 2000 m, made it possible to distinguish the North Atlantic Subsurface Waters (NASW). Other identified water masses in the Gulf were as follows: North Atlantic Common Water (NACW), Tropical Atlantic Central Water (TACW), North Atlantic Intermediate Water (NAIW), and North Atlantic Deep Water (NADW) (**Figure 3**).

As indicated earlier, the region where intensive water mixing occurs is near the surface of coastal waters. The salinity and density values indicated the intrusion

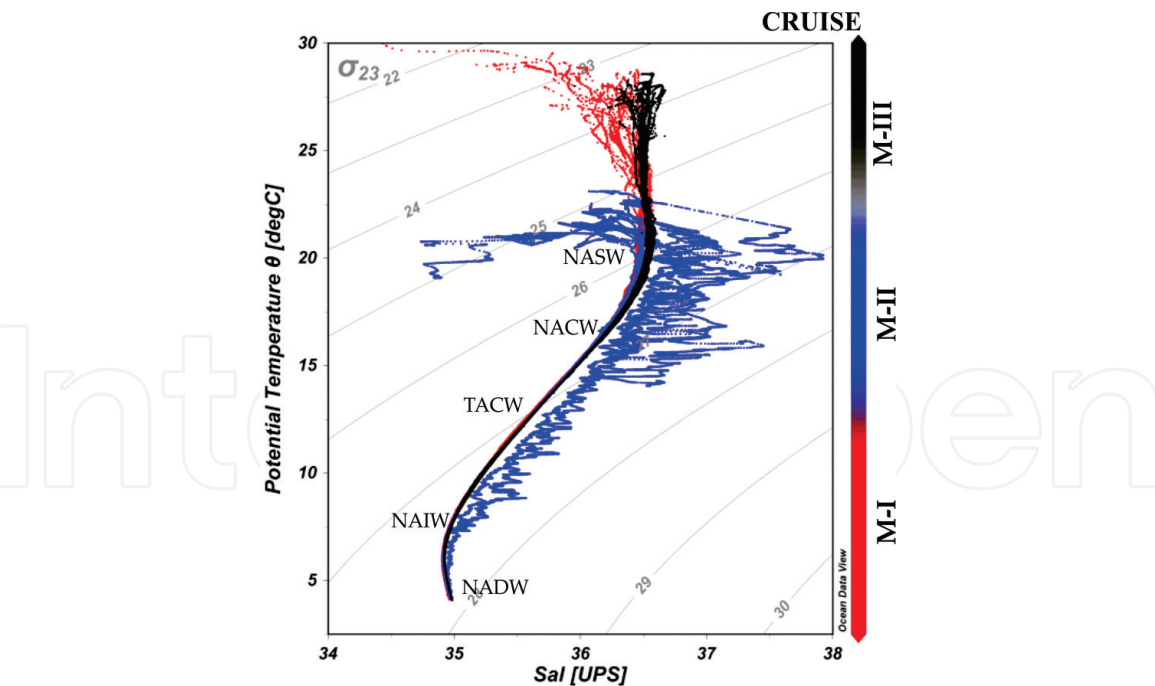


Figure 3. T-S diagrams showing the profiles obtained during M-I (in red), M-II (in blue), and M-III (in black). North Atlantic subsurface waters (NASW), North Atlantic common water (NACW), tropical Atlantic central water (TACW); North Atlantic intermediate water (NAIW), and North Atlantic deep water (NADW).

of fresh water from the river discharge onto the Tamaulipas continental shelf. The degree of water mixing of the water column was estimated by calculating the Brunt-Väisälä frequency (N). The results of this procedure revealed a significant stratification in the three oceanographic campaigns ($N > 0$). The average value for each campaign was 6.6 cycles/s for M-I, 4.12 cycles/s for M-II, and 5.0 cycles/s for M-III. Furthermore, in M-I the highest N values corresponded to the depth of 30 m, which coincide with the thermocline's depth recorded between 10 and 35 m. In M-II, the highest N value was recorded at 75 m and in M-III at 50–70 m. In both instances, the thermocline depth was of 70–90 m and 50–70 m, respectively (**Figure 4**).

During M-II and M-III, the oxygen, nutrients (nitrates, phosphates, and silicates) and the Chl-*a* concentrations maintained values that fall within the known ranges reported for the GoM ($0.05\text{--}2.5\text{ }\mu\text{M PO}_4$, $0\text{--}35\text{ }\mu\text{M NO}_3$; $<0.29 \pm 0.31\text{ }\mu\text{g/L Chl-}a$) [36, 37].

