Persistent organic pollutants in sediment cores of Laguna El Yucateco, Tabasco, Southeastern Gulf of Mexico

Contaminantes orgánicos persistentes en núcleos sedimentarios de la Laguna El Yucateco, Tabasco en el sureste del Golfo de México

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ABSTRACT

Information is presented on the content of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in sediment cores collected in the coastal ecosystem of Laguna El Yucateco, located in the tropical southeastern Gulf of Mexico. The ecosystem lies in a region where the human population is socially and economically limited, and it is subjected to great environmental pressure derived mainly from the oil industry. The vertical profiles data show that concentration of the various persistent organic pollutants (POPs) does not present a homogeneous pattern, making evident that the levels of these pollutants depend strongly on anthropological discharges from industrial, urban and farming sources, as well as on those originated by sanitary control measures for the prevention of tropical diseases such as malaria. Potentially carcinogenic compounds were found, including benzo(a)pyrene, aldrin and polychlorinated biphenyls congeners that have been classified as endocrine disruptors. The magnitude of the concentration of persistent organic pollutants is alarming, as values were above the sediment quality criteria established to prevent damage to benthic organisms. Coastal sediments also represent an environmentally risky secondary source of pollutants.

Key words: Carcinogenic compounds, industrial agricultural impact, POPs.

RESUMEN

Se presenta la información sobre el contenido de hidrocarburos aromáticos policíclicos, bifenilos policlorados y plaguicidas organoclorados en núcleos sedimentarios del sistema costero Laguna El Yucateco, localizado en el sureste tropical del Golfo de México, sometido a grandes presiones ambientales principalmente derivadas de la industria petrolera y con una población humana social y económicamente marginada. Los perfiles verticales, mostraron que las concentraciones de los diversos contaminantes orgánicos persistentes, no tuvieron un patrón homogéneo, evidenciando que los niveles de estos contaminantes están sujetos en gran medida, a las descargas antrópicas de fuentes industriales, urbanas, agropecuarias, así como las provenientes del control sanitario para la prevención de enfermedades tropicales como la malaria. Se encontraron compuestos con potencial carcinogénico como el benzo(a)pirene y el aldrín, así como congéneres de PCBs, catalogados como disruptores endocrinos. La magnitud de las concentraciones registradas de los COP’s evaluados, son una señal de alarma ya que fueron mayores a los criterios de calidad sedimentaria establecidos para evitar ocasionar daños a los organismos bentónicos. De igual forma, los sedimentos costeros representan una fuente secundaria de contaminantes de alto riesgo ambiental.

Palabras clave: Cancerígenos, impacto industrial y agropecuario.
INTRODUCTION

In order to evaluate pollution in the coastal area, it is vital to consider the historical behavior of the pollutants to better understand their origin, distribution patterns and temporal trends, as well as the complex interactions that may occur among them and the natural components of the ecosystem. Historical records are essential for the better management of polluting substances, as well as to make it possible to predict future trends in the polluting process, to establish effective measures to prevent habitat deterioration, and to look forward to have a cleaner environment (Boonyatumanond et al., 2007). Among persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs) are the most studied group in Mexico, mainly in the Gulf of Mexico, where oil industry has been present for 60 years. Reports exist on the level of PAHs in coastal lagoon water (Díaz-González et al., 1994), coastal and marine surface sediments (Botello et al., 1983, 1987, 1997, 2001; Sharma et al., 1997; García-Ruelas et al., 2004; Ponce et al., 2006), sediment cores (Calva et al., 2002) and benthic organisms (Gold-Bouchot et al., 1995b, 1997; Noreña et al., 1999; Botello et al., 2002). Data on molecular markers and isotopic records related to oil pollution were also published (Farrán et al., 1987). Concentrations of organochlorine pesticides (OCPs) have been reported in various coastal environmental matrices since the late 1970s. The present state of the ecosystems and the impact caused OCPs have been comprehensively discussed for the Gulf of Mexico coast (Rosales et al., 1979, 1985; Gold-Bouchot et al., 1993, 1995a; Botello et al., 1994; Albert, 1996; González-Farias, 2003; Díaz-González et al., 2005; Rendón-von Osten et al., 2005). Data on OCPs have also been gathered for commercially important species (mussels, oysters, shrimp and fish) of the Mexican Pacific (Gutiérrez-Galindo, 1983, 1984, 1988a,b, 1998; Galindo et al., 1996; Botello et al., 2000), water (Galindo et al., 1999; Hernández-Romero et al., 2004) and coastal sediments (Rueda et al., 1998; Galindo et al., 1999; González-Farias et al., 2002; Osuna-Flores & Riva, 2002; Leyva-Cardoso et al., 2003; Montes et al., 2011). Compared to PAHs and OCPs, polychlorinated biphenyls (PCBs) are less studied in Mexican ecosystems. A few coastal environmental evaluations included PCBs (Macías-Zamora et al., 2002; Páez-Osuna et al., 2002), but information for coastal sediment is limited (Calva et al., 2002, 2005; Lugo-Ibarra & Daesslé, 2010).

