

## ASSESSMENT OF TRACE ELEMENTS AND ORGANIC POLLUTANTS FROM A MARINE OIL COMPLEX INTO THE CORAL REEF SYSTEM OF CAYO ARCAS, MEXICO

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**Abstract.** Possible contaminants produced by the Petroleos Mexicanos (PEMEX) marine oil complex in the vicinity of the Cayo Arcas (Mexico) coral reef ecosystem were evaluated by analyzing sediments and sea water for hydrocarbons and metal elements. We found that the concentrations of aliphatic hydrocarbons in the sea water were generally low, with the highest values detected near the oil station; the concentration of polycyclic aromatic hydrocarbons (PAHs) was generally below the detection limit. The hydrocarbons found in the sediments seem to have a pyrogenic origin, and were probably produced by marine traffic in the study area. The total PAH concentration did not exceed the NOAA criteria, although levels of some individual PAHs did. The only metal detected in the sea water at high concentrations was nickel. The Ni/V ratio in the sediments indicates the contribution of crude oil to the system. The high content of Ni and Zn was attributed to the ballast waters from the oil tankers that load at the station's monobuoys. The presence of fine sediments that commonly originate from terrestrial ecosystems supported this assumption.

**Keywords:** ballast water, coral reef, trace elements, oil pollution, Southeast Gulf of Mexico

### 1. Introduction

Located in the Southeastern Gulf of Mexico, the 4.6 km long by 2.4 km wide Cayo Arcas group (Figure 1) forms part of the Campeche Bank Reefs. The nearest largest city is Merida, on the Yucatan mainland. The group consists of three sandy cays located approximately 128 km from the mainland: Cayo Centro (the largest cay), Cayo del Oeste, and Cayo del Este, which together form a "U" shape. Up to four people (lighthouse keepers and marines) live on each island. An elongated 3-km-long reef flat also forms part of the complex; the reef flat surrounds a sandy partial lagoon on the western side of the Cayo del Centro.

The Triangulos Reef is a complex of three coral reefs that lie within 1000 m of each other, approximately 70 km north of Cayo Arcas. The Triangulos group includes islands or simple reef walls with very steep sides and small reef flats. Because of its remoteness and inaccessibility, this reef complex is less exposed to anthropogenic contamination and can therefore be used as a reference example of an unaltered area.

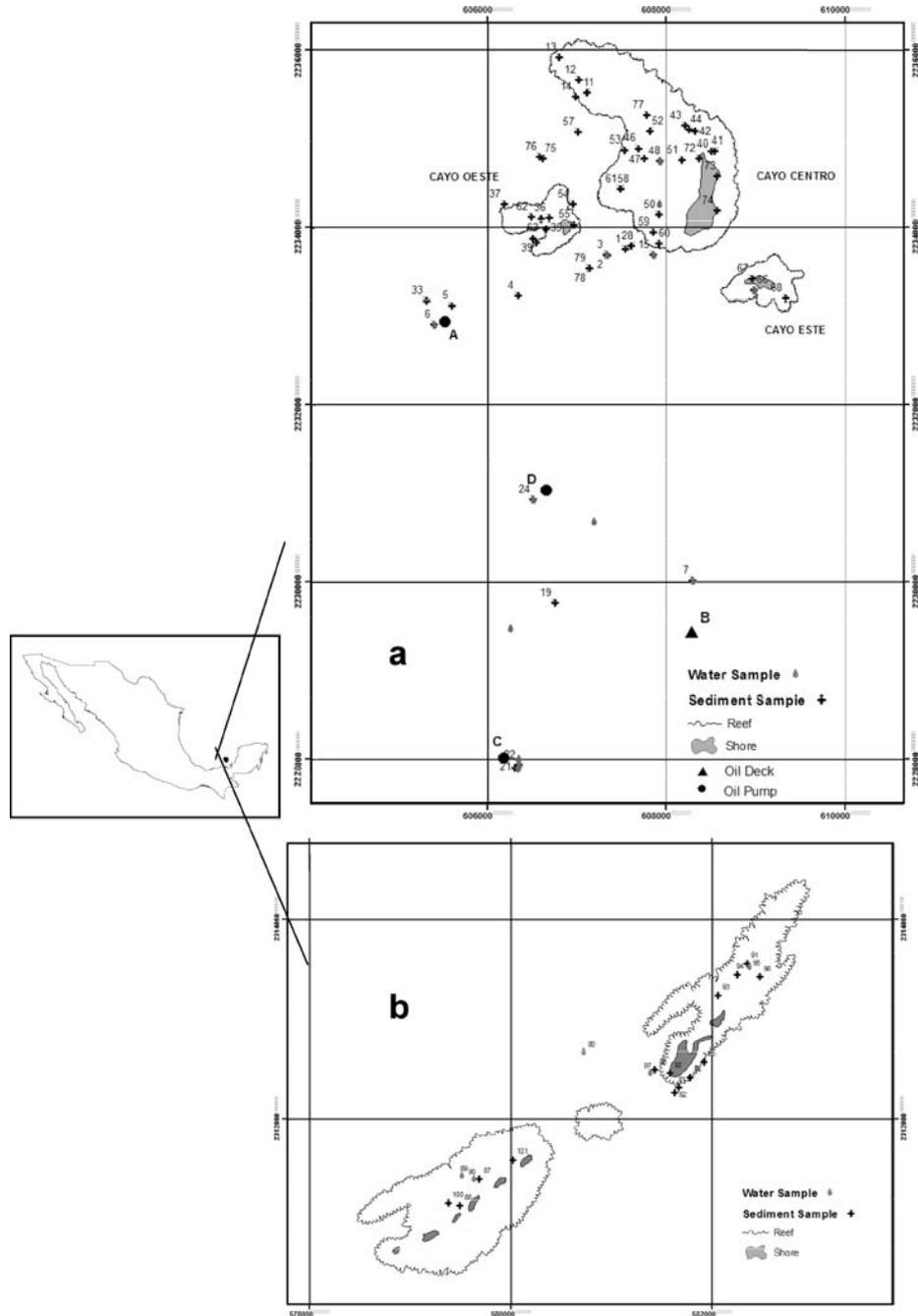


Figure 1. Location of the study area and (a) sampling locations for water and sediments at the Cayo Arcas coral reef on the Campeche Bank, Gulf of Mexico. (A, C, and D, monobuoys for oil tankers; B, marine oil platform terminal). (b) Study area and sampling locations for water and sediments at the Triangulos coral reef on the Campeche Bank, Gulf of Mexico.

The region of Campeche Bank, which encompasses Cayo Arcas and Triangulos, is an underwater extension of the Yucatan Peninsula, which gradually slopes northwards for about 200 km and descends abruptly into the Sigsby Deep. The Gulf of Mexico is basically an area of terrigenous sedimentation, but scattered reef growth is found off Mexico. Both emerged and submerged reefs are present, but all of them are platforms growing as incomplete cones, rising from a pre-Holocene base located at 50–60 m in depth. Campeche Bank Reefs, one of the more offshore reefs, present ecological and morphological characteristics that distinguish them from the nearby Caribbean reef. This region is of considerable value both from an ecological point of view and as a strategic site for the Mexican petroleum industry. The sea of the Cayo Arcas region, which lies 84 km north of the country's marine oil wells, offer high maneuverability to oil tankers and are naturally protected from winds, conditions that facilitate navigation and travel even in adverse weather. The Cayo Arcas petroleum complex, is one of Mexico's most important fueling oil stations for the export of Maya-type crude oil. This oil complex consists of three monobuoys, with a total capacity of 250,000 t dead weight and one platform station with a capacity of 350 000 t dead weight. In 2004, 64,500 896 t of crude oil were shipped from this station.