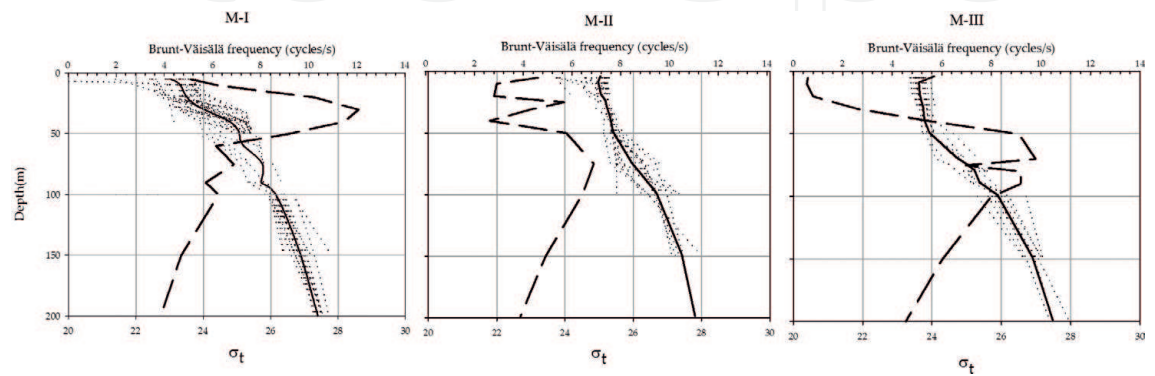


Figure 4. Density and Brunt-Väisälä profiles for the three oceanographic cruises: M-I, M-II, and M-III. The dotted lines depict individual profiles, and the black line is the average. The long dash line is the Brunt-Väisälä profile associated with the density average.

6. Polycyclic aromatic hydrocarbons (PAHs)

The PAH included a range of 16 individual compounds that are commonly analyzed [38] in monitoring programs. The concentrations of total PAH in sub-surface waters remained below the analytical detection limits ($<0.003\text{--}0.03\text{ }\mu\text{g/L}$) in the three surveys. Similarly, the Σ individual PAH ranged between 0.1 and $0.02\text{ }\mu\text{g/L}$. In M-I, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and indeno(1,2,3-cd)pyrene were recorded in 14.3% of the sites [39]. In M-II, only low concentrations of benzo(b)fluoranthene were recorded in seven sites which is equivalent to 28%. In W-III, the individual PAH identified were indeno(1,2,3-cd)pyrene, benzo(b)fluoranthene, benzo(a)pyrene, and pyrene. These compounds were detected in seven sites, representing 21.2%.

The concentrations of PAH contained in sediments fluctuated significantly among the three oceanographic campaigns. The values were similar to those previously recorded by [40] in the Tamaulipas continental shelf and by [41] in the Campeche and Tabasco continental shelves, regions widely exposed to intense oil activities. In M-I, the concentrations oscillated among 0.01 and 0.70 ($0.29 \pm 0.17\text{ }\mu\text{g/g}$). These values decreased in 90% of the sampling stations in M-II, presumably as a consequence of the Hurricane Alex and associated rains. In this period, concentrations of $0.03\text{--}0.51$ ($0.16 \pm 0.12\text{ }\mu\text{g/g}$) were recorded. Throughout the following winter (M-III), PAH increased, presenting values of $0.05\text{--}1.54$ ($0.44 \pm 0.03\text{ }\mu\text{g/g}$). This increase indicated a recent deposit of hydrocarbons, considering that the sedimentation rate is very low in the deep GoM [42].

The total PAH recorded in sediments exhibited a heterogeneous spatial distribution, but high concentrations were frequently recorded in the northern transect of the study area. In M-I, the highest concentrations were observed at 100 and 500 m depth, in M-II at 500 and 1500 m depth and in M-III at $>2000\text{ m}$ depth. The presence of high concentrations of PAH in deep sediments ($>500\text{ m}$) is not likely related to Rio Bravo runoff but rather to a far-field transport of hydrocarbons from other than local sources. The observed interannual heterogeneity (temporal/spatial) in the PAH concentrations in the NW Gulf can find an explanation in the geochemical processes acting upon different sources of hydrocarbon compounds. Indeed, one of such processes is the biodegradation of fossil fuels oil by oil-degrading bacteria [3, 43] that takes place when a massive oil spill occurs.

The distribution of individual PAH was heterogeneous throughout the study, but among the predominant were the chrysene in M-I ($0.06 \pm 0.02\text{ }\mu\text{g/g}$), the fluorene in M-II ($0.06 \pm 0.01\text{ }\mu\text{g/g}$), and the benzo(a)anthracene in M-III ($0.08 \pm 0.07\text{ }\mu\text{g/g}$). These are low molecular weight compounds generated from the burning of fossil fuels and are abundant in crude oil, so they are indicators of a recent input of anthropogenic hydrocarbons [44]. The benzo(a)anthracene and chrysene have acute toxicity and represent an environmental risk.

The primary origin of PAH in the area of study was pyrolytic. In some stations, the combustion of fossil fuels is predominated, while in others, the combustion of organic carbon, plants, wood, and other vegetal compounds prevailed. A mixture of PAH of pyrolytic and petrogenic sources was restricted to few stations throughout the study. Among the petrogenic sources, crude oil was remarkable. This indicates an anthropogenic input to the area of study because of the fossil fuel burning.

Total PAH concentrations were below sedimentary quality criteria (LRE and MRE), whose exceeded limits indicate a potential adverse effect on benthic biota. However, among individual PAH, acenaphthylene, fluorene, benzo(a)anthracene, and dibenzo(a,h)anthracene exceeded the low-range effect (LRE) criterion in four stations in M-I. In M-III, acenaphthene, fluorene, dibenzo(a,h)anthracene, and

anthracene exceeded the LRE in more than 23 stations. These results showed that the toxicity of the sediments caused by the presence of hydrocarbons increased throughout the study and hence the potential risk to the benthic fauna.