Sedimentary profiles may be used to estimate the historical deposit of POPs in coastal areas impacted by local and regional...
southern Mexico. The data were used to identify the principal origins, and to examine the relationships between pollutant concentration and sediment features like organic matter and ben
thic toxicity.

**MATERIALS AND METHODS**

The lagoon El Yucateco is located in the oil region of Tabasco, southeastern Gulf of Mexico, at 18°13'36" N and 94°10'36" W. It is one of the Mexican coastal ecosystems with more than 50 years of environmental perturbation that has resulted from oil industry and farming activities. This situation has caused a marked decrease in fishery catches, as well as the extinction of species. This lagoon has an area of 270 ha, and a water depth range of 1-5 m, (average 2 m). A considerable number of ducts were placed around the lagoon body and throughout the lagoon by Petróleos Mexicanos (PEMEX) in the 1950s, when exploration started in the "Cinco Presidentes" oil field.

The sites for core sampling were located in three areas: site A with a marked river influence, site B with estuarine conditions, and site C with a strong tidal effect. Four sediment cores were collected, two in 1998 (cores 98-1 and 98-2) and two in 2005 (cores 05-3 and 05-4) (Fig. 1 and Table 1). The cores were collected by scuba diving; the divers used manual acrylic tubes with 7 cm of diameter. The cores were frozen and transported. Later, their integrity was checked with X rays and they were sliced with a circular cutter. A total of 31 strata were obtained, including ten from core 98-1, nine from core 98-2, five from core 05-3 and seven from core 05-4, each 10 cm thick. The strata were unfrozen, dried at 45°C for 48 h, and sieved through a 250 µm mesh.

The samples were analyzed for the 16 priority PAHs (USEPA, 2009) following the method recommended by the UNEP/IOC/IAEA (1992) and used worldwide in marine pollution studies (Readman et al., 2002; Tolosa et al., 2004, 2009; Martins et al., 2005; Mzoughi et al., 2002, 2005; Darilmaz y Kucuksezgin, 2007; Mille et al., 2007; Kapsimalis et al., 2010). The PAHs were: naphthalene (NA), acenaphthylene (AC), acenaphthene (ACE), fluorene (FL), phenanthrene (PHE), anthracene (AN), fluoranthene (FLU), pyrene (PY), benzo(a)anthracene (BA), chrysene (CR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BP), indeno(1,2,3-cd)pyrene (IP), dibenzo(a,h)anthracene (DA) and benzo(g,h,i)perylene (BPE). ΣPAHs refers to the sum of the 16 PAHs. This method involves an organic extraction with n-hexane: methylene chloride 50:50 v/v, a saponification with methanol and KOH, a phase change to a non polar hexanic fraction, concentration of the extract, clean-up using a silica pack, aluminium oxide and anhydrous sodium sulphate, eluted with n-hexane 100% to obtain the aromatic fraction (PAHs). The samples were concentrated under a soft N2 current to dryness.

The PCBs determined as individual congeners were 28, 52, 101, 118, 138, 153 and 180; the total PCB concentration (ΣPCBs) was calculated from the sum of 7 major congeners mentioned. The OCPs included the HCH (alpha, beta, gamma and delta isomers), DDT and its metabolites (p,p′-DDT, p,p′-DDE and p,p′-DDD) and the cyclodiene group (heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, endrin aldehyde, endosulfan I, endosulfan II and endosulfan sulphate); the ΣOCPs was calculated from the sum of 16 organochlorine pesticides mentioned. The sediment samples were processed following the technique proposed by the UNEP/ IAEA (1982) reported in several studies (Hong et al., 1995; Morrison et al., 1996; Bakan & Ariman 2004; de Mora et al., 2010; Montes et al., 2011; Ramirez-Sandoval et al., 2011). It consists of extraction
with HPLC grade n-hexane, concentration of the organic extract, and cleanup by adsorption chromatography using Florisil and anhydrous sodium sulphate. The cleanup column was eluted with n-hexane 100% for the PCBs fraction, and using the mixtures n-hexane:ethylc ether 9:1 and 8:2 to obtain the OCPs. The final solution was concentrated with N$_2$ gas for GC analysis.