Even in the absence of spills, marine oil stations and its activities release a variety of contaminants into the environment that could adversely affect the coral reef ecosystems (Bak, 1987). Marine oil pollution spreads widely due to the presence of marine oil stations, traffic by oil tankers, and oil spills. The seriousness of coastal oil pollution depends on the amount of oil that is released and on the characteristics of the coastal environment. Gundlach and Hayes (1978) have ranked coastal environments in terms of their degree of susceptibility to oil deposition and the residence time of any deposited oil. According to their classification, sheltered rocky coasts, salts marshes, mangroves, and coral reefs are most likely to be adversely affected by oil contamination. The coral reef system of Cayo Arcas clearly falls into this category of vulnerability.

No serious attempt has previously been made to evaluate the impact of the Cayo Arcas marine oil station on the region's ecosystems. Gonzalez *et al.* (1992) evaluated the levels of aliphatic hydrocarbons in the region's sediments and organisms, but no attempt was made to correlate this data with the activities of the oil complex. Therefore, the objective of the present study was to evaluate the contaminants being released by the Cayo Arcas oil marine station operated by Petroleos Mexicanos (PEMEX) in the vicinity of the Cayos Arcas coral reef system and compare them with the contaminants present in the nearby Triangulos coral reef system, which we believed to be unaffected by the marine oil station since it is not surrounded by any marine oil activity.

The contaminants most commonly assessed in studies of oil pollution are polycyclic aromatic hydrocarbons (PAHs) and heavy metals. PAHs pose the greatest environmental risk, mainly because of their carcinogenic and mutagenic properties (Varanasi, 1989). However, ingested heavy metals can move up the food chain and

bioaccumulate over time, eventually reaching toxic concentrations in body fluids, tissues, or specific organs (Siegel, 2002).

In an attempt to determine the impact of contaminants in the environment, the Coastal Protection and Restoration Division of the U.S. National Oceanic and Atmospheric Administration (NOAA) has published a list of critical values to help identify the possible impact of toxic residues on coastal habitats and resources (Buchman, 1999). These values, referred to as Screening Quick Reference Tables (SQUIRTs), are used as reference values. They do not represent criteria for determining whether contamination has occurred, but rather represent a compilation of various studies that evaluated the toxicity of the contaminants for different biological species. Nevertheless, these values provide useful initial criteria for evaluating the possible impact of contaminants, and on this basis, we chose them for our study of the impacts of the Cayo Arcas marine complex.

Other substances can be used as indicator compounds for detecting oil pollution. For example, the analysis of aliphatic hydrocarbons can be used to fingerprint spilled oils and provide additional information on the source of a given hydrocarbon contamination. Metals such as vanadium (V) and nickel (Ni), which are found in high concentrations in crude oil, (Macias-Zamora *et al.*, 1999) are incorporated into marine sediments after an oil spill, therefore quantification of Ni and V has been used as an indicator of crude oil pollution (Khalaf *et al.*, 1982). Thus, we obtained oil samples from nearby marine stations (Cantarel crude oil from Sonda de Campeche and Cayo Arcas oil mixture, (both in the Gulf of Mexico) in order to profile the hydrocarbon and trace metal contents of these oils as a tool for assessing possible contamination of the Cayo Arcas ecosystem.

## 2. Materials and Methods

### 2.1. SAMPLE COLLECTION

The sediment and water sampling took place simultaneously during the Ar-Cor oceanographic survey conducted by the oceanographic ship *Justo Sierra*, which is owned and operated by the Universidad Nacional Autónoma de México (UNAM), from 16 to 26 August 2001. In total, 71 sediment and 25 water samples were obtained in the Cayo Arcas area and its surroundings, covering approximately 38 km<sup>2</sup>, and from the Cayo Triángulos control site, covering approximately 10 km<sup>2</sup>. (See Sections 2.1.2 and 2.1.3 for details of the sample size in each area).

In Cayos Arcas, the sampling design used three transects that ran from the PEMEX marine facilities toward the reef; these transects began at the three monobuoys (A, C, and D in Figure 1), where oil tankers from around the world unload their ballast water and load oil; a fourth transect began at the marine terminal (B in Figure 1), which was 3 km from the coral reef.

In Figures 1, 2, 5, and 6, the coordinates are the Universal Transverse Mercator (UTM) system so that the coordinates can be tied directly into a distance measuring system. The positions of the sample sites are shown in Figure 1 for the Cayo Arcas (Figure 1a) and Cayo Triángulos (Figure 1b) areas.

#### 2.1.1. *Sediment Sampling*

Of the 71 sediment samples, 56 were collected from the Cayo Arcas area and 15 were collected from the Cayo Triángulos area. In each case, we collected approximately 800 g (wet weight) of surface sediments (a depth of 0 to 5 cm) using a custom made bottom dredge sampler; the samples were then subdivided into glass containers for hydrocarbon determination and plastic bags for physicochemical characterization and metal determination. The samples were stored at 0 °C until laboratory analysis.

#### 2.1.2. *Oil and Diesel Sampling*

A sample of the diesel fuel used by the *Justo Sierra* was taken to let us account for any possible contamination of the samples, since this type of contamination has been reported in previous sampling studies (Hellmann, 1995). Oil samples from Cantarel and Cayo Arcas were obtained to provide a basis for comparison with the contaminants found in the samples.

#### 2.1.3. *Water Sampling*

Simultaneously with some of the sediment sampling, approximately 3 liter water samples were obtained. Of the 25 samples, 18 were collected from the Cayo Arcas area and 7 from the Triángulos area. The samples were of surface water (to a depth of 20 cm). Temperature and dissolved oxygen were determined *in situ*. The samples were transported in dark containers stored at 4 °C to the shipboard laboratory, where we performed the following analysis:

1. All samples were filtered through pre-weighed 45- $\mu$ m filters (Millipore Corp., Bedford, MA, USA).
2. The filters were dried at 105 °C to constant weight and weighed in order to quantify the suspended solids.
3. We performed an extraction on 2 L from 12 selected samples (collected near the oil station and the ship) using 100 mL of hexane. The extract was stored in hermetically sealed tubes until we were able to perform the hydrocarbon quantification analysis.
4. We acidified 250 mL from each of the 12 selected samples (from the same sites as in step 3) with nitric acid to the nearest 2% before transportation and subsequent determination of trace metal contents.
5. We used 250 mL from the surface water samples for determination of the physicochemical parameters in the ship's onboard laboratory.

## 2.2. SAMPLE ANALYSIS

### 2.2.1. Sediment Analysis

The sediments were air-dried at ambient temperature in a closed room designed for the specific purpose, then were sieved through a 2-mm sieve. We then determined the particle size distribution using 2.38-, 1.68-, 1.0-, 0.5-, 0.21-, and 0.074-mm sieves. In three samples with very fine sediments, we used the Bouyoucos-hydrometer method (Tan, 1996). We also determined the organic carbon and trace metal (Al, Ni, V, Pb, Cu, Cr, Fe, Zn, Ba, Cd, and Hg) contents. Organic matter was determined using a potassium dichromate digestion with subsequent quantification of Cr(III) in a UV spectrophotometer (UV Varian model CARY3E, Melbourne, Australia) according to the Walkley-Black method, (ISO14235, 1987), with calibration performed using blanks and duplicates every 10 samples. We subdivided the 800 g of sediment into two. We then air-dried the first subsample at 105 °C to determine the results on a dry-weight basis. We performed hydrocarbon determination on the second subsample while it was still wet.

