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# Temporal Variation of Persistent Organic Pollutant (POP) Residue Concentrations in Sediments from the Bay of Chetumal, Mexico

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**Abstract** Bay of Chetumal is a transboundary priority area for the Mesoamerican Barrier Reef Systems project, which has been studied because it is the receiving body of pollutants from a large agricultural area and the city of Chetumal. Levels of persistent organic pollutants in sediments from the Bay were assessed a few years after a mass mortality event of Mayan catfish (*Ariopsis assimilis*) occurred in 1996. Recent sediments were collected in the rainy season (1999) and dry season (2000); results show concentrations in general lower than those reported after the fish kill, and a change of chemical profiles in chemical pollution.

## Introduction

The Bay of Chetumal, a coastal system in the Yucatan Peninsula shared by Mexico and Belize, is a protected area designed to preserve the habitat of the West Indies manatee (*Trichechus manatus manatus*) (Lock, 1997) and is one of the priority transboundary areas for the Mesoamerican barrier reef ecosystems project, a program that coordinates the conservation efforts of four countries: Mexico, Belize, Guatemala and Honduras. A mass mortality event of Mayan catfish (*Ariopsis assimilis*) in 1996 in the Bay made evident the need to investigate the status of the area with regard to potentially toxic substances. Therefore, in the last decade, several efforts have been made to assess chemical pollution in the Bay, following from an environmental evaluation made in October 1996 to determine hydrocarbon and organochlorine residue concentrations in sediments (Noreña Barroso et al., 1998) and in catfish liver (Noreña Barroso et al., 2004), a study of the toxicity of sediments from the Bay (Zapata-Pérez et al., 2000), and community structure of benthic organisms and parasites in response to organic pollutant levels (Salazar-Silva, 1998; Vidal-Martínez et al., 2003). In order to compare the levels of organochlorine pesticides, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) with those found in 1996 and to investigate any temporal changes in contaminant loads, spatial distributions and geochemical signatures, recent sediment samples were collected in the two extreme climatic seasons (rainy and dry season) with the aim of establishing possible seasonal changes.

## Materials and Methods

The Bay of Chetumal is located in the Mexican state of Quintana Roo, between 18° 21′ and 18° 52′ N, and 87° 54′ and 88° 23′ W (Fig. 1). It is a shallow lagoon 67 km long and 20 km wide with a mean depth of 3.30 m. The bay is influenced by the city of Chetumal on the west side, the capital of the state with about 200,000 inhabitants in the urban area (INEGI 2001), the Hondo River that flows into the bay near to the city of Chetumal, and a 19 km opening to the southeast that connects the bay to the Caribbean Sea. Freshwater input to the Bay comes mainly from the Hondo River in the south of the system, which defines the border between Mexico and Belize, and is a major source of or-

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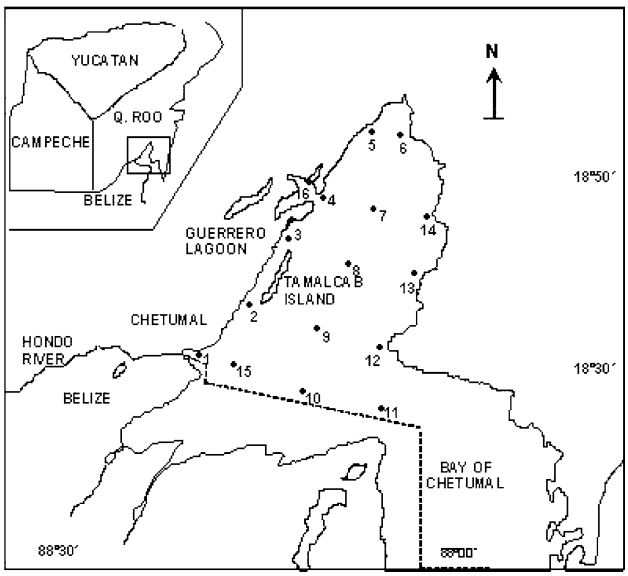


**Fig. 1** Location of the Bay of Chetumal and the sampling stations considered

ganic pollutants to the bay due to sugar cane and jalapeño pepper cultivation and processing, and wood extraction and preparation activities in its catchment area (Rojas and Morales, 2002).