All analytes were quantified using a Hewlett–Packard 5890 series II gas chromatograph (GC) equipped with an HP-5 silica fused capillary column (30 m X 0.25 mm i.d. with 0.25 µm film thickness). A flame ionization detector (FID) and an electron capture detector (ECD) were used for PAHs and the organochlorine compounds, respectively. Quantification was carried out using the internal calibration method based on a five-point calibration curve for individual components.

Four perdeuterated PAHs (naphthalene-d$_8$, acenaphthene-d$_{10}$, phenanthrene-d$_{10}$ and chrysene-d$_{12}$) and 4,4-dichlorobiphenyl (DCB) were added to duplicate samples prior to extraction in order to quantify procedural recoveries. The percentage of recovery of PAHs and organochlorine compounds ranged from 85% to 105%. For each batch of 10 samples, a procedural blank, a spiked blank and reference standard material were processed (IAEA-417). The analytical blank contained no detectable amounts of target analytes. Detection limits (DLs) were 0.01 µg g$^{-1}$ for PAHs and 0.01 ng g$^{-1}$ for OCPs and PCBs. The DLs were calculated considering the average + 3S for each analyte after obtaining the chromatographic data of 15 injections of the lowest standard. All data are referred to dry weight.

Organic carbon determination was based on method of Gaudette et al. (1974) in which exothermic heating and oxidation with K$_2$CrO$_7$ and concentrated H$_2$SO$_4$ are followed by titration of the excess dichromate with 0.5N Fe(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O.

### RESULTS

The presence of organic matter (OM) is one of the environmental characteristics in coastal ecosystems that affect the accumulation of POPs in the sediments. The sediment from three of the four cores presented similar OM levels, with averages of 7.4 ± 3.5% (core 98-1, site A), 10.1 ± 3.4% (core 98-2, site B) and 9.8 ± 10.4% (core 05-4, site C) (Table 2). The high content of organic matter in core 05-3 from site A is notable, as it was three times greater than that in core 98-1 (23.4 ± 2.1%) from the same area.

#### PAHs. The average ΣPAHs in each core, the Pearson’s ($r$) correlation coefficient, as well as the significance ($p$) obtained from the relationship between ΣPAHs and the organic matter content are presented in Table 2. Only 98-2 and 05-4 cores showed a significant correlation between ΣPAHs and OM as a result of their

![Figure 2. Depth profiles of the ΣPAHs in the sediment cores.](image)
similar seasonal inputs to the lagoon ecosystem. For PAHs, core 98-1 has the greatest average with 3.25 µgg⁻¹, followed by core 05-4 with 1.10 µgg⁻¹. The other cores had lower averages, from 0.80 to 0.31 µgg⁻¹ for 98-2 and 05-3, respectively. In the 1998 cores, the general trend indicates that the upper layers, between 0 and 40 cm depth, had the greatest levels of ΣPAHs; exceptions were recorded for both cores of this year. In 98-1 the greatest value of 7.06 µgg⁻¹ was found in the deepest layer (90 cm) and in 98-2 this was recorded at a depth of 80 cm. In contrast, the 2005 cores presented a different pattern; for 05-3, the ΣPAHs was approximately one order of magnitude lower, and was detected only in three layers, in the two upper layers (0-20 cm) and in the deeper layer at 50 cm depth. For core 05-4 the aromatic hydrocarbon concentrations were higher at greater depths, particularly at 40 to 70 cm (Fig. 2).