We determined concentrations of aromatic hydrocarbons and examined for n-alkanes determined by means of gas chromatography with a flame ionization detector (GC-FID Varian model 3400CX Melbourne, Australia) using UNEP method No. 20 (1992). We extracted 5 g of dry weight from the sediment with hexane-dichloromethane (1:1 v:v) in a Soxhlet extractor for 8 hours. This extract was evaporated to a 5-mL volume in a Rotavapour evaporator (Heidolph Laborota 4003), after which we obtained the aliphatic and aromatic fractions by passing the extract through a glass column; the column was filled with fiberglass, silica gel (5%, deactivated), alumina (5%, deactivated), and anhydrous sodium sulfite that had been pre-washed three times with 30 mL of hexane for determination of the aliphatic hydrocarbons and with 30 and 20 mL of hexane-dichloromethane (9:1 and 1:1 v:v, respectively) for determination of the aromatic hydrocarbons. The extracts were concentrated again to a 5 mL final volume using the Rotavapour evaporator. Next, the extracts were dried in a nitrogen flow, redissolved the extract in 1 mL of isooctane, then homogenized the solution in an ultrasound bath for 30 min before injection into the GC. Every 15 samples, we recalibrated the GS using blanks that were analyzed together with duplicates of the samples.

For the determination of trace metals, the samples were microwave-digested according to method EPA 3051(EPA-3051, 1994) and metal concentrations were quantified by means of AAS or hydride generation (for Hg) (Elrick *et al.*, 1987). For quality control, duplicate samples were digested and analyzed, as were spiked samples and a standard reference material Estuarine Sediment NBS 1646 (Gaithersburg, MD, USA).

We determined the soluble form of the metals according to method ASTM D 3987–85. (ASTM, 1982). In this approach, we dried 10 g of dry weight of the sediment and sieved it into a PVC bottle. We then extracted the sediment with

200 mL of distilled water, with agitation for 18 h at 240 rpm. We determined levels of extracted Pb, Cu, Cd, Zn, Ni, Ba, V, Cr, Fe and Al (Hg was not determined since it was not detected in the sediment samples) by means of AAS. The instruments used were a Varian SpectraAA 110 and a SpectraAA 10 plus with air-acetylene and nitrous oxide acetylene burners and hollow cathode lamps for each of the elements. We prepared different standards for each element from a stock solution of 1000 mg/L (Merck KGaA, Darmstadt, Germany) and constructed calibration curves. The extracts were then quantified against these calibration curves.

### 2.2.2. Marine Diesel and Crude Oil Analysis

The aromatic and aliphatic fractions of the oil samples were separated and identified in the same manner as for the sediments as described in Section 2.2.1, and the trace elements were quantified by means of an atomic-absorption spectrophotometer (AAS) Spectra AA 10 plus Varian Australia, Ltd. Victoria, Australia.

### 2.2.3. Water Analysis

We determined the total suspended solids gravimetrically (i.e., by filtering and weighing). We determined the concentrations of aromatic and aliphatic hydrocarbons by means of GC-FID according to UNEP Method No. 20. (1992) We extracted the sea water with 50 mL of hexane per 1 L of marine water on the ship. The extract was then refrigerated at 4 °C until further treatment in the laboratory. We concentrated the extract to 10 mL using the Rotavapour evaporator, and separated the aliphatic and aromatic fractions using laboratory made silica gel and alumina (both 5% deactivated) column, packed with de-ionized water (18.3 MΩ). The aliphatic fraction was extracted four times using 30 mL of hexane, and the aromatic fraction was extracted with 30 and 20 mL of a hexane-dichloromethane mixture (9:1 and 1:1 v:v, respectively). The extract was then concentrated using the Rotavapour evaporator to a 10-mL volume. Both extracts were dried in vials with a nitrogen flow. The extracts were redissolved with 0.25 mL of isooctane prior to analysis by means of GC-FID. The concentrations of the aliphatic and aromatic hydrocarbons were calculated using a calibration curve created from commercial standards (polycyclic aromatic hydrocarbon mixture PPH-10RPM and diesel mixture 2 GRO/DRO; Chem Service, West Chester, Philadelphia, USA).

We determined nitrate, nitrite, and phosphate concentrations with a field spectrophotometer (DR model 2000, HACH Company, Loveland, CO, USA) according to methods 8039, 8507, and 8048, respectively, following the manufacturer's instructions. We determined electrical conductivity using a conductimeter (HACH model 441, Corning, NY, USA), silicates using ASTM method D859/88, colorimetry by means of UV-visible spectrophotometer, and alkalinity (HACH model 441, Corning, NY, USA).

### 3. Results

#### 3.1. SEDIMENTS

##### 3.1.1. *Physicochemical Properties*

Figure 2a and b show the particle size spatial distributions for the Cayos Arcas and Triángulos samples, respectively. In general, the samples sites were predominantly

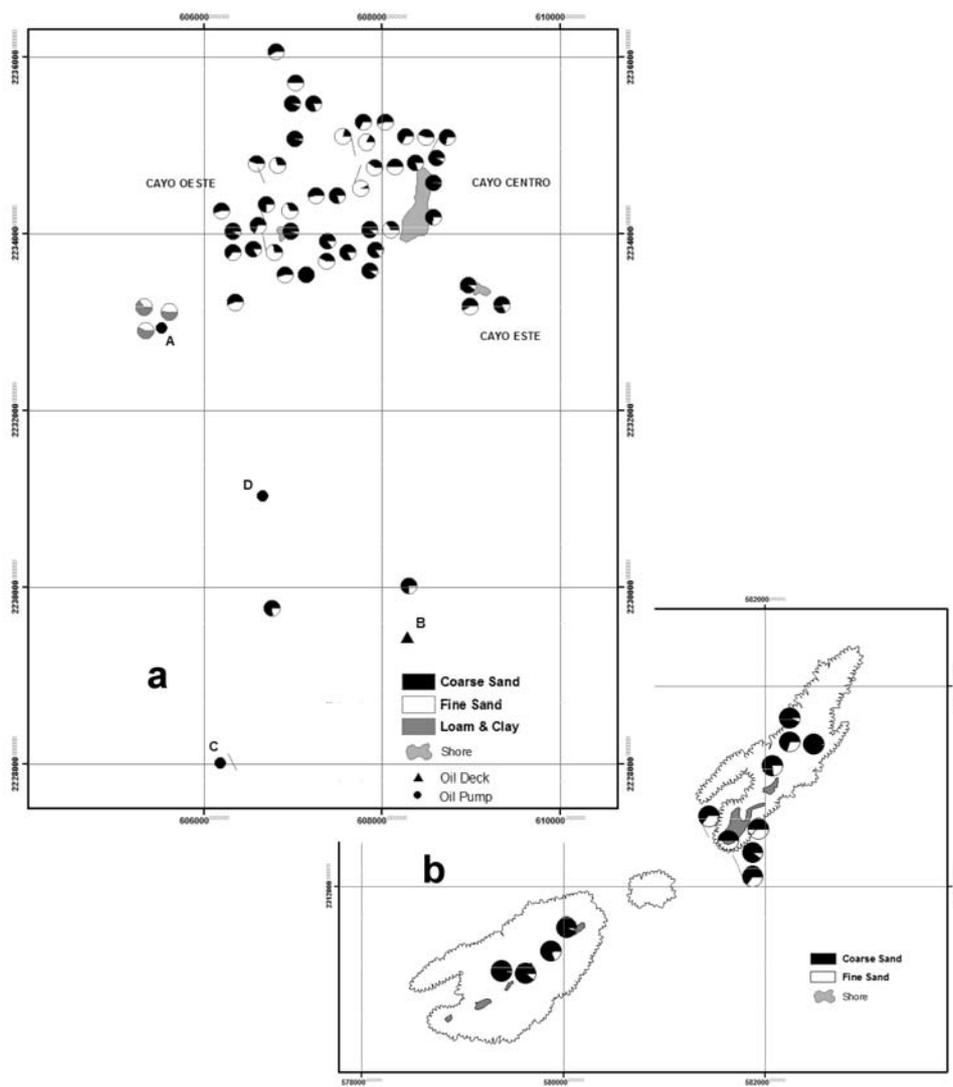


Figure 2. (a) Particle size distribution of the sediments at the Cayo Arcas coral reef, Campeche, Gulf of Mexico. (b) Particle size distribution of the sediments at the Triángulos coral reef, Campeche, Gulf of Mexico.