7. Trace metals

The concentrations of vanadium increased significantly over time in both the continental shelf and the continental slope (from $121.74 \pm 14.44 \mu\text{g/g}$ in M-I to $144.86 \pm 28.51 \mu\text{g/g}$ in M-III), showing a recent input. The values observed in this study in some deep regions of the northwestern Gulf may constitute evidence of the influence of the 1500 m depth plume oil derived from the accidental DWH oil spill. The concentrations of certain trace metals increase as the oil weathering increases [45]. Similarly, the concentration of nickel increased gradually and significantly over time (from $31 \pm 4.87 \mu\text{g/g}$ in M-I to $42.16 \pm 8.52 \mu\text{g/g}$ in M-III) exceeding the sediment quality criteria LRE in most of the stations throughout the study, particularly in sites deeper than 1500 m. The detection of values higher than the MRE during M-III indicated the potential damage to the benthic fauna. The concentration of this metal in deep sites may be linked to processes of sediment transport from the northern Gulf, which includes degraded petroleum products. The concentration of cobalt also increased slightly over time (from $12.51 \pm 1.6 \mu\text{g/g}$ in M-I to $16.08 \pm 2.61 \mu\text{g/g}$ in M-III). This trace element was mostly concentrated along the outer continental shelf and upper slope of the area of study, showing a similar pattern to that of vanadium and nickel. The chrome maintained dissimilar concentrations during the 3-year monitoring period of observation. The highest concentrations of Cr were detected in coastal areas exposed to the intensive river runoff from the Bravo River and Pánuco River.

8. Organic matter (OM) and stable carbon isotope ($\delta^{13}\text{C}$)

The inner continental shelf extended from Rio Soto La Marina River and the Laguna Madre represented vital deposition area of sedimentary organic matter of continental origin. The applied geochemical analysis revealed significant shifts in the concentrations of organic matter (OM) and organic carbon (OC) throughout the 3-year period of observation, showing a progressive increase over time. However, the values remained within the known ranges of concentrations previously recorded in the Gulf of Mexico. No significant changes were detected in the spatial pattern of distribution of organic inputs during the three periods of observation. However, the estimated OC percentages did show significant variability over time; such variability was more evident in deep sites ($>1000 \text{ m}$), where presumably, there is a substantial accumulation of OM caused by processes of deposition or sediment transport on the continental slope.

The $\delta^{13}\text{C}$ values during the three campaigns fluctuated between -20.16 and -21.66‰ with an average of $-21.02 \pm 0.34\text{‰}$. There seems to be an impoverished gradient of $\delta^{13}\text{C}$ values from the northwestern corner close to the coast, which gradually increased outward to the oceanic region, following a southeast pathway. The $\delta^{13}\text{C}$ results highlighted the predominance of autochthonous organic matter (marine) as the primary source of sedimentary OC over that of terrigenous origin, particularly at remote sites from the coast. However, as expected, near the coast, where there are important inputs of terrestrial organic matter derived primarily from C_4 plants, the OC isotopic signature is masked by the mixture with the

autochthonous organic matter. In the present investigation, the isotopic fingerprint belonging to the Deepwater Horizon oil spill ($-27.23 \pm 0.03\text{‰}$ for weathered petroleum and $-27.34 \pm 0.34\text{‰}$ for crude oil) was not detected.

9. Ecotoxicology

9.1 Genotoxicity and bioassays

The short-term bioassays conducted to assess the toxicity of surface sediments, employing biomarkers, *Tetraselmis suecica* (microalgae), *Artemia franciscana* (crustacean), and *Brachionus plicatilis* (rotifers), revealed different responses (**Table 1**). The evaluation of toxicity using as indicator *T. suecica* showed a significant relationship with the presence of PAH, AH, and Fe. In contrast, *A. franciscana* showed distinct mortality pattern when exposed experimentally to the sediments from certain sites of the study area. For instance, significant toxicity was well-defined at sites on the continental shelf and slope just off the Rio Bravo, Soto La Marina, and Carrizales Rivers. The geochemical variables with the highest correlation with mortality of this species were the Zr and Rb during M-I, Ni in M-II, and PAH in M-III. The rotifer *B. plicatilis* served for the identification of areas of low and high toxicity through time. Not a defined pattern for both conditions was recognized, but there was clearly an increase in the temporary toxicity; during M-I, the high toxicity was reduced to two sites: one in front of Laguna Madre and another next to the Soto La Marina River. In the subsequent winter periods (2011–2012), the high toxicity initially corresponded to sites located between 500 and 1500 m of depth and then expanded onto the continental shelf. The mortality of this rotifer showed a significant correlation with the presence of Zr, Nb, Rb and SiO₂ in M-I, and PAH in both winter seasons.