Ratios of the principal mass 178, 202, 228 and 276 parent PAHs such as AN/(AN+PHE) to identify oil combustion, FLU/(FLU+PY) to identify oil combustion from other types of combustion, and BA/(BA+CR) and IP/IP+BPE to identify sources of combustion (Yunker et al., 2002; Arias et al., 2010; da Silva & Bicigo, 2010) (Table 3). Due to the low record of individual PAHs, it was only possible to calculate these ratios for some of the layers of the analyzed cores. Globally, for core 98-1 a dominant source from plant pyrolysis was obtained, in core 98-2 it was estimated only for layer 8 at 80 cm depth originated from plant pyrolysis, in core 05-3 they were estimated only in the first two layers. In the surface layer (0-10 cm) there was a mixture of sources, of the pyrolysis of fossil combustion and the burning of plant matter, and in the next layer (10-20 cm) the dominant footprint was that of the combustion of seagrasses, wood and carbon. In core 05-4 more compounds were detected, and the pattern obtained for the origin of the PAHs showed dominant plant combustion processes, with a lower contribution from oil combustion in the surface layer (0-10 cm), as well as from mixed sources in the 60 cm deep layer (Fig. 3). In order to complement this information on the main sources of the PAHs, the ratio LMW/HMW was used to indicate the relationship between the low molecular weight PAHs (≤ 3 rings) and those of high molecular weight (≥ 4 rings) (Ping et al., 2007; Arias et al., 2010; Sánchez-García et al., 2010). Practically all the strata of the sedimentary columns presented the same pattern. They indicated an old PAH contamination, with a dominance of high molecular weight hydrocarbons (≥ 202) that remain for longer in the environment, and have been reported to be generated by pyrolytic processes. The exception was core 98-1 at a depth of 90 cm with a LMW/HMW value of 7.1, which indicates a dominant source from oil, possibly produced by natural filtrations that are characteristic of the region (Table 3) (Tam et al., 2001; Yuam et al., 2001).

The most relevant PAHs recorded in these cores were benzo(k)fluoranthene, dibenzo(a,h)anthracene and benzo(g,h,i)-perylene. Low molecular weight compounds were also recorded, including acenaphthylene and acenaphthene of the petrogenic type (Table 4). Benzo(a)pyrene and dibenzo(a,h)anthracene were also detected, which were classified by the IARC (2010) as carcinogenic for humans (group 1) and probably carcinogenic (group 2A), respectively. Both had maximum concentrations up to one order of magnitude greater than the value established by the international criteria of sediment quality effects range-low (ERL), (Buchman, 2008), that gives an indication of the real risk of damage to the benthic community.

PCBs. PCBs were only recorded in the 2005 cores. The greatest concentrations of ΣPCBs were found in core 05-4 with maximum of 33.92 ngg⁻¹ at a depth of 30 cm and an average value of 13.28 ± 16.7 ngg⁻¹; the core 05-3 had average of 2.28 ± 3.7 ngg⁻¹ with maximum of 8.56 ngg⁻¹ at 20 cm; for the core 05-4, the first two strata were the only ones with biphenyl contents below the ERL. In contrast, strata 3 (20-30 cm), 4 (30-40 cm) and 5 (40-50 cm) of core 05-4 had concentrations of these compounds greater than the ERL (Table 5). The molecular profile of the congeners was also different among the studied cores. PCB52 and PCB101, with 4 and 5 molecular chlorines respectively, dominated in core 05-4, whereas in core 05-4 there was a greater abundance of PCB138, PCB153 and PCB180, with 6 or 7 chlorines in their chemical
structure, that were more persistent and lipophilic. Correlations between PCBs and organic matter to the cores of 2005 were not significant ($p>0.05$).

**OCPs.** Organochlorine pesticides were only analyzed in the 2005 cores, as well as the polychlorinated biphenyls. There were no significant correlations between OCPs and organic matter in spite of having complete data for the cores of 2005 ($p>0.05$). Averages values were $56.3 \pm 73.1$ ngg$^{-1}$ and $152.42 \pm 133.4$ ngg$^{-1}$ for the cores 05-3 and 05-4 respectively. In general terms, the $\Sigma$OCPs in core 05-4 was greater than those recorded in core 05-3, particu-

![PAH cross plots for the ratios of (a) AN/178 vs FLU/FLU+PY, (b) BA/228 vs FLU/FLU+PY and (c) IP/IP+BPE vs. FLU/FLU+PY.](image-url)

Figure 3. PAH cross plots for the ratios of (a) AN/178 vs FLU/FLU+PY, (b) BA/228 vs FLU/FLU+PY and (c) IP/IP+BPE vs. FLU/FLU+PY.
Table 4. Average concentrations of individual PAH compounds (± SD, maximum in µg g\(^{-1}\) dry wt) in sediment cores of El Yucateco lagoon and toxicity guideline.