Figure 3. An oil tanker loading crude oil near monobuoy A. Note the area of ballast water around the ship.

coarse sand (2.38 to 0.50 mm). However, in the Cayo Arcas area near buoy A, the sediments had finer particles (less than 0.074 mm) classified as clays and loams, suggesting a possible terrestrial origin. The origin of the clays and loam may have been ballast water from the oil tankers. Figure 3 shows an oil tanker loading crude oil at one of the monobuoys; the lighter shape spreading from the ship corresponds to the ballast water.

In the middle part of Cayo Centro, between two emerged cays with a small water depth (20 to 30 m), there was also an accumulation of fine sand (0.21 to 0.074 mm), which can probably be explained by the lack of strong water currents that would favor the accumulation of such sediments.

Organic matter concentrations in the sediments from the Cayos Arcas and Triángulos areas ranged between 0.12 and 1.00%, and did not differ significantly between the two reefs.

### 3.1.2. Hydrocarbons

In general, the sediments had a low concentration of aliphatic hydrocarbons (1.5 to 26.4 mg kg<sup>-1</sup>; Figure 4a). The aliphatic hydrocarbon profile was dominated by nC24, which was characteristic of the Cantarel crude oil (Figure 7). The highest concentration in the samples was found in the enclosed area west of Cayo Centro (20.9, 25.4, 26.4, 18.4, and 19.7 mg kg<sup>-1</sup>), where no strong currents occur. This pattern matches the accumulation of fine sand shown in Figure 2.

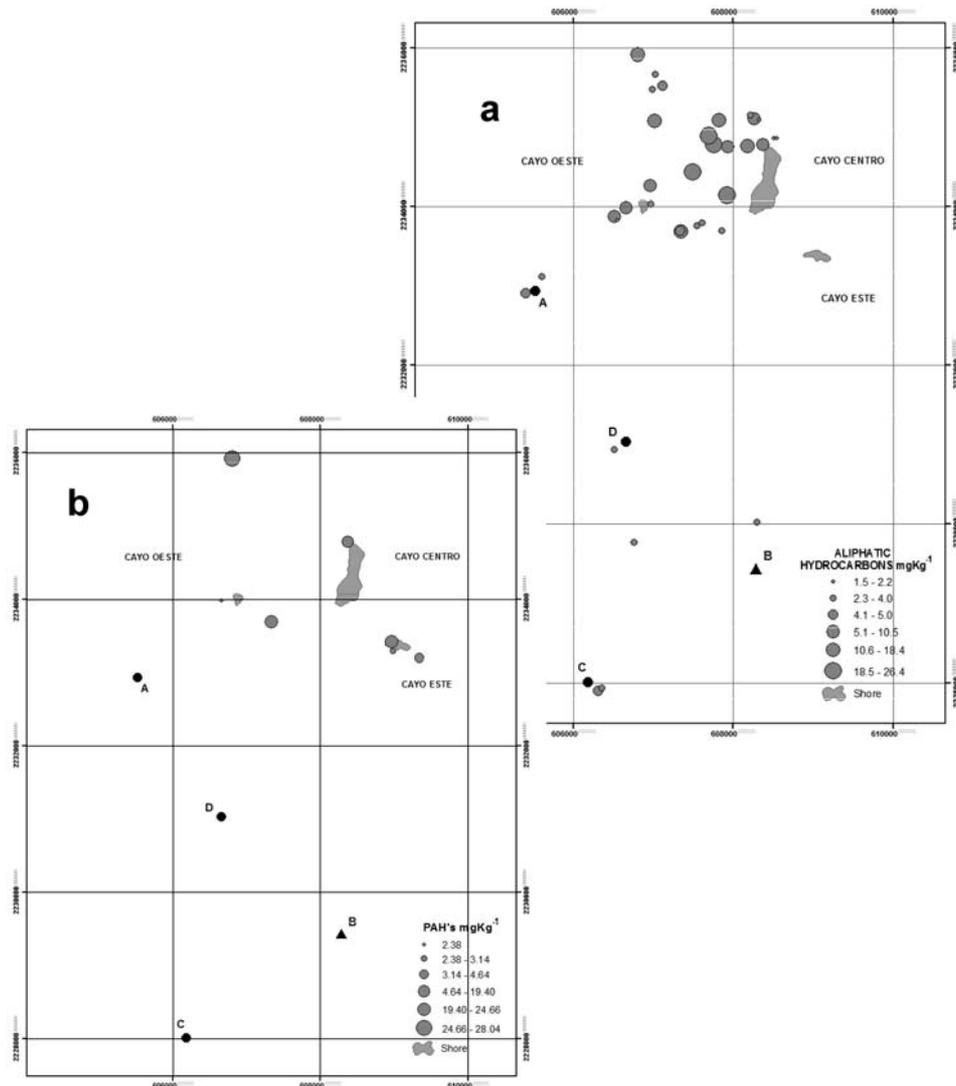


Figure 4. Spatial distribution of (a) aliphatic hydrocarbons and (b) polycyclic aromatic hydrocarbons (PAH) in sediment samples from the Cayo Arcas coral reef, Campeche, Gulf of Mexico.

Only seven sediment samples showed the presence of PAHs, with concentrations ranging between 3 and 28  $\text{mg kg}^{-1}$ . The individual PAHs that we detected were anthracene, pyrene, chrysene, benz(a)anthracene, benzo(a)pyrene, and benzo(b)fluoranthene. The spatial allocation of these samples did not show a clear pattern (Figure 4b) with respect to the locations of the monobuoys and platform. This suggests that the PAH pollution might have a different origin from the aliphatic pollution.

### 3.1.3. Trace Elements

**3.1.3.1. Barium, Iron and Aluminum.** There were no significant differences between the Ba concentrations in the Cayo Arcas and Triángulos sample areas, with mean values of 102 and 113 mg kg<sup>-1</sup>, respectively, therefore we assume that either these are typical background levels for the study area or are part of the global pollution of the Gulf of Mexico. Vazquez and Sharma (2004) have reported values of Ba in sediments in the south of the Gulf of Mexico for up to 2400 mg kg<sup>-1</sup>. In contrast, Fe and Al differed between the Cayo Arcas and Triángulos areas. In the Cayo Arcas area, values of up to 4829 mg kg<sup>-1</sup> Fe and 5360 mg kg<sup>-1</sup> Al were found, versus 243 and 434 mg kg<sup>-1</sup>, respectively, in the Triángulos area.

When the spatial distribution of Fe and Al is mapped (Figure 5a and b), the highest concentrations appear near buoy A, where fine sediments (loams and clays) had accumulated. Near buoys C and D and near terminal B, Fe and Al concentrations were lower than those near buoy A, but were still sufficiently high to be considered atypical for the region (since the majority of the values are within 200 mg kg<sup>-1</sup> or less).

### 3.1.3.2. Other Metals (Hg, Cd, Cu, Cr, V, Ni, Zn, Pb).

**Hg and Cd:** The concentrations of Hg and Cd were below the detection limits (0.1 and 2 mg kg<sup>-1</sup>, respectively) in all samples.

**Cu:** A large proportion of the samples (93%) showed undetectable (<6 mg kg<sup>-1</sup>) levels of Cu, but samples in the Cayos Arcas area towards the middle of Cayo Centro and north and south of Cayo Centro showed concentrations of 97, 43, and 41 mg kg<sup>-1</sup>, which could represent toxic concentrations for sensitive organisms (NOAA, 1999).

**Cr:** Only five samples showed concentrations above the limit of detection (10 mg kg<sup>-1</sup>). The highest concentrations were found near the middle of Cayo Centro (34 mg kg<sup>-1</sup>). None of the samples were above the NOAA (1999) criteria of 160 to 370 mg kg<sup>-1</sup>.