Regarding the genotoxic effects of sediments analyzed, we were able to establish a significant correlation in the 3-year monitoring study, between the damage in the DNA structure and the concentration of PAH. Most of the stations with the highest levels of genotoxicity also presented the highest PAH concentrations. Statistically, we demonstrated an interannual decline of genotoxicity values. However, the percentage of sites containing sediments with substances fostering genotoxicity increased in M-III. The toxicity and genotoxicity are strongly linked to factors such as wastewater and industrial discharge and agrochemicals inputs in the coastal zone. However, in

Species	Toxicity level	M-I	M-II	M-III
<i>Tetraselmis suecica</i>	Low	17	20	6
	Medium	60	72	64
	High	23	8	30
<i>Artemia franciscana</i>	Low	6	92	6
	Medium	74	8	73
	High	20	0	21
<i>Brachionus plicatilis</i>	Low	29	24	6
	Medium	66	64	67
	High	5	12	27

Table 1.
Stations percentage by level of toxicity for each species, in the three MARZEE campaigns.

	Species	Vanadium		Nickel		Cadmium		Lead	
		Muscle	Liver	Muscle	Liver	Muscle	Liver	Muscle	Liver
M-I	<i>Cyclopsetta chittendeni</i>	0.19 ± 0.36	0.03 ± 0.028	2.24 ± 1.798	3.77	0.21 ± 0.484	1.44 ± 1.981	0.32 ± 0.363	1.24 ± 1.701
	<i>Harengula pensacolatae</i>	0.13 ± 0.12		1.52 ± 0.019		0.02 ± 0.03		0.07 ± 0.034	
	<i>Prionotus longispinosus</i>	0.07 ± 0.02		4.40 ± 3.849		0.028 ± 0.033		0.1 ± 0.08	
	<i>Pristipomoides aquilonaris</i>	0.07 ± 0.007	1.72 ± 1.253	0.82 ± 0.319	4.34 ± 3.203	0.053 ± 0.053	1.54 ± 0.927	0.04 ± 0.02	0.37 ± 0.084
	<i>Stenotomus caprinus</i>	0.16 ± 0.25		3.7 ± 3.307		0.054 ± 0.049		0.09 ± 0.021	
	<i>Synodus foetens</i>	0.03 ± 0.01	0.03 ± 0.001	1.16 ± 0.566	3.65 ± 2.288	1.79 ± 3.052	8.73 ± 9.151	0.06 ± 0.03	0.21 ± 0.027
	<i>Trachurus lathami</i>	0.096		2.34		0.115		0.061	
	<i>Centropristis philadelphica</i>	0.01 ± 0.001	0.24 ± 0.145	0.46 ± 0.236	2.81 ± 1.344	0.01 ± 0.001	20.15 ± 15.798	0.03 ± 0.013	0.19 ± 0.042
M-II	<i>Cyclopsetta chittendeni</i>	0.03 ± 0.02		2.25 ± 1.463		0.01 ± 0.006		0.06 ± 0.05	
	<i>Lutjanus synagris</i>	0.01 ± 0.008	0.9 ± 0.026	1.37 ± 0.734		0.007 ± 0.003	0.19 ± 0.105	0.04 ± 0.009	1.38 ± 1.555
	<i>Prionotus longispinosus</i>	0.02 ± 0.005	0.52 ± 0.403	1.55 ± 1.17	16.69 ± 15.632	0.003 ± 0.004	26.68 ± 2.339	0.14 ± 0.079	1.14 ± 0.971
	<i>Pristipomoides aquilonaris</i>	0.02 ± 0.003	4.93 ± 3.51	0.46 ± 0.137	4.68 ± 2.968	0.006 ± 0.004	9.15 ± 7.653	0.02 ± 0.018	0.48 ± 0.379
	<i>Synodus foetens</i>	0.01 ± 0.009	0.15 ± 0.231	1.18 ± 0.904	0.38 ± 0.194	0.017 ± 0.006	3.02 ± 1.992	0.12 ± 0.11	0.96 ± 1.554
	<i>Balistes capriscus</i>	0.095	4.704	0.112	0.573		0.68	0.058	2.74
M-III	<i>Cyclopsetta chittendeni</i>	0.08 ± 0.04	0.80 ± 0.909	0.08 ± 0.035	0.67 ± 0.947	0.002 ± 0.002	0.082 ± 0.064	0.11 ± 0.067	1.33 ± 1.987
	<i>Diplectrum bivittatum</i>	0.10 ± 0.09	2.90 ± 4.472	0.14 ± 0.055	1.82 ± 1.928	0.004 ± 0.002	0.44 ± 1.019	0.15 ± 0.134	5.19 ± 9.038
	<i>Lutjanus synagris</i>	0.088	0.618	0.127	1.59		0.106	0.071	1.96
	<i>Porichthys plectrodon</i>	0.06 ± 0.05	0.89 ± 0.973	0.11 ± 0.094	0.30 ± 0.258	0.017 ± 0.014	0.65 ± 0.475	0.21 ± 0.186	0.48 ± 0.497
	<i>Prionotus stearnsi</i>	0.07 ± 0.008	4.39 ± 2.393	0.38 ± 0.438	1.09 ± 0.938	0.005	0.17 ± 0.095	0.11 ± 0.095	1.77 ± 0.722
	<i>Prionotus spp</i>	0.05 ± 0.01	0.31 ± 0.532	0.13 ± 0.025	0.18 ± 0.096	0.003	0.18 ± 0.341	0.09 ± 0.039	0.16 ± 0.085
	<i>Raja texana</i>	0.067	0.004	0.52	0.006		0.001	0.085	0.002
	<i>Stenotomus caprinus</i>	0.09 ± 0.07	0.25 ± 0.122	0.08 ± 0.02	0.51 ± 0.251		0.055 ± 0.026	0.023 ± 0.029	0.51 ± 0.447
	<i>Synodus foetens</i>	0.08 ± 0.06	3.06 ± 7.688	0.13 ± 0.106	1.48 ± 3.313	0.004 ± 0.003	0.30 ± 0.717	0.09 ± 0.072	1.66 ± 3.37

Table 2.