<table>
<thead>
<tr>
<th>PAH compound</th>
<th>Abb’\’n</th>
<th>MW</th>
<th>98-1</th>
<th>98-2</th>
<th>05-3</th>
<th>05-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>NA</td>
<td>128</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>AC</td>
<td>152</td>
<td>0.14 ± 0.43 (1.36)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.02 ± 0.02 (0.05)</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>ACE</td>
<td>154</td>
<td>0.22 ± 0.71 (2.24)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Fluorene</td>
<td>FL</td>
<td>166</td>
<td>0.26 ± 0.82 (2.58)</td>
<td>&lt;0.01</td>
<td>0.01 ± 0.01 (0.03)</td>
<td>0.02 ± 0.02 (0.06)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>PHE</td>
<td>178</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.01 ± 0.03 (0.06)</td>
<td>0.02 ± 0.02 (0.06)</td>
</tr>
<tr>
<td>Anthracene</td>
<td>AN</td>
<td>178</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.03 ± 0.02 (0.07)</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>FLU</td>
<td>202</td>
<td>0.03 ± 0.09 (0.28)</td>
<td>0.02 ± 0.07 (0.22)</td>
<td>0.02 ± 0.03 (0.07)</td>
<td>0.13 ± 0.12 (0.34)</td>
</tr>
<tr>
<td>Pyrene</td>
<td>PY</td>
<td>202</td>
<td>0.05 ± 0.10 (0.24)</td>
<td>&lt;0.01</td>
<td>0.02 ± 0.05 (0.11)</td>
<td>0.11 ± 0.11 (0.31)</td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>BA</td>
<td>228</td>
<td>0.28 ± 0.37 (0.89)</td>
<td>0.05 ± 0.16 (0.47)</td>
<td>0.01 ± 0.03 (0.07)</td>
<td>0.03 ± 0.03 (0.07)</td>
</tr>
<tr>
<td>Chrysene</td>
<td>CR</td>
<td>228</td>
<td>0.35 ± 0.41 (1.06)</td>
<td>0.04 ± 0.12 (0.35)</td>
<td>0.03 ± 0.06 (0.13)</td>
<td>0.06 ± 0.05 (0.11)</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>BbF</td>
<td>252</td>
<td>0.48 ± 0.59 (1.89)</td>
<td>0.19 ± 0.24 (0.56)</td>
<td>0.02 ± 0.05 (0.12)</td>
<td>0.04 ± 0.03 (0.09)</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>BkF</td>
<td>252</td>
<td>0.25 ± 0.35 (0.97)</td>
<td>&lt;0.01</td>
<td>0.02 ± 0.03 (0.05)</td>
<td>0.29 ± 0.13 (0.44)</td>
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<tr>
<td>Benzo(a)pyrene</td>
<td>BP</td>
<td>252</td>
<td>0.32 ± 0.52 (1.13)</td>
<td>0.06 ± 0.19 (0.56)</td>
<td>0.04 ± 0.08 (0.18)</td>
<td>0.14 ± 0.04 (0.21)</td>
</tr>
<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
<td>IP</td>
<td>276</td>
<td>NA</td>
<td>0.07 ± 0.21 (0.67)</td>
<td>&lt;0.01</td>
<td>0.01 ± 0.02 (0.05)</td>
</tr>
<tr>
<td>Dibenz(o,h)anthracene</td>
<td>DA</td>
<td>278</td>
<td>0.61 ± 0.55 (1.45)</td>
<td>0.16 ± 0.32 (0.76)</td>
<td>0.08 ± 0.17 (0.38)</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Benzo(g,h,i)perylene</td>
<td>BPE</td>
<td>276</td>
<td>NA</td>
<td>0.21 ± 0.23 (0.53)</td>
<td>0.27 ± 0.35 (0.95)</td>
<td>0.05 ± 0.07 (0.15)</td>
</tr>
</tbody>
</table>

\*ERL effects range-low (Buchman, 2008); NA not available.

Table 5. PCBs content in the 2005 sediment cores of El Yucateco lagoon. Values in ng g\(^{-1}\) dry weight.