**V:** Only 11 samples had levels above the detection limit (60 mg kg<sup>-1</sup>); 10 were in the Cayo Arcas area and 1 was in the Triángulos area, with concentrations ranging between 60 and 170 mg kg<sup>-1</sup>. NOAA (1999) establishes a baseline concentration of 50 mg kg<sup>-1</sup> for V, but does not define toxic levels. The spatial distribution of V was similar to that of Al and Fe, suggesting that its source is the monobuoys, and originates either from ballast waters or from minor oil spills.

**Ni:** A large proportion (84%) of the samples showed Ni concentrations between 10 and 20 mg kg<sup>-1</sup> (Figure 6), which are considered typical of the study area since similar values were found in both the Cayo Arcas and the Triángulos areas. Values above this range (three samples) were found near the monobuoys and near the middle of Cayo Centro (two samples). Of the latter two samples, one (41.9 mg kg<sup>-1</sup>) was slightly above the NOAA (1999) toxic level (35.9 mg kg<sup>-1</sup>).

The V/(V+Ni) ratio for the sediment samples that contained both V and Ni was 0.86; this ratio was similar to the one obtained for the Cantarel and Cayo

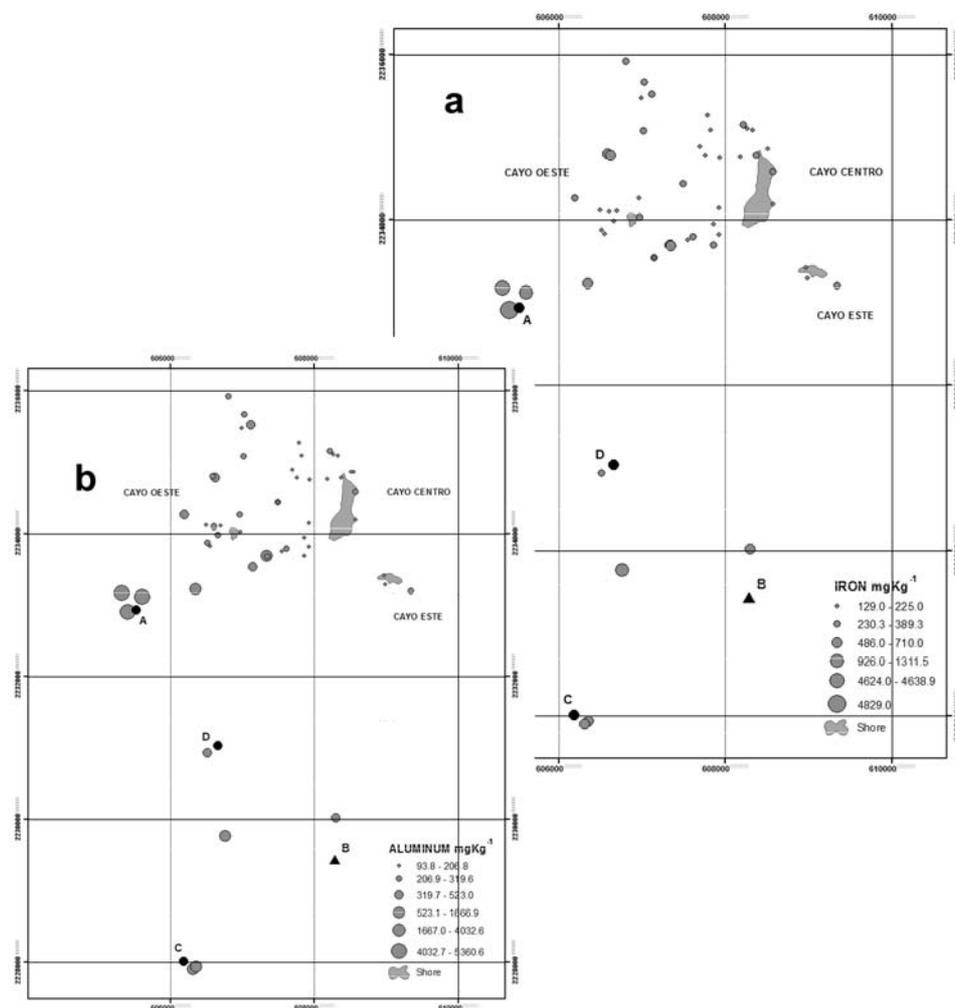


Figure 5. (a) Spatial distribution of iron in sediment samples from the Cayo Arcas coral reef, Campeche, Gulf of Mexico. (A, C, and D, monobuoys; B, marine oil terminal). (b) Spatial distribution of aluminum in sediment samples from the Cayo Arcas coral reef, Campeche, Gulf of Mexico.

Arcas crude oils, suggesting that the source of these contaminants was the crude oil produced in the Campeche Bank region.

Zn: A moderate proportion (62%) of the samples showed Zn concentrations very near to or below the detection limit ( $2 \text{ mg kg}^{-1}$ ), and these values were less than the baseline values reported by NOAA (1999) (7 to  $38 \text{ mg kg}^{-1}$ ; Figure 6). As with the rest of the metals, the highest concentrations were found near buoy A (20 to  $24 \text{ mg kg}^{-1}$ ). These values are less than the NOAA (1999) values ( $271$  and  $410 \text{ mg kg}^{-1}$ ) that are considered to be detrimental to the environment.

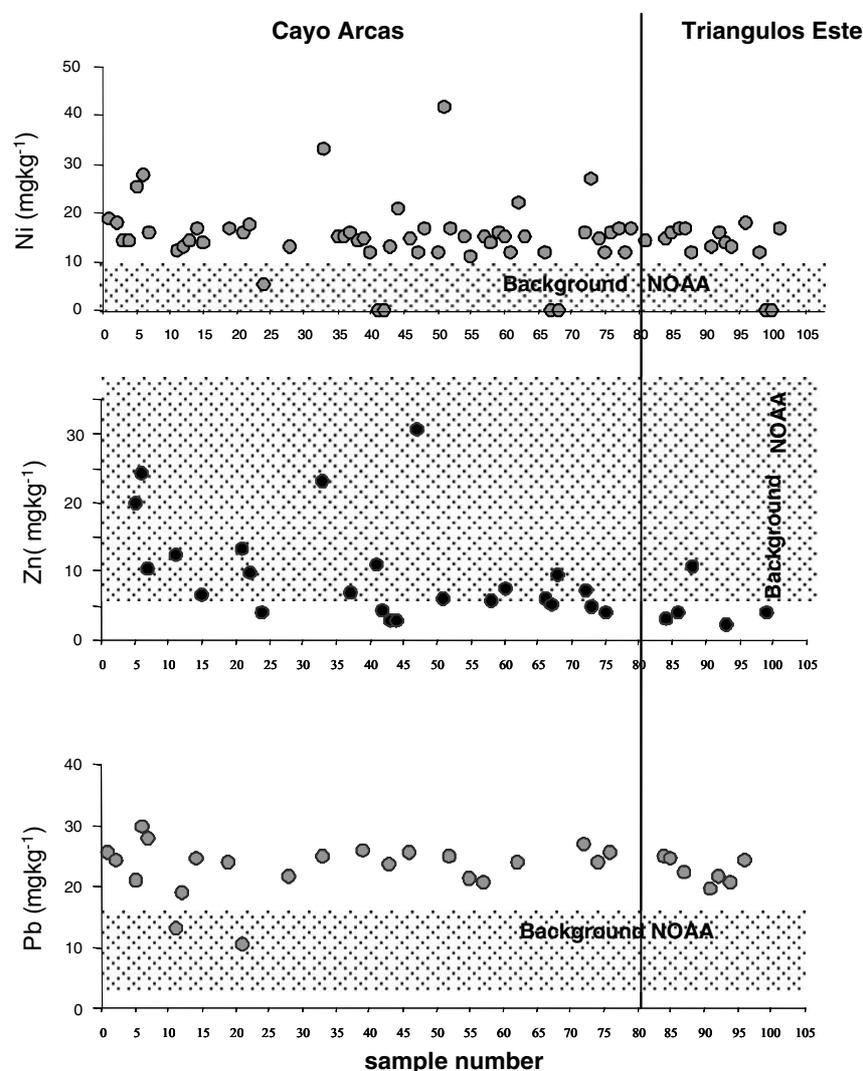


Figure 6. Nickel, zinc, and lead concentrations in sediments from the Cayo Arcas and Triángulos areas. The shaded area shows the background concentration for marine sediments reported by NOAA (Buchman, 1999).