Average concentrations ($\mu\text{g/g}$) and standard deviation of the metals detected in muscle and liver tissues of fish in the three MARZEE campaigns.

deep zones (>500 m), the levels herein detected in both variables reflect the influence of different sources other than the regionals. Both the toxicity and genotoxicity of sediment can be attributed to the synergy between the PAH and other contaminants detected in sediments, including trace metals such as V, Ni, Cr, Co, Fe, and Al.

9.2 Trace metals in demersal fauna

The toxicity analysis of trace metals (vanadium, nickel, cadmium, and lead) in 250 tissues samples of demersal fauna (fish, crustaceans, and mollusks) showed that the vanadium was the metal less concentrated in the muscle tissue of fish. Concentrations of this metal showed variability over time, decreasing sequentially toward the M-III in muscle, and increasing in liver tissue, reflecting a null or low recent exposure to this metal. In contrasts, the nickel presented the highest concentration average values in liver tissue, in comparison with the muscle, throughout the three oceanographic campaigns. The high concentrations of Ni in some demersal fish may reflect its incorporation by benthic pray or sediment ingestion. The cadmium reached significant concentrations in the liver tissue of demersal fishes but lower concentrations in the muscle. Hence, according to the standard guidelines for human health, such concentrations did not pose any risk for direct consumption. The concentrations of lead recorded in muscle and liver tissues of fish did not exceed critical values of intake and therefore did not represent a risk for its consumption either (Table 2).

The vanadium appeared with a higher concentration in the muscle of macroinvertebrates (mollusks and crustaceans) (Tables 3 and 4). Nickel was also a persistent metal in macroinvertebrates, with highest concentrations at the end of the study (M-III). This metal showed different concentrations between crustaceans and mollusks, presumably due to their different capacities for bioaccumulation

	Species	Vanadium	Nickel	Cadmium	Lead
M-I	<i>Farfantepenaeus aztecus</i>	0.501 ± 0.528	0.095 ± 0.175	0.025 ± 0.071	0.026 ± 0.08
	<i>Sicyonia</i> sp.	1.013 ± 1.144	0.048 ± 0.059	0.001 ± 0.001	0.005 ± 0.004
	<i>Squilla</i> sp.	0.396 ± 0.233	0.064 ± 0.05	0.591 ± 0.393	0.006 ± 0.006
M-II	<i>Farfantepenaeus aztecus</i>	1.053 ± 0.747	0.006 ± 0.001		0.003 ± 0.001
	<i>Squilla</i> sp.	1.847 ± 0.164	0.022 ± 0.009	0.332 ± 0.206	0.002 ± 0.0008
M-III	<i>Farfantepenaeus aztecus</i>	0.19 ± 0.105	0.413 ± 0.371	0.043 ± 0.085	0.142 ± 0.116
	<i>Rimapenaeus similis</i>	0.199 ± 0.051	0.476 ± 0.101	0.014 ± 0.008	0.095 ± 0.069
	<i>Sicyonia dorsalis</i>	0.139	0.28		0.195
	<i>Sicyonia typica</i>	0.323 ± 0.238	1.828 ± 2.416	0.052 ± 0.070	0.623 ± 0.460
	<i>Solenocera necopina</i>	0.096 ± 0.057	0.170 ± 0.129	0.01	0.139 ± 0.142
	<i>Solenocera vioscai</i>	0.208	0.556	0.017	0.131
	<i>Squilla chydaea</i>	0.778 ± 0.405	1.402 ± 0.942	0.387 ± 0.069	0.863 ± 0.593

Table 3.
Average concentrations (µg/g) and standard deviation of the trace metals detected in crustaceans during the three MARZEE campaigns.

	Species	Vanadium	Nickel	Cadmium	Lead
M-I	<i>Loligo</i> sp.	0.149 ± 0.05	0.007 ± 0.005	0.039 ± 0.027	0.002 ± 0.001
	<i>Amusium papyraceum</i>	4.646	0.003	0.013	0.0001
	<i>Mercenaria campechiensis</i>	7.768	0.02	0.001	0.003
M-II	<i>Loligo</i> sp.	0.091 ± 0.084	0.013 ± 0.016	0.001 ± 0.001	0.0006 ± 0.0002
	<i>Amusium papyraceum</i>	7.251 ± 0.855	0.054 ± 0.0003	1.029 ± 0.019	0.004 ± 0.001
M-III	<i>Loligo</i> sp.	0.32 ± 0.271	0.408 ± 0.213	0.044 ± 0.023	0.384 ± 0.132

Table 4.
Average concentrations (µg/g) and standard deviation of the trace metals detected in mollusks during the three MARZEE campaigns.

and regulatory mechanisms of excretion. The cadmium represented the metal with lower concentrations in the tissue of macroinvertebrates. The recorded values of Cd did not exceed those established by the safety guidelines for human health. Only in the case of a crustacean predator (*Squilla* sp.), an average concentration of $0.592 \pm 0.394 \mu\text{g g}^{-1}$ was registered during M-I, which exceeded the safety limits. In the case of lead, its concentration in the muscle of crustaceans and mollusks fit for human consumption remained below $1 \mu\text{g/g}$, except for three species of crustaceans recorded in M-III. This value is considered as critical threshold for human health. In summary, the analysis conducted of metals in tissues of demersal fish, crustaceans, and mollusks did not indicate life-threatening concentrations for the individuals nor to the human health in most of the cases. However, one cannot overrule the possible existence of bioaccumulation and biomagnification phenomena that eventually might affect the demersal trophic web.