Recent sediments were collected at 16 sampling stations in the Mexican part of the Bay of Chetumal (Fig. 1) during the extreme climate seasons for this area: the rainy season (August 1999), and the dry season (June 2000). Sediments were obtained using a 0.1 $m^2$ van Veen grab, frozen and transported to the laboratory for further analysis.

Levels of hydrocarbons and organochlorine compounds in the sediments were determined according to the procedures described in Sericano et al. (1990). Briefly, 30 g of freeze-dried sediments were extracted with hexane and methylene chloride. Extracts were concentrated and then fractionated by alumina-silica column chromatography and the aromatic fraction (containing chlorinated pesticides, PCBs and PAHs) was obtained by sequential elution. Analytes were separated and quantified by gas chromatography using a Hewlett Packard 5890 series II gas chromatograph equipped with a 30 m x 0.25 mm HP-5 capillary column and working in the splitless mode. Hydrocarbons were quantified with a flame ionization detector (FID) and organochlorine pesticides and PCBs with an electron capture detector (ECD). Individual compounds were identified and quantified using authentic standards from Ultra Scientific. Quality assurance of the analytical procedure included the addition of internal standards and the analysis of a procedural and a spiked blank for each set of samples. In addition, sediment grain size was determined by the Bouyoucos hydrometer method and the percentage of organic matter in each sample was measured using the Walkley and Black wet oxidation method (Franco et al., 1985). Non-parametric statistical procedures were run to evaluate differences in median values [Mann-Whitney *U* test and the Kruskal-Wallis analysis of variations (ANOVA)] and correlations (the Spearman rank test), using Statistica software (StatSoft, 1991).

## Results and Discussion

Levels of POPs found in sediments of the Bay of Chetumal for both climatic seasons are shown in Table 1. Twenty individual chlorinated pesticides were identified in recent sediment collected in the rainy and dry season. In the rainy season, total pesticides ranged from 0.45 to 39.82 ng $g^{-1}$, with a median concentration (± one interquartile range) of 4.84 ± 4.24 ng $g^{-1}$. For the dry season, levels found were lower, with a median of 2.47 ± 3.97 ng $g^{-1}$, a minimum of 1.55 ng $g^{-1}$ and a maximum of 12.10 ng $g^{-1}$. Hexachlorocyclohexanes (HCHs) was the group of pesticides with the highest concentration in the rainy season (0.80 ± 0.63 ng $g^{-1}$) and dichlorodiphenyltrichloroethane (DDT) and its metabolites were highest during the dry season (0.58 ± 0.38 ng $g^{-1}$). Statistical analysis showed no significant difference between seasons regarding either total pesticide content or any individual pesticide in the sediments.

There were fewer PCB congeners than chlorinated pesticides, 10 and nine compounds for the rainy and dry seasons, respectively. PCB concentrations were also lower than those of pesticides for both seasons. Total PCBs had a minimum of 0.37 ng $g^{-1}$ and a maximum of 2.17 ng $g^{-1}$, with a median of 0.82 ± 0.93 ng $g^{-1}$ during the rainy season, but they reached higher levels during the dry season, ranging from 0.74 to 4.26 ng $g^{-1}$, with a median value of 1.63 ± 1.59 ng $g^{-1}$ (Table 1). According to their degree of chlorination, in the rainy season PCBs with three chlorine atoms in their structure (TriCBs) were the highest with 0.75 ± 0.67 ng $g^{-1}$ and for the dry season four chlorine atoms in their structure (TetraCBs) had the highest level with 1.56 ± 0.89 ng $g^{-1}$. A Mann-Whitney *U* test showed statistically significant differences ($p$-value ≤ 0.05) in the levels of total PCBs, triCBs, tetraCBs and heptachlorinated biphenyls between seasons. Low-chlorinated congeners, such as those found in the bay in high concentrations, are more soluble in water and more biodegradable than high-chlorinated congeners (Nie et al., 2005). The lowest- and highest-chlorinated congeners (bi- and nona- and decachlorinated biphenyls, respectively) found in 1996 (21 individual analytes), were not present in the 1999-2000 sampling. Changes in PCB profiles could be due to a reduction of PCB sources to the bay.