<table>
<thead>
<tr>
<th></th>
<th>CB28 (3 Cl)</th>
<th>CB52 (4 Cl)</th>
<th>CB101 (5 Cl)</th>
<th>CB118 (5 Cl)</th>
<th>CB138 (6 Cl)</th>
<th>CB153 (6 Cl)</th>
<th>CB180 (7 Cl)</th>
<th>ΣPCBs</th>
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<td>Core 05-3 Depth (cm)</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>0-10</td>
<td>&lt;0.01</td>
<td>1.75</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>1.07</td>
<td>&lt;0.01</td>
<td>2.82</td>
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<tr>
<td>10-20</td>
<td>1.61</td>
<td>2.69</td>
<td>2.56</td>
<td>1.70</td>
<td>&lt;0.01</td>
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<td>20-30</td>
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<tr>
<td>30-40</td>
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<td>&lt;0.01</td>
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<tr>
<td>40-50</td>
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<tr>
<td>Core 05-4 Depth (cm)</td>
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<tr>
<td>0-10</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
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<td>31.85</td>
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<td>40-50</td>
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ERL = 22.7 and ERM = 180.0 for ΣPCBs (Buchman, 2008)
larly at 30 and 40 cm deep (Fig. 4). Core 05-3 presented a low diversity of organochlorine pesticides, aldrin was the only compound detected throughout the sediment column. Heptachlor epoxide at 40 and 50 cm deep, lindane at 40 cm and \( \text{p,\text{-}}\text{DDT} \) in the deepest layer (50 cm) were also found. The molecular pattern in core 05-4 was different; the first three strata, from 0 to 30 cm presented a great variety of pesticides, of this layers, beta-HCH had the greatest concentration at 134.24 ng g\(^{-1}\); only in layer 4 (40 cm) lindane was found as the dominant compound at 1.95 ng g\(^{-1}\). Of the aromatic family of the organochlorine pesticides, there was more \( \text{DDT} \) than its metabolites; \( \text{p,\text{-}}\text{DDE} \) was detected at 40 cm only. Cyclodiene, endosulfan sulphate and heptachlor epoxide were the most relevant; the first one had the highest concentration of OCPs with 163.2 ng g\(^{-1}\). From the point of view of the intrinsic toxicity of the sediments in relation to the benthos, the OCPs group counts only with reference values such as the ERL (effects range-low) and the ERM (effects range-medium), for the \( \text{p,\text{-}}\text{DDT} \) (1.0-7.0 ng g\(^{-1}\)) and the dieldrin (0.02-8.0 ng g\(^{-1}\)) (Buchman, 2008). The concentrations obtained for the DDT were above these sedimentary quality guides, mainly at 30 and 40 cm in core 05-4, with 23.9 and 21.7 ng g\(^{-1}\) of this xenobiotic, which means there is a greater probability of causing damage to the benthos. In the case of dieldrin, this was detected only in core 05-4 at the surface (0-10 cm) at 2.65 ng g\(^{-1}\), and at 30 cm at 1.91 ng g\(^{-1}\). These concentrations were >ERL but <ERM, suggesting there is a lower probability of affecting the benthic community. Environmental monitoring is required because of the persistence, lipophylicity and synergism of these compounds.

**DISCUSSION**

The greater content of organic matter in the station A, detected in core 05-3, in comparison with the previous record of core 98-1, may have resulted from the accumulation of sediments over the past seven years, mainly due to the input of terrigenous material, principally from mangroves, and the increase in agricultural activities with the use of fertilizers that are transported by the Chicozapote river.

Sedimentation rates vary in agreement with the dynamics and the inputs from particular areas (Calva et al., 2002; Yim et al., 2005; Gong et al., 2007). Site B has the greatest rate as it is located in an area with little circulation and scarce river and tidal influence, which allows sedimentary accumulation. Comparatively, site A has an intermediate rate as there is a greater tidal influence and input from the Chicozapote river. Site C has the lowest rate due to the marked influence of the tide, the greater hydrodynamics and the geomorphology of the area (Gutiérrez & Galavíz, 1983; Calva et al., 2002).