10. Plankton

10.1 Phytoplankton

According to the taxonomic composition and abundance of phytoplankton algae, it was found that the values obtained coincided with those previously reported for this region (Table 5) [46]. These results suggest oligotrophic conditions, as confirmed by the low nutrients (nitrates, 29.3–37.9 µM; silicate, 3.5–8.2 µM; phosphates, 1.9–3.4 µM) and chlorophyll-*a* concentrations ($>0.25 \pm 0.14 \mu\text{g/L}$). The abundance of dinoflagellates and phytoflagellates, and the low diatom abundance in most of the analyzed samples, adds support to the oligotrophic condition of this region in the summer and winter seasons. The Chlorophyceae algae were responsible for the blooms recorded in coastal waters (652, 179 cells/L). No significant differences were found in abundance among the three campaigns.

10.2 Zooplankton

The zooplankton biomass values registered in the three oceanographic campaigns fluctuated between 1.20 and 19.38 g/100 m³. These values were considered impoverished when compared to those registered in the SW Gulf, which exceed 40 and 100 g/100 m³ [47]. In the two winter seasons (2011 and 2012), the

	M-I	M-II	M-III
Stations	35	25	33
Samples	282	188	230
Abundance (cell L ⁻¹)	35–19.6 × 10 ⁴	12–7.75 × 10 ⁴	66–66.5 × 10 ⁴
Groups			
• Diatoms	145	104	89
• Dinoflagellates	175	62	58
• Silicoflagellates	16	3	2
• Cocolithophorids	8	1	0
• Cyanophytes	7	1	2
• Chlorophytes	2	1	1
• Ciliated	1	1	0
• Total species	354	173	152

Table 5.
Phytoplankton abundance by groups (cells/L) recorded in the water samples obtained during the three MARZEE campaigns.

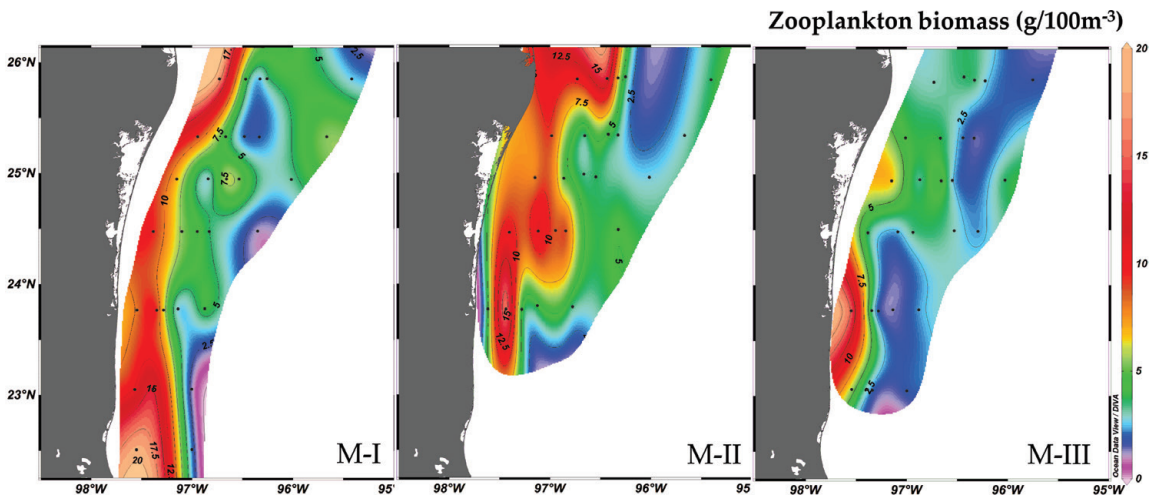


Figure 5.
Zooplankton biomass (g/100 m³) distribution for the three campaigns M-I, M-II, and M-III.

zooplankton revealed a significant decrease in biomass in both neritic and oceanic waters. In 2011 the biomass varied between 2.9 and 19 g/100 m³, and in 2012 it reached 1.2–15.8 g/100 m³. The neritic waters showed high variability in biomass (2–7 g/100 m³), due to the influence of river discharges and the intrusion of ocean water near the coast. The zooplankton biomass was less than 8 g/100 m³ in M-I and in M-II, while in M-III, it was less than 3 g/100 m³ (**Figure 5**).