Pb: The baseline value for Pb established by NOAA (1999) is between 4 and 17 mg kg<sup>-1</sup>, but the highest concentration found in the Triángulos area (which we took as the baseline value for our study) was 25 mg kg<sup>-1</sup>, which was higher than the NOAA (1999) value (Figure 6). Macias *et al.* (1999) reported an average Pb concentration of 4.3 mg kg<sup>-1</sup> for the southern Gulf of Mexico; in contrast, Vasquez *et al.* (2002) (Vasquez *et al.*, 2002) initially reported Pb concentrations between 67.3 and 263 mg kg<sup>-1</sup>, then in a more detailed study (Vasquez *et al.*, 2004) reported

TABLE I  
Suspended solids and metal concentrations in the ballast waters of oil tankers that loaded crude oil at the Cayo Arcas oil terminal (internal report of PEMEX 98–99)

|                  | Range (mg L <sup>-1</sup> ) | Mean (mg L <sup>-1</sup> ) | Monthly total* |
|------------------|-----------------------------|----------------------------|----------------|
| Suspended solids | 120–8                       | 70                         | 73.4 t         |
| Cd               | 0.01–0.05                   | 0.023                      | 24 kg          |
| Cu               | 0.02–1.0                    | 0.06                       | 62 kg          |
| Cr               | 0.01–0.37                   | 0.12                       | 125 kg         |
| Ni               | 0.04–9.3                    | 2.1                        | 2200 kg        |
| Pb               | 0.01–0.52                   | 0.17                       | 178 kg         |
| Zn               | 0.11–4.47                   | 0.56                       | 586 kg         |

\*The mean concentration was multiplied by the volume of ballast water in the oil tankers (the Cayo Arcas area receives a monthly average of 29 oil tankers, each with ca. 36 163 t of ballast; 1 t = 1000 L of ballast water).

a mean value of 11.1 mg kg<sup>-1</sup> for the same region. Therefore, no real consensus for the background concentrations of Pb has been made. The spatial distribution of Pb did not show a clear contribution of Pb from the monobuoys or platform terminal, with the exception of slightly higher concentrations (30 and 28 mg kg<sup>-1</sup>, respectively) found near monobuoy A and the platform terminal.

Some metals were found at high levels near the monobuoys and in the area of the Cayo Centro key. The internal PEMEX report 98-99 suggests that these metals originated in the ballast waters of the oil tankers (Table I). The table shows that the input of metals is large, especially for Ni and Zn (2200 and 586 kg per month, respectively). Therefore, ballast waters represent a considerable source of metal pollution, especially at sites where tankers dump their ballast waters and replace it with oil.

*3.1.3.2. Soluble Metals in Sediments.* To evaluate the presence of soluble metals in the sediments, we used the water samples with the highest concentrations of metals. None of these samples showed detectable levels of soluble metals.

## 3.2. CRUDE OIL AND DIESEL

### 3.2.1. Hydrocarbons

Figure 7 shows the aliphatic hydrocarbon profile for the two different crude oils for the diesel fuel from the ship. The ship's diesel fuel had the highest concentration of aliphatic hydrocarbons, dominated by nC8 to nC17, with nC10 most abundant. The aliphatic fraction of the Cayo Arcas crude oil had a homogeneous distribution of aliphatic hydrocarbons with low and high molecular weights, but with some dominance by the even-numbered n-C pairs from nC8 to nC36. The Cantarel crude oil had aliphatic hydrocarbons from n-C8 to n-C30, with n-C11 and n-C24 being

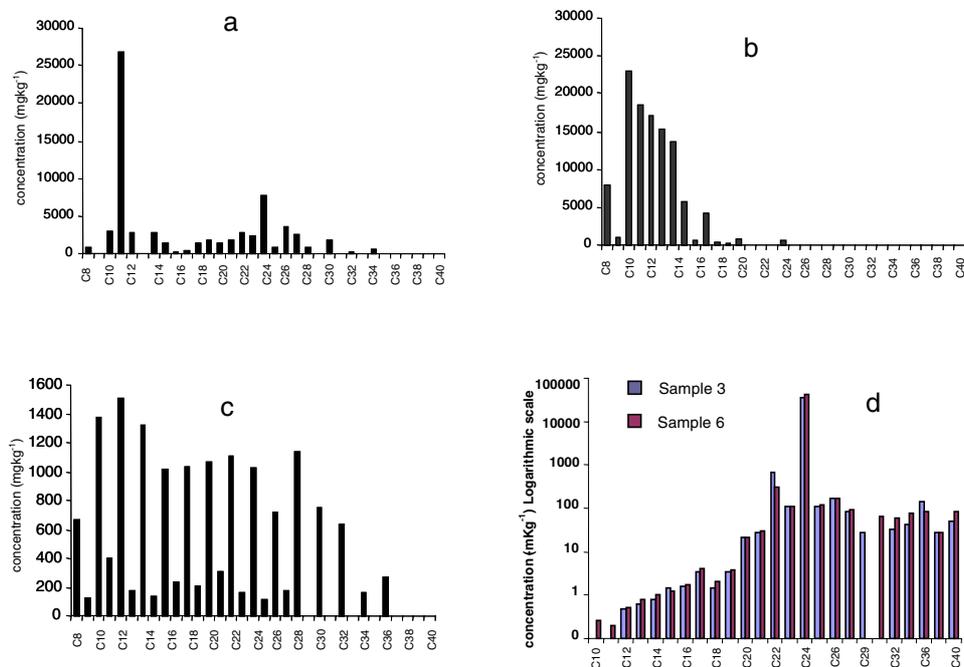


Figure 7. Aliphatic hydrocarbon profile for the (a) Cantarel crude oil, (b) diesel fuel from the ship, (c) Cayo Arcas crude oil, and (d) two seawater samples.

the dominant species. The values of the carbon preference index (CPI) were 0.60 for the Cayo Arcas crude oil, 0.57 for the Cantarel crude oil, and 0.75 for the ship's diesel fuel. We found no unresolved complex mixture (UCM).

Table II shows the PAH concentration for the two crude oils and the diesel fuel. The Cayo Arcas crude oil contained most of the individual PAHs that we measured (12), at concentrations ranging between 14 and 137 mg kg<sup>-1</sup> and with a total PAH concentration of 745.00 mg kg<sup>-1</sup>. The Cantarel crude oil PAH fraction contained only 8 of the compounds we detected, with anthracene, fluoranthene, and pyrene having the highest concentrations and with a total PAH concentration of 1001.57 mg kg<sup>-1</sup>. The diesel fuel's PAH fraction had the lowest number of individual PAHs (7), but the highest total PAH concentration (1772.07 mg kg<sup>-1</sup>).

### 3.2.2. Trace Elements

The only trace elements that we measured in these samples were V and Ni, since the relationship between these two elements can be used to trace the geochemical origin of a sample (Botello, 1995; Lewan, 1984). Any hydrocarbon contamination that has the same V-Ni relationship, i.e. V/(V + Ni), as a hypothetical source of contamination probably originated from that source.