Five-ringed PAHs dominated the three analyzed cores (43-57%) and four-ringed compounds were very important in core 05-4 (45.5%). In more detail, core 98-1 from the northern area (site A) presented polyaromatic groups with four and five rings in similar concentrations (0.28 and 0.33 \( \mu \)g g\(^{-1}\)), the two-ringed group had a lower level (0.15 \( \mu \)g g\(^{-1}\)) and the three-ringed group recorded levels at the detection limit (0.01 \( \mu \)g g\(^{-1}\)). Core 98-2 from site B presented five-ringed PAHs in greater abundance (53.3%) and thus, pyrolytic processes were the main origin of these hydrocarbons. However, the average concentration of this group

![Figure 4. Depth profiles of the \( \Sigma \)OCPs in the 2005 sediment cores.](http://example.com/figure4.png)
of hydrocarbons was lower than that recorded for core 98-1. In the cores 05-3 and 05-4, considering the rings, the average values of the PAHs decreased significantly by more than one order of magnitude; the pattern showed a predominance of combustion processes, particularly in core 05-3 with an abundance greater than 50%, while in core 05-4 four-ringed PAHs dominated with a 45% abundance. The molecular behavior indicates a clear presence of pyrolysis compounds in the region that are related to the burners of the oil company around the ecosystem which are transported by air and deposited in the lagoon. In addition, the petrogenic component is more evident in certain areas of the lagoon, as site A which had a 19% abundance of this group of hydrocarbons. This provides information on the natural filtrations that occur in the Gulf of Mexico, as well as on the accidental spills that have taken place since the start of the oil industry activities in Mexico. This vertical pattern of the PAHs has been described for the coastal lagoon of Sontecomapan on the coast of the Gulf of Mexico, considered a pristine area (Calva et al., 2002). Similarly, pyrolysis is the dominant process in the older sediments in Asian coastal environments (Boonyatumanond et al., 2007). The result is a mixture of pyrogenics and petrogenics in the most recent sediment strata, and provides evidence of the contribution made by internal combustion motors through vehicle emissions and combustion of plant material (Boonyatumanond et al., 2007; Arias et al., 2010). Ancestral agricultural practices such as chopping and burning, by which crop land is burned in between sowing and harvesting cycles, still take place in Mexican rural areas. These periodic activities, when carried out in areas of natural oil seeps, contribute to the production of high molecular weight PAHs that are dispersed and distributed to distant areas by air or rain. This is followed by the washing of higher altitude areas and transportation to the coast and sea, becoming one of the main sources in areas where no industry or city could be recognized as a source of emission of these compounds.

Site A receives permanent fluvial discharges that generate an estuarine-type mixed area, site B is a typically tropical lagoon area characterized by estuarine conditions and the presence of pumping stations that have remained from the oil operations that took place in the area during many years, and in site C the dominant effect is tidal and there is a greater amount of marine sediments.

About PCBs, these are the first data that are reported for vertical profiles collected in coastal ecosystems of the Gulf of Mexico. Core 05-4, collected from site C where both the tide and the Chicozapote river permanently renew the water, had the greatest average level of PCBs. Additionally, this area receives allochthonous materials and substances that are transported by the tides from the Tonalá river and the Gulf of Mexico, as well as from the adjacent crop lands where it is known that these residual oils are used as pesticides. In Mexico, the use of PCBs dates from the 1970s, when these industrial products were imported mainly from the United States, and later from Japan. Recently, the Mexican federal government published a document containing data on the national inventory of PCBs, as well as historical and legal aspects related to these POPs; approximately in the country in the 1995-2006 period, the ΣPCBs was 18,862.6 metric tons which location is unknown (SEMARNAT, 2007). Mexican legislation considers them as dangerous residues, nevertheless, there is no clear norm for their prohibition, restriction of use, management and final disposal, particularly for coastal areas. The data on the chlorinated compounds reported in this study make evident the historical industrial and human effects that have impacted the coastal ecosystems that receive these xenobiotics, mainly through fluvial runoff and transportation by air. The vertical pattern presented by the PCB congeners was different in the analyzed cores. Core 05-3 had most of its records at a depth of 20 cm, represented mainly by the less chlorinated molecules like tri-PCB 28 and tetra-PCB 52. The exception was hexa-PCB 153 that was detected only in the surface layer (0-10 cm). In contrast, core 05-4 showed a migration down to below the hexa and hepta-PCBs, which have a greater environmental persistence and were detected at 50 cm depth. Studies from the mid 1990s focused on researching the physicochemical characteristics of these organic semi-volatile compounds, and the environmental processes that influence their distribution, degradation and storage to explain their presence in ecosystems far from the sources, like the polar areas, and to contribute to the adequate management of this type of dangerous materials and their worldwide prohibition (Wania et al., 2006). Data on PCBs are available on the dominant molecular profile present in the diverse compartments of the planet. For example, in the atmosphere it has been estimated that the PCBs with a lower and higher degree of chlorination have not been transported great distances, as the first may be degraded efficiently, the heavy ones stick to atmospheric particles and are deposited at short distances, and only those that have an intermediate degree of coloration may remain in the atmosphere enough time to be transported greater distances (Shen et al., 2006). It has also been reported that, for a particular area, the input from rivers and the hydrodynamic conditions such as the currents, are more important sources of this group of pollutants than atmospheric deposits (Ricking et al., 2005). Also, the biological activity is very important; Giuliani et al (2011) reported that PCBs composition may change under aerobic and anaerobic conditions. In the first process, these compounds are converted to its constituent elements while in the second, common in the sediments, chlorine atoms are removed from highly chlorinated PCBs. Although, this mechanism is slow in natural environments (Borja et al., 2005; Sahu et al., 2009).