Levels of chlorinated compounds in recent sediments of the Bay for both seasons are low if compared with other

**Table 1** Concentrations of persistent organic pollutants (POPs) in sediments from the Bay of Chetumal, Mexico

| Station | TCBs* ng/g | ΣHCHs* ng/g | Chlordanes* ng/g | Drins* ng/g | DDTs* ng/g | ΣPesticides† ng/g | ΣPCBs ng/g | ΣPAHs μg/g |
|---|---|---|---|---|---|---|---|---|
| Rainy season | | | | | | | | |
| 1 | n.d. | 1.55 | 0.09 | 0.03 | n.d. | 2.42 | 0.46 | 0.11 |
| 2 | n.d. | 0.14 | n.d. | n.d. | n.d. | 0.45 | 1.03 | 0.11 |
| 3 | 0.56 | 0.58 | n.d. | n.d. | n.d. | 2.70 | 1.94 | 0.19 |
| 4 | 0.61 | 0.71 | n.d. | n.d. | n.d. | 7.50 | 1.15 | 0.29 |
| 5 | 0.48 | 0.71 | n.d. | 0.05 | n.d. | 3.88 | 0.75 | 0.51 |
| 6 | 0.27 | 0.81 | 0.65 | n.d. | n.d. | 7.18 | 0.89 | 0.22 |
| 7 | 0.20 | 0.60 | 0.59 | n.d. | 0.59 | 4.30 | 0.40 | 0.08 |
| 8 | 0.18 | 1.88 | 0.35 | 0.01 | 0.14 | 5.54 | 1.78 | 0.22 |
| 9 | 2.20 | 4.47 | 6.39 | n.d. | 0.10 | 39.82 | 2.17 | 0.97 |
| 10 | 0.93 | 0.56 | 1.03 | n.d. | n.d. | 5.37 | 0.61 | 0.51 |
| 11 | n.d. | 0.93 | 0.00 | n.d. | n.d. | 7.67 | 1.48 | 0.44 |
| 12 | n.d. | 0.08 | 1.01 | n.d. | n.d. | 3.44 | 0.37 | 0.03 |
| 13 | n.d. | 0.79 | 0.31 | n.d. | n.d. | 2.76 | 0.57 | 0.43 |
| 14 | n.d. | 0.85 | 0.12 | 0.03 | n.d. | 4.27 | 0.52 | 0.28 |
| 15 | n.d. | 1.31 | 2.10 | 0.15 | n.d. | 9.73 | 1.47 | 0.10 |
| 16 | 0.01 | 1.14 | 0.89 | n.d. | n.d. | 6.08 | 0.59 | 0.08 |
| Median | 0.18 | 0.81 | 0.35 | 0.00 | 0.00 | 5.37 | 0.89 | 2.50 |
| IQ | 0.56 | 0.71 | 1.01 | 0.03 | 0.00 | 4.06 | 0.91 | 3.95 |
| Dry season | | | | | | | | |
| 1 | n.d. | 0.32 | 0.22 | 0.19 | 0.80 | 2.02 | 0.99 | 0.09 |
| 2 | n.d. | 0.31 | n.d. | n.d. | 0.58 | 1.64 | 2.52 | 1.04 |
| 3 | 1.18 | 0.42 | n.d. | n.d. | 1.04 | 6.21 | 2.90 | 0.97 |
| 4 | 0.07 | 0.23 | 0.12 | 0.16 | 0.58 | 2.76 | 1.64 | 0.91 |
| 5 | n.d. | 1.18 | n.d. | n.d. | 0.08 | 2.26 | 3.41 | 0.37 |
| 6 | 0.02 | 0.45 | n.d. | 0.09 | 0.77 | 2.44 | 2.73 | 0.92 |
| 7 | n.d. | 0.23 | n.d. | 0.18 | 0.81 | 1.82 | 3.72 | 0.20 |
| 8 | 0.04 | 0.26 | n.d. | 0.13 | 0.42 | 2.26 | 1.45 | 0.52 |
| 9 | 0.04 | 0.35 | n.d. | 0.11 | 0.65 | 2.50 | 1.81 | 0.40 |
| 10 | 0.84 | 0.26 | n.d. | 0.74 | 1.09 | 6.01 | 4.26 | 0.95 |
| 11 | 0.02 | 0.29 | n.d. | n.d. | 0.38 | 1.55 | 1.63 | 0.14 |
| 12 | n.d. | 0.58 | n.d. | n.d. | n.d. | 6.80 | 1.63 | 0.46 |
| 13 | n.d. | 0.94 | 0.11 | n.d. | n.d. | 5.83 | 0.74 | 0.07 |
| 14 | n.d. | 1.17 | 0.81 | 0.02 | 0.04 | 2.35 | 1.00 | 0.09 |
| 15 | n.d. | 0.63 | 0.10 | n.d. | n.d. | 6.73 | 0.92 | 0.04 |
| 16 | n.d. | 2.21 | 1.92 | n.d. | 0.55 | 12.10 | 1.63 | 0.14 |
| Median | 0.00 | 0.42 | 0.00 | 0.02 | 0.58 | 2.50 | 1.64 | 0.40 |
| IQ | 0.04 | 0.65 | 0.12 | 0.16 | 0.72 | 3.95 | 1.45 | 0.78 |