The total V concentrations for the Cayo Arcas and Cantarel samples were 339 ± 10.6 and 462 ± 10.9 mg kg<sup>-1</sup>, respectively, versus values of 65.3 ± 2.0

TABLE II  
Concentrations of polycyclic aromatic hydrocarbons in the marine diesel fuel and crude oil samples

| Polycyclic aromatic hydrocarbon | Concentration (mg kg <sup>-1</sup> ) |                    |                           |
|---------------------------------|--------------------------------------|--------------------|---------------------------|
|                                 | Cayo Arcas crude oil                 | Cantarel crude oil | Diesel fuel from the ship |
| Naphthalene                     | 137.0                                | 39.28              | 208.62                    |
| Acenaphthylene                  | 52.0                                 | 72.58              | 593.51                    |
| Acenaphthene                    | 97.0                                 | 70.03              | 199.07                    |
| Fluorene                        | 81.0                                 | 107.75             | 454.39                    |
| Phenanthrene                    | 93.0                                 | 45.45              | 111.84                    |
| Anthracene                      | 121.0                                | 273.03             | 127.31                    |
| Flouranthene                    | 17.0                                 | 128.67             | 77.33                     |
| Pyrene                          | 50.0                                 | 264.78             | N.D.                      |
| Benzo(a)anthracene              | 50.0                                 | N.D.               | N.D.                      |
| Chrysene                        | 17.0                                 | N.D.               | N.D.                      |
| Benzo(b)fluorene                | 16.0                                 | N.D.               | N.D.                      |
| Benzo(k)fluorene                | 14.0                                 | N.D.               | N.D.                      |
| Benzo(a)pyrene                  | N.D.                                 | N.D.               | N.D.                      |
| Indene                          | N.D.                                 | N.D.               | N.D.                      |
| Dibenzo anthracene              | N.D.                                 | N.D.               | N.D.                      |
| Benzo(ghi)perylene              | N.D.                                 | N.D.               | N.D.                      |
| Total PAH                       | 745.00                               | 1001.57            | 1772.07                   |

N.D., not detected.

and  $75.5 \pm 2.4$  mg kg<sup>-1</sup>, respectively, for Ni (All values represent 95% confidence intervals) The V/(V + Ni) ratio equaled  $0.86 \pm 0.19$  for the Cayo Arcas crude oil and  $0.86 \pm 0.16$  for the Cantarel crude oil.

### 3.3. SEA WATER

#### 3.3.1. Physicochemical Characterization

The mean value of the physicochemical parameters of the sea water (Table III) showed only small variations between the two sampling areas, the reference site Triangulos and Cayo Arcas.

#### 3.3.2. Hydrocarbons

In general, the hydrocarbon concentrations in the water were low, except for one sample near buoy A in the Cayo Arcas area (sample 3) and an intermediate point along the transect between buoy A and south of Cayo Centro (sample 6). The hydrocarbon analysis of these samples (Figure 7d), showed that nC24 was the dominant species, that was also common in the Cantarel crude oil (produced in

TABLE III  
 Physicochemical characteristics of water samples from the coral reefs at Cayo Arcas and Triángulos, Gulf of Mexico

| Sample number | pH  | Temp. (°C) | Diss. O <sub>2</sub> (mg L <sup>-1</sup> ) | NO <sub>2</sub> <sup>-</sup> (mg L <sup>-1</sup> ) | NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> ) | PO <sub>4</sub> <sup>-3</sup> (mg L <sup>-1</sup> ) | Elec. cond. (mS cm <sup>-1</sup> ) | Suspended solids (g L <sup>-1</sup> ) | Silicates (meq L <sup>-1</sup> ) | CO <sub>3</sub> <sup>-</sup> (meq L <sup>-1</sup> ) |
|---------------|-----|------------|--|--|--|---|------------------------------------|---------------------------------------|----------------------------------|---|
| Cayos Arcas   |     |            |  |  |  |   |                                    |                                       |                                  |   |
| 3             | 8.5 | nd         | nd   | 0.011  | 0.7  | 0.18  | 52.2                               | 0.07                                  | 0.318                            | 2.50  |
| 6             | 8.5 | nd         | nd   | 0.008  | 0.9  | 0.15  | 52.6                               | 0.07                                  | 0.273                            | 2.50  |
| 7             | 8.6 | 29.3       | 6.4  | 0.012  | 0.6  | 0.17  | 52.9                               | 0.06                                  | 0.211                            | 2.50  |
| 15            | nd  | 29.3       | 7.4  | nd   | nd   | nd  | nd                                 | 0.06                                  | nd                               | nd  |
| 16            | nd  | 29.2       | 7.4  | nd   | nd   | nd  | nd                                 | 0.06                                  | nd                               | nd  |
| 17            | nd  | 29.3       | 7.3  | nd   | nd   | nd  | nd                                 | 0.06                                  | nd                               | nd  |
| 18            | nd  | 29.3       | 7.4  | nd   | nd   | nd  | nd                                 | 0.06                                  | nd                               | nd  |
| 19            | nd  | 29.3       | 6.6  | nd   | nd   | nd  | nd                                 | 0.06                                  | nd                               | nd  |
| 22            | 8.5 | 29.4       | 7.7  | 0.010  | 0.9  | 0.12  | 52.8                               | 0.07                                  | 0.428                            | 2.50  |
| 23            | 8.5 | nd         | nd   | 0.008  | 0.9  | 0.14  | 52.9                               | 0.06                                  | 0.393                            | 2.50  |
| 24            | 8.5 | nd         | nd   | 0.016  | 1.0  | 0.12  | 52.7                               | 0.07                                  | 0.857                            | 2.50  |
| 27            | nd  | 29.5       | 7.6  | nd   | nd   | nd  | nd                                 | 0.06                                  | nd                               | nd  |
| A 130         | 8.6 | 29.5       | 7.6  | 0.012  | 0.8  | 0.14  | 52.8                               | 0.07                                  | 0.420                            | 2.50  |

(Continued on next page)

TABLE III  
(Continued)

| Sample number  | pH  | Temp. (°C) | Diss. O <sub>2</sub> (mg L <sup>-1</sup> ) | NO <sub>2</sub> <sup>-</sup> (mg L <sup>-1</sup> ) | NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> ) | PO <sub>4</sub> <sup>-3</sup> (mg L <sup>-1</sup> ) | Elec. cond. (mS cm <sup>-1</sup> ) | Suspended solids (g L <sup>-1</sup> ) | Silicates (meq L <sup>-1</sup> ) | CO <sub>3</sub> <sup>-</sup> (meq L <sup>-1</sup> ) |
|----------------|-----|------------|--|--|--|---|------------------------------------|---------------------------------------|----------------------------------|---|
| 48             | 8.6 | nd         | nd   | 0.009  | 0.6  | 0.09  | 52.5                               | 0.06                                  | 0.313                            | 2.60  |
| 49             | 8.6 | nd         | nd   | 0.011  | 0.7  | 0.12  | 52.5                               | 0.06                                  | 0.216                            | 2.64  |
| 56 (surface)   | 8.7 | nd         | nd   | 0.008  | 1.0  | 0.08  | 53.5                               | 0.07                                  | 0.129                            | 2.50  |
| 56 (3-m depth) | 8.7 | nd         | nd   | 0.009  | 0.7  | 0.14  | 53.5                               | 0.07                                  | 0.832                            | 2.65  |
| 66             | 8.7 | nd         | nd   | 0.012  | 0.9  | 0.10  | 52.7                               | 0.06                                  | 0.362                            | 2.50  |
| Triangulos     |     |            |  |  |  |   |                                    |                                       |                                  |   |
| 80 (surface)   | 8.7 | 29.2       | 6.4  | 0.012  | 0.7  | 0.14  | 52.8                               | 0.07                                  | 0.674                            | 2.56  |
| 80 (3-m depth) | 8.7 | nd         | nd   | 0.011  | 1.0  | 0.10  | 52.6                               | 0.07                                  | 0.267                            | 2.62  |
| 89             | 8.7 | 30.0       | 6.6  | 0.008  | 0.7  | 0.07  | 52.6                               | 0.07                                  | 0.501                            | 2.50  |
| 90             | 8.7 | 29.8       | 6.6  | 0.010  | 0.9  | 0.09  | 52.7                               | 0.06                                  | 0.683                            | 2.60  |
| 95             | 8.7 | 29.5       | 6.6  | 0.010  | 1.0  | 0.18  | 52.8                               | 0.07                                  | 0.485                            | 2.59  |
| 97 (surface)   | 8.7 | 29.8       | 6.3  | 0.009  | 1.0  | 0.14  | 52.7                               | 0.07                                  | 0.525                            | 2.54  |
| 97 (3-m depth) | 8.7 | nd         | nd   | 0.010  | 1.0  | 0.06  | 52.9                               | 0.06                                  | 0.414                            | 2.50  |

nd: not determined.

the Sonda Campeche, in the Campeche Bank, Gulf of Mexico). The CPI for both samples was 0.53, which is close to the value for the Cantarel crude oil (CPI = 0.57). We detected no unresolved complex mixtures in any of the samples. The samples that contained detectable levels of PAHs had a concentration barely above  $10 \text{ mg kg}^{-1}$ , the detection limit of our method.

