

^{210}Pb -derived history of PAH and PCB accumulation in sediments of a tropical inner lagoon (Las Matas, Gulf of Mexico) near a major oil refinery

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Abstract

Concentrations of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were measured in a sediment core from the tropical freshwater inner lagoon of Las Matas, near the petroleum industrial area of Minatitlán-Coatzacoalcos, in the Gulf of Mexico. A ^{210}Pb -derived chronology was used to reconstruct the historical PAH and PCB accumulation in the site during one century (1906–2005). Both geochemical and sedimentological data indicated that a major change occurred in 1947 ± 4 , including a shift to coarser sediments and a significant decrease of Al, Li, Fe, organic C and total N contents. This was likely due to the changes in hydrology caused by the confinement of Las Matas Lagoon due to the construction of the Trans-Isthmus road in 1946. PAHs in these samples show relatively low concentrations ($259\text{--}1176 \text{ ng g}^{-1}$), and the congener relative abundances indicate the influence of pyrogenic (petroleum combustion) sources. Total PCB concentrations in the sediments ranged from 24 to 77 ng g^{-1} , and are composed by low chlorinated PCBs, with 3- and 4-CB as the prevalent species (51–65% and 29–40%, respectively). PAHs and PCBs were detected at depths corresponding to the early 1900s, when Minatitlán refinery started operations, although their time evolution appears to be influenced by different accumulation processes. The PCB background is most likely produced by the combustion of natural organic matter, and an industrial contribution can be recognized when normalizing with OC contents. We concluded that atmospheric deposition is the most significant source of PAHs and PCBs for this water body. This study also provided evidence of the alteration of the wetlands surrounding this industrial area due to urbanization; the fragmentation and alteration of Las Matas Lagoon hydrology contributes to the gradual loss of the wetlands in the zone.

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1. INTRODUCTION

Increasing habitat destruction and ecosystem alteration either by physical (e.g., landfills, urbanization, infrastructures, siltation, etc.), chemical (e.g., pollution) or biological means (e.g., the introduction of non-indigenous species) constitutes the most widespread, frequently irreversible, human impact on the coastal zone. Poorly planned urban and industrial growth (residential development as well as building of roads, utility rights of way and large recreational facilities) have significantly reduced the areas previously covered by dunes, mangroves and wetlands. Additionally, these fragile ecosystems have been often used as dumping sites either for urban or industrial wastes, and have been extensively damaged by the discharges of sewage and chemical compounds such as nutrients, metals (e.g., Hg, Cd, Sn and Cu), persistent organic pollutants and petroleum hydrocarbons (GESAMP, 2001).

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are ubiquitous and persistent compounds that can be found in various environmental media, and are considered as dangerous chemicals because of their potential effects on both biota and human beings. PAHs are originated by combustion of fossil fuels, waste incineration and oil spills (e.g., Lake et al., 1979; Neff, 1979; Law, 1994; Savinov et al., 2000); 16 of them are considered by the USEPA as priority micropollutants (USEPA, 1982) because they are known to have mutagenic and carcinogenic properties (e.g., Conney, 1982; Connel et al., 1997).

PCBs were discovered in 1865 as a by-product of coal tar, first synthesized in 1881 (Myers, 2007) and industrially produced since the 1930s in large amounts, primarily used as dielectric fluids in electrical transformers and capacitors, and also in carbonless copy papers and inks (Harrison, 2001). PCBs releases into the environment include improper disposal, leakage, incineration and volatilization (Rappe, 1993); they do not easily break down and can bioaccumulate in the fatty tissues of fish and mammals. The production of PCBs was banned in the United States since 1976 under the Toxic Substance Control Act, but they are still of major concern due to the multiplicity of sources and transport mechanisms (Hutzinger et al., 1974; Atlas et al., 1986; Lakshmanana et al., 2010). However, little is known about PCB pollution of tropical environments and, although the tropics contribute to the global PCB contamination (Wilcke et al., 1999), data on Mexican aquatic systems are surprisingly scarce.