(n.d. = not detected)

* TCBs = 1,2,4,5-TCB + 1,2,3,4-TCB; HCHs = $\alpha$-HCH + $\beta$-HCH + $\gamma$-HCH + $\delta$-HCH; chlordanes = heptachlor + heptachlor epoxide + $\alpha$-chlordane + *Cis*-nonachlor; Drins = aldrin, dieldrin, endrin; DDTs = op-DDE + pp-DDE + op-DDT + pp-DDT

† ΣPesticides also includes endosulfan II, mirex, hexachlorobenzene, pentachloroanisole and pentachlorobenzene

studies. Median concentrations of total DDTs for the rainy and dry seasons (0.37 and 0.58 ng $g^{-1}$, respectively), total chlordanes (0.65 and 0.22 ng $g^{-1}$) and total PCBs (0.82 and 1.63 ng $g^{-1}$) are between one and three orders of magnitude lower than the unadjusted mean values reported by the national status and trends program for the northern Gulf of Mexico (O'Connor, 1990) of 3.2 ng $g^{-1}$ for chlordanes, 24 ng $g^{-1}$ for DDTs and 120 ng $g^{-1}$ for total PCBs. Moreover, concentrations of chlorinated compounds in the Bay are lower than the effects range-low (ERL) and effects range-

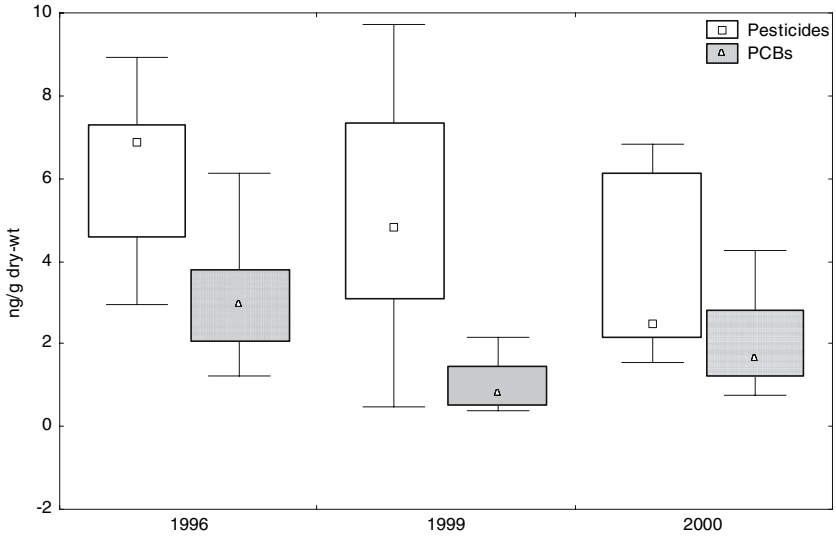


**Fig. 2** The temporal variation of chlorinated organic compound content of sediments from Bay of Chetumal, Mexico

median (ERM) reference values reported by the US National Oceanic and Atmospheric Administration (NOAA) (Buchman, 1999), so that chlorinated compounds in the sediments are not likely to cause deleterious biological effects.