### 3.3.3. Trace Elements

The only trace element that we detected in the seawater was Ni, with concentrations ranging from 0.38 to  $0.42 \text{ mg L}^{-1}$  at all sample sites.

## 4. Discussion

### 4.1. SEDIMENTS

The high content of fine particles in certain sediments clearly indicates contamination caused by activities related to operation of the marine oil complex. According to an internal report from PEMEX 98-99, the contribution of solids and metals from ballast waters to the local seawater was considerable (73 t of sediments per month, versus up to 2.2 t of metals such as Ni). The high Al and Fe content in the sediments suggests the terrestrial origin of this contamination. Several studies have shown that ballast waters can contribute identifiable and measurable collections of pollutants (Anil *et al.*, 2002; Blanchard *et al.*, 2003; Goldberg, 1995) that have serious consequences for the ocean ecosystem. Therefore, the disposal of ballast waters should be examined more closely.

The sediment samples showed the same PAH profile as that of the Cantarel crude oil, with the exception of benzo(a)pyrene. This suggests that the origin of the PAHs in the sediment samples is the Cantarel crude oil, but no oil spills have been reported from the oil complex. On the other hand, the individual PAHs that we found are all parent compounds with a molecular weight  $> 178$ , and are thus classified as pyrolytic in origin. Thus, another possible explanation for their presence is that they resulted from combustion processes, (Mastral *et al.*, 2000) in which compounds with low molecular weight can combine into compounds with larger molecular weight, such as benzo(a)pyrene, by means of pyrosynthesis reactions. An additional indicator of pyrogenic processes is the dominance of PAHs with high molecular weight (4 to 6 rings) compared with the quantity of PAHs with low molecular weight (2 to 3 rings) (Wang *et al.*, 1999). The sediment samples showed a ratio of compounds with low molecular weight to those with high molecular weight between 0.00 and 0.03, which suggests dominance by the larger molecules; in contrast, the ratio for the Cayo Arcas and Cantarel crude oils was greater than 1, further supporting the hypothesis of pyrogenic origin. Pyrogenic PAHs may originate from ships and boats (tourists, fishermen, the Mexican navy, PEMEX ships, and oil tankers), which are continuously present in the area.

The total concentration of PAHs does not exceed the NOAA (1999) quality criterion of  $44 \text{ mg kg}^{-1}$ , although some individual PAHs do exceed their individual criterion level. That is the case for benz(a)anthracene, whose NOAA (1999) control value is  $1.60 \text{ mg kg}^{-1}$  (effects range median); nine samples had benzo(a)pyrene levels above the NOAA (1999) limit, and two of these levels were an order of magnitude larger. The locations of these samples (near coral reef sites visited frequently by tourists) again suggests a pyrogenic origin for the benz(a)anthracene.

Furthermore, the sample obtained near Cayo Este, where there are few waves and therefore a favorable route for ships traveling to the cay, we identified three PAHs (benz(a)anthracene, chrysene, and benzo(a)pyrene) whose concentrations exceeded the NOAA (1999) quality criteria.

Another possible explanation for the presence of benzo(a)pyrene is residual petroleum dumped into the ocean along with the ballast waters from the tankers. Hydrocarbon in sediments originated in ballast waters has been reported (Blanchard *et al.*, 2002).

The concentrations of Cu, Cr, V, Ni, Zn, and Pb were similar in both reefs for most sediment samples; the exceptions were higher levels at Cayo Arcas. In order to positively identify an anthropogenic contribution of the metals, it would be necessary to perform a more intensive study of the region.

The unusually high concentrations of Fe and Al could be attributed to terrestrial sediments dumped into the sea in the ship's ballast water during loading of oil at Cayo Arcas. These sediments are taken from the ship's port of origin, where they are present because rivers that end in the sea near the original port carry erosion sediments. These sediments are rich in Fe and Al silicates that are part of the terrestrial matrix, but not part of the matrix of the ocean sediments (Doherty *et al.*, 2001). We observed a reduction in the Fe and Al concentrations near monobuoy A, south of Cayo Centro, and north of Cayo Centro, that seem to reflect the influence of local sea currents. Sampling sites with a high percentage of fine-grained sediments showed a similar distribution pattern to the patterns for Fe and Al, and this supports the hypothesis that local currents may be responsible for spreading fine-grained sediments with high Fe and Al contents.

#### 4.2. SEA WATER

The values of the seawater's physicochemical parameters were all within the common ranges for the Gulf of Mexico (Lanza, 2001). The values for dissolved oxygen and suspended solids showed an oxygenated environment. The low nutrient content, stable and warm temperatures, and stable salinity were appropriate values for the development of a coral reef ecosystem (Souter *et al.*, 2000).

The sea water showed little significant contamination by hydrocarbons. The samples that did reveal hydrocarbon pollution were near monobuoy A and south of Cayo Centro. According to the aliphatic profile and the CPI values, this contamination probably originated from the Cantarel crude oil. Surface transport of

hydrocarbons by local winds over large distances in the Gulf of Mexico has been reported by Botello and co-workers (Botello *et al.*, 1995). Contamination of our samples by diesel fuel from the ship during sampling was ruled out because the profile of the hydrocarbons did not match that of the diesel fuel samples. The PAH concentrations in the samples was well below the values cited by NOAA (Buchman, 1999) as posing a concern for effects on living organisms ( $300 \text{ mg kg}^{-1}$ ).

The concentration of Ni exceeded the maximum permitted value; (Buchman, 1999) if these concentrations remain continuously high for more than 3 months, the Ni can become toxic to sensitive species. Nevertheless, these values resulted from one sampling of the surface waters, therefore the Ni values indicate a potential concern that should be monitored by means of further sampling.

Only two of our samples showed significant concentrations of Ni or of aliphatic and PAH compounds. The presence of these contaminants in seawater was generally detected near the oil station facilities, suggesting that any pollution of concern arises from the marine oil station's activities.

The effects of sub-lethal concentrations of oil pollution on coral reefs may not manifest themselves except over very long periods of time (Bak, 1987). In order to verify the adequacy of the environment for the development of coral reefs, sampling should be continued throughout a longer time period than that in the present study.

## 5. Conclusions

Our study revealed that the oil fueled by the oil compound in the study area could not be directly associated for the observed contamination, but that some contamination was related to the oil complex activities and could adversely affect the coral reef ecosystem. Ballast waters seem to be the primary source of these contaminants, and results from residual hydrocarbons in the oil tankers that mix with the ballast waters. In addition, the fine-grained sediments that probably originated in ballast water appear to have contributed to the high levels of anthropogenic metals such as Fe and Al in some areas. The high level of marine traffic in the region, which is related to both the activities of the oil station and other human uses of the Gulf of Mexico, is also a contributing factor. This traffic may be a large source of the hydrocarbon contamination.

The results of our study were obtained from a short sampling period, thus the data presented in this paper are not sufficient to definitively evaluate the possible effects on the study area's ecosystem. To provide the necessary data, a longer-term monitoring strategy must be implemented.

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