In aquatic ecosystems PAHs and PCBs partition preferentially to sediments because of their hydrophobicity. Therefore, sediments might act as recorders of the contaminant inputs as well as of other environmental changes over time (e.g., Kannan et al., 2005; Sanchez-Cabeza and Druffel, 2009), provide useful information to understand the cycling of toxic chemicals in aquatic ecosystems and allow assessing the effectiveness of environmental legislations to reduce the impact of anthropogenic activities.

The industrial corridor of Cosoleacaque–Minatitlán–Coatzacoalcos (Gulf of Mexico) is one of the major petrochemical production areas of Mexico that hosts around 65 petrochemical plants, including the oil refinery “Lázaro-

Cárdenas”, which is the oldest facility of the six Mexican refineries. It is located along the margins of the lower reaches of Coatzacoalcos River, which flows into the Gulf of Mexico and serves as the main transportation channel for crude oil and refined products. The river and its associated wetlands have served as repository of wastes since the establishment of the oil refinery in 1906. Huge areas of the swamps located between the cities of Minatitlán and Coatzacoalcos have been massively burned and infilled to build roads, to serve as open dumping grounds, to support new urban settlements and, currently, to support the expansion of the old refinery.

Previous studies showed that the Coatzacoalcos River and wetlands surrounding the industrial area are contaminated by trace metals and hydrocarbons due to the discharges of untreated wastes and oil spills (Páez-Osuna et al., 1986; Vazquez et al., 1991; Rosales-Hoz and Carranza-Edwards, 1998). More recently, high levels of PCBs and other persistent organic compounds were detected in chicken eggs collected in the vicinity of the study area, suggesting atmospheric dispersion of these pollutants from waste incinerators (Bozada Robles and Bejarano González, 2006). The area has been recognized as a critical zone for ecologic regulation and environment protection by the Mexican Government since early 1990s (SEMARNAT, 1993, 2005).

The objective of this study was to reconstruct the history of organic pollution in Las Matas Lagoon, a small freshwater wetland close to the most important petrochemical industrial area of Mexico, recorded in a ^{210}Pb -dated sediment core collected in the lagoon. Results were expected to improve the knowledge on temporal trends, congener distribution and deposition fluxes of PAHs and PCBs in tropical areas, and contribute to understand the relative importance of the potential sources (e.g., atmospheric deposition, biomass burning and river runoff).

2. STUDY AREA

Las Matas is a shallow fresh water lagoon (1.5 m maximum depth) located in the South of Veracruz State (Gulf of Mexico coast, Isthmus of Tehuantepec). It is part of the lower basin water bodies of the Coatzacoalcos River system and is one of the small remnants ($\sim 0.3 \text{ km}^2$) of an ancient wetland, currently integrated by $\sim 200 \text{ km}^2$ of swamps. Fig. 1 compares the extension of the lagoon in 1970s and in the present (PEMEX, 1991). The drying out process was initiated by the fragmentation and confinement of Las Matas Lagoon, due to the construction of the Trans-Isthmus road, which interrupted the water exchange between the lagoon and the Calzadas River by the end of 1940s.

The lagoon sustains a small scale fishery of tilapia (*Chichlasoma urophthalmus*) and prawns (*Macrobrachium* sp.) and has abundant free floating weeds (genera *Pistia*, *Lemna*, *Pontederia* and *Eichhornia*; PEMEX, 1991). It is surrounded by the industrial area of Minatitlán–Coatzacoalcos–Cosoleacaque considered to be one of the most industrialized and polluted areas of Mexico (GEV, 2005).