11. Infaunal benthic community

The taxonomic composition, density, and biomass of the infaunal benthic biota constituted a valuable analytical asset in the effort of identifying the magnitude of natural changes opposed to those potentially caused by anthropogenic disturbances. In M-I, an impoverished infaunal benthic community was recorded, with only five taxa recorded and an average density value of 4.64 ± 7.03 individuals/10 cm². In M-II, the diversity of taxa continued being poor, recording seven taxa (**Table 6**), but

Taxa	M-I	M-II	M-III
Annelida	10.97	98.44	209.63
Arthropoda	9.20	17.70	48.15
Mollusca	40.01	4.24	16.99
Nematoda	101.27	60.19	155.80
Priapulida	0	0.70	4.72
Sipunculida	0	0.70	3.30
Nemertea	0	1.41	8.97
Kinorhyncha	1.06	0	3.77

Table 6.
Densities per taxon (ind/10 cm²) recorded in the three MARZEE campaigns.

the density values showed a small increase: 7.33 ± 8.48 individuals/10 cm². In M-III, the highest diversity and density values were recorded: eight taxa and 13.67 ± 22.71 individuals/10 cm², respectively [48]. The pattern of density in both seasons maintained the same negative exponential correlation with respect to the depth. Interestingly, there were significant density values at sites on the shelf rich in organic materials exported from the coastal zone; similar density values were also recorded in deeper sites in which presumably deposition and sediment transport occur. The nonmetric multidimensional scaling (nMDS) analysis applied to the estimated infaunal density in the three campaigns confirmed that M-I was different to the winter of 2011 and 2012; while the latter were similar to each other.

Significant temporal differences among the three campaigns were detected through the PERMANOVA analysis. Pairwise test indicated that such differences were interannual rather than seasonal. Spatially, only significant bathymetrical differences were detected; no latitudinal significant differences were noted. The pairwise test showed differences among the benthic infauna of the inner continental shelf (50 m) and deeper strata [48].

Based on the interpretation of abundance/biomass comparison curves (ABC) of the macroinfaunal community, it was possible to assess its interannual ecological equilibrium expressed as a stress factor. A clear trend of position of the curves since 2010–2012 revealed an interannual intensification of the stress degree. We inferred that the proliferation of nematodes in the latter season is symptomatic of such stress condition (**Figure 6**) [48].

In M-III, the infaunal community experienced a substantial change in its composition. The nematode worms reached a high dominance (44%). Even though no statistically significant latitudinal or bathymetric patterns of dispersion were distinguished, high density values were concentrated near the 50 m isobaths. The notorious abundance of the genus *Sabateria* in our samples deserves special attention. This genus represents an invaluable biomarker due to its tolerance to high concentrations of organic matter, degraded, heavy metals, and hydrocarbons [49]. *Sabateria* is known as an opportunistic nematode which, together with other infaunal dwellers like *Terschellingia*, *Paracomesoma*, and *Daptonema*, are normally found in highly contaminated sediments by organic matter characterized by a low redox potential [49, 50].

Metazoan organisms that make up the infaunal community are particularly sensitive to alterations in the geochemical properties of the sediments. A multivariate analysis BIO-ENV was performed to relate the set of environmental sedimentary variables to the macrofauna community structure. The correlation values obtained

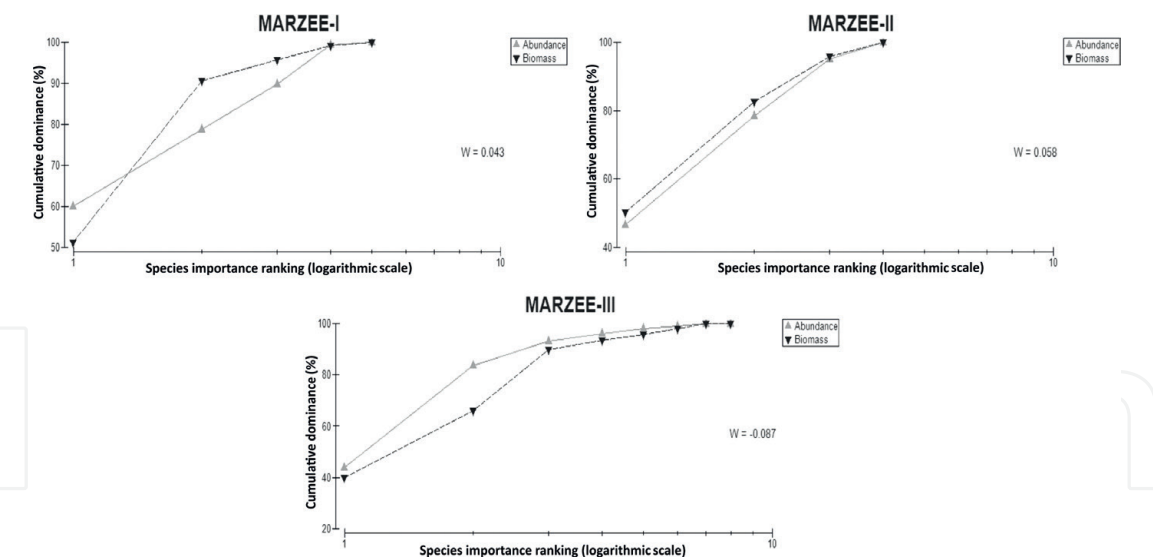


Figure 6.
Abundance/biomass comparison curves (ABC) for the three MARZEE campaigns.