Similarly to PCBs, the concentrations of the organochlorine pesticides in the vertical profiles are the first records for this coastal ecosystem. The high levels of the individual OCPs and of
the ΣOCPs, as well as the greater detection of these chlorinated hydrocarbons in core 05-4, indicate a strong agricultural influence in this sediment profile. The inputs from the crop lands along the northern coastline and those transported by the tides are the most important in explaining the presence of these compounds in site C. However, the low diversity of these pesticides in the older strata also points to an allochthonous contribution of these persistent pollutants that may be transported by air to other latitudes. The presence of lindane (γ-HCH) in both cores was evaluated to determine its origin, whether from the technical mixture or the compound by itself (99% lindane). This, in Mexico, has had predominantly agricultural and domestic uses. In both cores, at 40 cm depth, this isomer presented a γ-HCH/ΣHCHs>0.5 ratio, which indicates that it was applied in its individual form (Doong et al., 2002; Gong et al., 2007). Likewise, in the first layers of core 05-4 (0-30 cm) and in the 50 cm layer, the beta-HCH presented the greatest concentrations of this group of pesticides with a ratio γ-HCH/ΣHCHs <0.5, indicating a recent use of Technical HCH, which is inexpensive and is available to the rural sector. The recent use of the pesticide p,p'-DDT (DDD+DDE/ΣDDTs < 0.5) is confirmed through its values in the cores of El Yucateco lagoon, in the southeastern Gulf of Mexico, particularly in core 05-4 of site C, where this metabolite was detected only in the 40 cm layer (Doong et al., 2002; Gong et al., 2007). Its presence in the study area reflects the combination of massive use in the past, and its current illegal use, since the Mexican law having classified it as restricted for exclusive use of the public health national agencies in the fight against malaria, a tropical disease that is still present in these areas of the Gulf of Mexico (CICOPLA FEST, 2008). Vertical migration processes may also influence this pattern, especially in environments with abundant organic matter. The effect of a great microbial community and interstitial pores that contribute to the selective transportation of this type of molecules towards sedimentary depths has to be considered (Boonyatumanond et al., 2007; Gong et al., 2007).

The vertical distribution of PAHs found in sediment cores from El Yucateco lagoon, clearly contrast with those reported for the PCBs and the OCPs. Both the oil industry activities and the natural contributions are reflected in the vertical sediment profiles of this group of hydrocarbons. The data also respond to the particular conditions in the study area, as an important variability in POPs levels was recorded along the cores, reflecting the environmental conditions and point-source human activities. The record of the OCPs provides data on the area, a region that has been agricultural since prehispanic times, after which this primary human activity combined with the industrial and oil development, as may be confirmed by the PCBs values recorded. Detected POPs such as benzo(a)pyrene, dibenz(a,h)anthracene and aldrin, represent an environmental risk, in view of the potential damage they can cause to the benthos and to human health when they are biomagnified through the trophic chain; also, have been studied for their carcinogenic properties and for acting as endocrine disruptors, moreover, their use is forbidden in most of the countries. The POPs concentrations recorded in this study provide a warning of environmental risk, in particular for biological damage to coastal species, and indicate that sediments represent a secondary source of ecotoxic pollutants.

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