According to the Köppen classification (modified by García, 1981) the weather in the area is a Amw^{v} (i) type (warm humid with abundant rain in summer). The area receives high rainfall along the year (up to 520 mm per

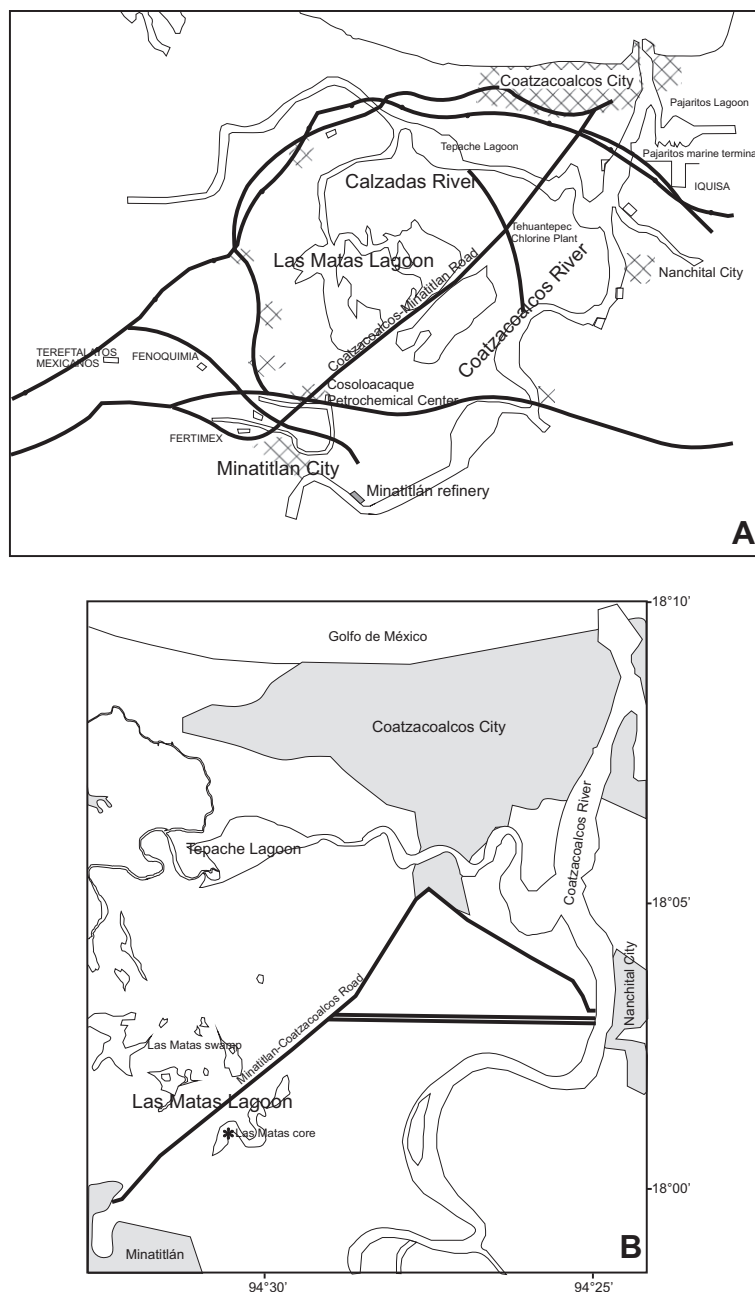


Fig. 1. Study area (A) in the 1970s, and (B) at present, including the sampling location.

month, between September and October) and the temperature typically ranges from 12 °C in January to 41 °C in June. Wildfires are frequent events in the surroundings of Las Matas wetland, being mostly anthropogenically triggered, in conjunction with the seasonal “Suradas” (warm, dry winds coming from the South).

3. MATERIALS AND METHODS

3.1. Sampling

Las Matas sediment core was collected in September 2005 at 1 m depth (18° 02.42' N and 94° 30.52' W) by man-

ually inserting a sharpened acrylic liner (8 cm inner diameter) into the sediment. Neither laminations nor evidences of sediment disturbance (sediment cracks, gas bubbles, infaunal burrows) were observed. The sediment core was extruded and subsampled at 1 cm intervals.