The chlorinated organic compound content of the sediments of the Bay in this study were compared with the levels registered after the catfish mortality event in 1996 (Fig. 2). Pesticides show a decreasing pattern from 1996 to 2000 and statistically significant differences between years were observed by a Kruskal-Wallis ANOVA ($H = 9.32$; $p = 0.0095$). On the other hand, PCB concentrations decreased between 1996 and 1999, but increased again in 2000; significant differences between years were also observed ($H = 22.81$; $p = 0.0000$). A decrease in the levels of chlorinated pesticides is also reported in a study made by Álvarez (2002) with levels of total pesticides going from 52.66 ng $g^{-1}$ in 1996 to 7.12 ng $g^{-1}$ in 1999. The decreasing pattern of chlorinated pesticide concentrations in the sediments of the Bay could be due to changes in the products used as pesticides in agricultural activities. A study of non-point sources of agricultural pollution in the area made in 1999 (Euan-Ávila et al., 2002) shows that Endosulfan is the only chlorinated pesticide currently used for jalapeño pepper crops.

For PAHs, like PCBs, there was a reduction of more than 50% in individual analytes registered compared to those reported in the 1996 sampling. For the rainy season, total PAHs ranged from 0.03 μg $g^{-1}$ to 0.97 μg $g^{-1}$ (Table 1). During the dry season, PAHs showed some increase, with a median value of 0.39 ± 0.80 μg $g^{-1}$ and had a minimum of 0.04 μg $g^{-1}$ and a maximum of 1.04 μg $g^{-1}$. A Mann-Whitney *U* test showed statistically significant differences on the levels of three- and five-ring PAHs between seasons ($U = 21$, $p = 0.0372$; $U = 9$, $p = 0.0114$, respectively). As for chlorinated compounds, levels of PAHs are lower than those reported for other coastal systems in Mexico influenced by the oil industry, like the Carmen, Machona and Mecoacan lagoons in the state of Tabasco, with total PAHs values of 7.05 to 19.7, 2.57 to 36.1 and 3.92 to 18.5 μg $g^{-1}$, respectively (Gold-Bouchot et al., 1997). They are one order of magnitude lower than the mean concentration of 7.87 ± 7.66 μg $g^{-1}$ reported by Alvarez and Sáenz (2005) for sediments of the Bay of Chetumal in 1998. In addition, levels of PAHs for the rainy and dry seasons are low if compared with effects-based guideline values, such as the effects range-low (ERL) and effects range-median (ERM) values set by the national oceanic and atmospheric administration (NOAA) (Long et al., 1995). The highest total PAHs found in the sediments of the Bay for both seasons are much lower than the ERL value (4.02 μg $g^{-1}$), and thus biological effects caused by PAHs are not likely to occur.

For the rainy season, median concentration of low-molecular-weight (LMW) PAHs (Σ two- and three-ring compounds) was 0.10 ± 0.13 μg $g^{-1}$, and that of high-molecular-weight (HMW) PAHs (Σ four- and five-ring compounds) was 0.03 ± 0.33 μg $g^{-1}$. On the other hand, for the dry season median concentrations for low and high molecular weight PAHs were 0.24 ± 0.70 μg $g^{-1}$ and 0.08 ± 0.10 μg $g^{-1}$, respectively (Fig. 3). A Mann-Whitney *U* test indicated significant differences between LMW and HMW PAH concentration in the dry season ($Z = 2.22$; *p*-value = 0.02). Given that LMW PAHs had higher levels, the origin of PAHs in sediments collected during the dry season could be considered petrogenic. The results obtained in this study for both seasons are opposite to those reported in 1996, changing the origin signal of PAHs from pyrogenic with a clear predominance of HMW PAHs over LMW compounds (Noreña-Barroso et al., 1998), to petrogenic with higher proportions of LMW PAHs. Alvarez and Saénz