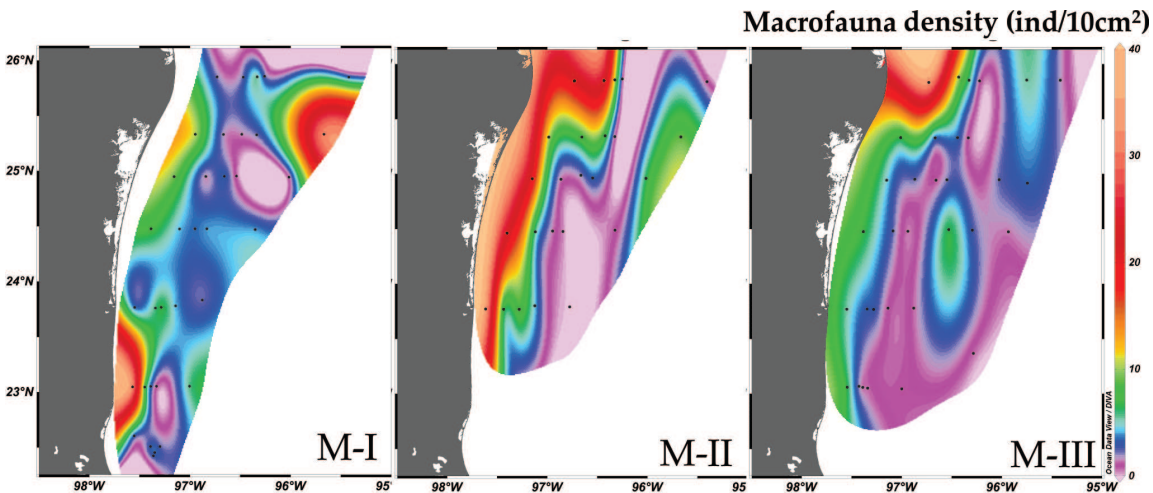


Figure 7.
Spatial distribution of macrofauna density values (individuals/10 cm²) in the three MARZEE campaigns.

from the BIO-ENV were rather low in the three campaigns (<0.4). However, it was possible to identify the geochemical variables that seem to govern the macroinfauna distribution in each season. In M-I the variables were percentage of sand, the concentration of Al and V, and the $\delta^{15}\text{N}$ values. In M-II, important variables were Al PAH, Ni, and AH. In M-III, the variables were Al, V, and AH. However, the correlation values were not significant. Nonetheless, in the summer season (2010), the influence of natural variables is more obvious than in the following periods (2011 and 2012), in which variables linked to crude oil become more relevant (**Figure 7**).

The changes observed in the community variables such as taxonomic composition and density of the macroinfaunal components were attributed to the gradual increase recorded in the study area of MO, HA, PAH, and metals such as Ni, V, and Co.

12. Final remarks

Many are the factors that determine the final destiny of complex oil molecules in the marine ecosystem. Coastal habitats (lagoons, coral; reefs, marsh; and lands,

mangroves), open waters, and seabed are vulnerable to oil contaminants due to lasting effects of toxic compounds incorporated in the trophic web or deposited in shallow and deep sediments. Our research revolved around two major premises: (a) the existence of trans-boundary pollutants in the GoM and (b) the high connectivity of oceanographic processes within the GoM. For Mexico, these two concepts are essential in understanding the potential environmental consequences of a massive oil spill in its EEZ and shoreline. The above two conditions facilitate the active transport of contaminants across different sectors of the Gulf. There are no physical barriers or other sort of factors that impede the free passage from the US waters toward Mexico's EEZ and vice versa. Migratory species (trans-boundary species) and planktonic larvae take advantage of the ocean circulation to extend their fundamental niche (growth-reproduction-nutrition) within the Gulf, regardless of international legal boundaries.

During the 3-year monitoring program in Mexico's EEZ in the aftermath of a major oil spill in the northern Gulf of Mexico caused by the Deepwater Horizon event in April of 2010, our research efforts focused on the assessment of crude oil compounds in water, sediments, plankton, and benthos of the NW Gulf. The high-connectivity and the trans-boundary mechanisms that facilitate the dispersion of larvae and pollutants within the GoM were the essential premises in examining the far-field effects of the DWH oil spill in Mexican waters. Therefore, it was doubtful that the DWH harmful effects were confined to a restricted area near the Macondo's wellhead.

The information contained in this chapter is an excellent baseline environmental data from more than 35 hydrographic variables, biogeochemical and biological properties of the benthic and pelagic ecosystems of the continental shelf, and the upper slope of the NW Gulf of Mexico. The analyses and interpretation so far achieved in this first multidisciplinary effort do serve to recognize the significant alterations in the sedimentary quality standards and the risk of harmful effects on benthic organisms, attributable to anthropogenic factors.

The lack of knowledge on the long-term environmental damage compels us to implement innovative research approaches. If we consider the short-term monitoring operations, it is necessary to adjust the network of observation sites and optimize the number of variables focusing on the detection of toxic elements in water, sediment, and the trophic web. In a long-term scenario, it is essential to continue with multidisciplinary monitoring programs involving research vessels and stationary observational buoys.

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