3.2. Preparation of samples

Sediment samples were frozen and freeze-dried before the analyses; wet and dry weight were recorded for calculation of porosities and dry bulk densities according to Berner (1971), assuming a particle density of 2.55 g cm⁻³. Dry sediment samples (except those for grain size analysis)

were ground by using an agatha mortar and pestle (except those for grain size analysis) and ground samples were stored in polyethylene bags until analysis.

3.3. Laboratory analysis

Particle-size analyses were performed by the X-ray attenuation method (Sedigraph). Samples for magnetic susceptibility were collected using 1 cm⁻³ polythene vials and were measured with a Bartington MS2G sensor.

The carbonate content (as CaCO₃) was determined by treating the sediments with 1 M HCl, and the excess of acid was quantified by back-titration with 0.5 M NaOH using phenolphthalein as an indicator (Rauret et al., 1988). For organic carbon (C_{org}) analyses, sediment samples were oxidized with a mixture of K₂Cr₂O₇ + Ag₂SO₄ + H₂SO₄ and the excess was back-titrated with Fe(NH₄)₂(SO₄)₂ (El Rayis, 1985). Precision was 4% for the determination of CaCO₃ and C_{org} contents. Selected samples were analysed for organic carbon (OC), total nitrogen (TN) and δ¹³C with a CHN-MS analyser.

Metal analyses were performed by atomic absorption spectrophotometry (Al, Fe and Mn by flame, and Li by graphite furnace). Aliquots of 0.25 g of dried, ground and homogenized sediments were transferred into Savillex™ PFA vessels (100 mL) and digested in a mixture of 5:4:1 HNO₃ + HCl + HF on a hot plate (150–180 °C) overnight. Solutions were then transferred into polypropylene tubes containing 5 g of boric acid and diluted to 50 cm³ with water Milli-Q. Accuracy and precision of metal analyses were evaluated through six replicates of the certified reference material IAEA-356 (except for Li). Metal recovery ranged from 90% to 110% and the uncertainties of the metal concentration values were 7% for Al and Fe, and 10% for Mn. A few duplicate analyses of samples indicated a precision of 5% for Li.

²¹⁰Pb activities were obtained by measuring its daughter product ²¹⁰Po assuming secular equilibrium between the two isotopes (Schell and Nevissi, 1983; Sanchez-Cabeza et al., 1998). Aliquots of 0.3 g of sediments were spiked with ²⁰⁹Po as yield tracer, and were digested in Saville PFA containers, in a 5:4:1 mixture of HNO₃ + HCl + HF on a hot plate (150–180 °C) overnight. The residue was converted to a chloride salt by repeated evaporation with 12 M HCl, then dissolved in 0.5 M HCl with 2.5 g of H₃BO₄, and 0.2 g of ascorbic acid were added to the solution. Po isotopes were deposited on a spinning Ag disc (Hamilton and Smith, 1986) and the activity measured by α-spectrometry using ORTEC silicon surface barrier detectors coupled to a PC running under Maestro™ data acquisition software. Blanks were run in parallel to correct for any contamination.

¹³⁷Cs (661.7 keV), and ²²⁶Ra were measured by γ-ray spectrometry in a HPGe well-detector at GEOTOP-University of Quebec in Montreal. Samples were stored in sealed glass vials (8 × 40 mm, 1 mL capacity) for 21 days and counted for a minimum of 48 h to obtain an uncertainty <10%. ²²⁶Ra was determined through its decay chain descendants ²¹⁴Pb (241.9, 295.2 and 351.9 keV) and ²¹⁴Bi (609.3 keV), assuming secular equilibrium.

Replicate analyses (*n* = 12) of the standard reference material IAEA-300 (Radionuclides in Baltic Sea sediment) confirmed good agreement for ²¹⁰Pb and ¹³⁷Cs values (within the reported confidence intervals). Accuracy and precision of the ²¹⁰Po method were 99% and 4.6%, respectively. Uncertainty for ²¹⁰Pb data, estimated through quadratic uncertainty propagation, was less than 7% in all cases.