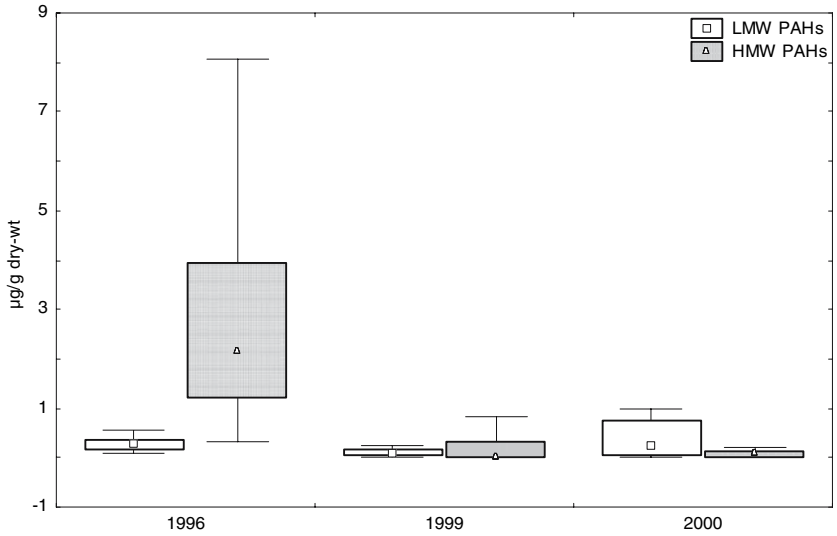


**Fig. 3** Temporal variation of low-molecular-weight (LMW) and high-molecular-weight (HMW) PAHs in sediments of the Bay of Chetumal, Mexico

(2005) also report a pyrogenic origin of PAHs detected in sediments collected in the bay in 1998. However, it is important to consider that it can be difficult to identify petrogenic sources of PAHs using PAH concentrations ratios alone, since PAH profiles are normally dominated by pyrogenic PAHs due to the chronic input of these compounds into the environment, and any petrogenic input may be masked. Also, weathering may alter PAH profiles.

Results of the study carried out in 1996 after the fish mortality indicated the presence in the Bay of Chetumal of many individual POPs that could represent a risk to the entire ecosystem. This evaluation, made a few years later, as well as other studies, suggests that concentrations of organic pollutants are decreasing; that is, the system is recovering and environmental management is effective in the bay. The decrease in POPs concentration in recent years supports the idea of a special set of conditions in the Bay of Chetumal in 1996 that led to an increase of contamination loads in the sediments.

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## References

Álvarez LMT (2002) Plaguicidas organoclorados en sedimentos de la Bahía de Chetumal y del río Hondo. Una revisión de los estudios realizados de 1993 a 1999. In: Rosado-May FJ, Romero R, de Jesús-Navarrete A (Eds.). Contribuciones de la ciencia al manejo costero integrado de la Bahía de Chetumal y su área de influencia. Universidad de Quintana Roo, México. pp 171–178

Álvarez LT, Sáenz MR (2005) Hidrocarburos aromáticos policíclicos en sedimentos de la Bahía de Chetumal. In: Vazquez-Botello A Gold-Bouchot G Rendón-Von Osten J (Eds). Golfo de México, Contaminación e Impacto Ambiental: Diagnóstico y Tendencias. Universidad Autónoma de Campeche, Campeche, México. pp. 299–310

Buchman MF (1999) NOAA Screening Quick Reference Tables, NOAA HAZMAT Report 99-1, Seattle WA, Coastal Protection and Restoration Division, National Oceanic and Atmospheric Administration, 12 pp

Euán-Ávila J, Liceaga-Correa MA, Rodríguez SH (2002) Caracterización de fuentes no puntuales de contaminación agrícola en el municipio de Othón P. Blanco en Quintana Roo, y su potencial influencia en la Bahía de Chetumal. In: Rosado-May FJ, Romero R, de Jesús-Navarrete A (Eds.). Contribuciones de la ciencia al manejo costero integrado de la Bahía de Chetumal y su área de influencia. Universidad de Quintana Roo, México. pp 197–204

García-Ríos V, Gold-Bouchot G (2003) Trace metals in sediments from Bahia de Chetumal, Mexico. Bull Environ Contam Toxicol 70:1228–1234

Gold-Bouchot G, Zavala-Coral M, Zapata-Pérez O, Ceja-Moreno V (1997) Hydrocarbon concentrations in oysters and recent sediments from three coastal lagoons in Tabasco, Mexico. Bull Environ Contam Toxicol 59:430–437

INEGI (2001) Tabulados Básicos Nacionales y por Entidad Federativa. Base de Datos y Tabulados de la Muestra Censal. XII Censo General de Población y Vivienda, 2000. Aguascalientes, Ags., México

Lock N (1997) Transboundary protected areas between Mexico and Belize. Coast Manage 25:445–454

Long ER, McDonald DD, Smith SL, Smith SL, Calder FD (1995) Incidence of adverse biological effects within range of chemical concentrations in marine and estuarine sediments. Environ Manage 1(19):81–97

Nie X, Lan C, Wei T, Yang Y (2005) Distribution of polychlorinated biphenyls in the water, sediment and fish from the Pearl River estuary, China. Mar Pollut Bull 50:537–546

Noreña-Barroso E, Zapata-Pérez O, Ceja-Moreno V, Gold-Bouchot G (1998) Hydrocarbon and organochlorine residue concentrations in sediments from Bay of Chetumal, Mexico. Bull Environ Contam Toxicol 61:80–87

Noreña-Barroso E, Simá-Álvarez R, Gold-Bouchot G, Zapata-Pérez O (2004) Persistent organic pollutants and histological lesions in Mayan catfish *Ariopsis assimilis* from the Bay of Chetumal, Mexico. Mar Pollut Bull 48:263–269

O'Connor TP (1990) Coastal environmental quality in the United States, 1990. Chemical contamination in sediment and tissues.

National Oceanic and Atmospheric Administration, Rockville, Maryland

Rojas MA, Morales VB (2002) Metales en hueso y sangre de manatíes (*Trichechus manatus manatus*) de la Bahía de Chetumal, Quintana Roo, México. In: Rosado-May FJ, Romero R, de Jesús-Navarrete A (eds.). Contribuciones de la ciencia al manejo costero integrado de la Bahía de Chetumal y su área de influencia. Universidad de Quintana Roo, México. pp 133–142

Salazar-Silva P (1998) Cambios en la estructura de la comunidad del macrobentos y su relación a contaminantes orgánicos de la Bahía de Chetumal, Quintana Roo, México. Tesis de Maestría en Biología Marina. CINVESTAV Unidad Mérida. Mérida, Mexico

Sericano JL, Atlas EL, Wade TL, Brooks JM (1990) NOAA's Status and Trends Mussel Watch Program: Chlorinated pesticides and PCBs in oysters (*Crassostrea virginica*) and sediments from the Gulf of Mexico, 1986–1987. Mar Environ Res 29:161–203

StatSoft, Inc. (1991) CSS:STATISTICA. Tulsa, Oklahoma, USA

Vidal-Martínez V, Aguirre-Macedo ML, Noreña-Barroso E, Gold-Bouchot G, Caballero-Pinzón PI (2003). Potential interactions between Metazoan parasites of the Mayan Catfish *Ariopsis assimilis* and chemical pollution in Chetumal Bay, Mexico. J Helminthol 77:173–184

Zapata-Pérez O, Simá-Álvarez R, Noreña-Barroso E, Güemes J, Gold-Bouchot G, Ortega A, Albores-Medina A (2000) Toxicity of sediments from Bahía de Chetumal, México, as assessed by hepatic EROD induction and histology in Nile tilapia *Oreochromis niloticus*. Mar Environ Res 50:385–391