PAHs analysis included the 16 USEPA priority congeners (based on their potential to cause cancer in animals and humans): naphthalene (Na), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (An), fluoranthene (Flt), pyrene (Py), benzo(a)anthracene (BaAn), chrysene (Ch), benzo(b)fluoranthene (BbFlt), benzo(k)fluoranthene (BkFlt), benzo(a)pyrene (BaPy), benzo(g,h,i)perylene (BgHiPe), indeno(1,2,3-cd)pyrene (Ipy), dibenzo(a,h)anthracene (DahAn). Perylene (Pe) and benzo(e)pyrene (BePy) were also determined. PAHs were extracted from ~ 2 g of freeze-dried sediment by means of accelerate solvent extraction (DIONEX ASE 200) using hexane/acetone (80:20 v/v). For quantification, a solution of six deuterated PAHs (Ace d-10; Flt d-10; Phe d-10; BaAn d-12; BaPy d-12; DahAn d-12) was added as internal standards to the samples before extraction. The extracts, dissolved in cyclohexane, were purified by column chromatography using solid phase extraction cartridges containing 2 g silica, eluted first with 10 ml of *n*-hexane and then with 20 ml cyclohexane:acetone (70:30). The final extracts were concentrated and re-dissolved with 400 μl of two deuterated PAHs (acenaphthylene d-8 and chrysene d-12) and finally analysed by GC-MS. The injection volume was 1 μL in splitless mode. The mass spectrometer was operated at electron impact (EI) of 70 eV in selective ion monitoring (SIM) mode. Laboratory quality control procedures included analyses of blanks, a reference material (BCR 535 Standard Reference Material) and spiked samples. Instrument stability and response was checked using NIST standard solutions. Reference material concentrations were in the reported confidence intervals. Estimated recoveries for each analyte ranged between 94–107% for PAHs and the estimated accuracy was better than ±7% for each single congener. Repeatability, based on six analyses of the reference material and four triplicate samples was ~10% for the sum of congeners, and ranged 7–21% for the single homologues. The detection limit was estimated <3 ng g⁻¹ for each PAH. Total PAHs is the sum of the 16 USEPA priority congeners. Low molecular weight PAHs (LMW) included Ace, Acy, An, Fl, Na and Phe, and the high molecular weight (HMW) included Flt, Py, BaAn, Ch, BbFlt, BkFlt, BaPy, Ipy and DahAn.

PCBs were extracted from 0.5 to 2.0 g of dry sediment with a Pressure Solvent Extractor (PSE one®, Applied Separations, LabService Analytica). The clean-up procedure was performed with a Power-Prep™ System (Dioxin Prep, Fluid Management System Inc., LabService Analytica) using a column of neutral silica and elution with *n*-hexane and then *n*-hexane/dichloromethane (1:1 v/v). PCBs were determined by High Resolution Gas Chromatography–Low Resolution Mass Spectrometry (HRGC–LRMS) with a Hewlett Packard Gas-chromatograph (Model 6890)

coupled with a Hewlett Packard Mass Selective Detector (model 5973; quadrupole mass analyzer). The analytical details are described elsewhere (Moret et al., 2001; Piazza et al., 2008).

For quantification, six ^{13}C labeled PCBs (EC-4058 mixture, Cambridge Isotope Laboratories, Andover, Massachusetts, USA) were added to the samples as internal standards before extraction. Namely, ^{13}C -PCB28 was used for the quantification of 1-CB, 2-CB- and 3-CB congeners, ^{13}C -PCB52 for the 4-CBs, ^{13}C -PCB101 for the 5-CBs, ^{13}C -PCB153 for the 6-CBs, and ^{13}C -PCB180 for 7- and 8-CBs. Rough concentration values were corrected with congener-specific instrumental response factors obtained by measuring four PCB standard solutions (C-CS01, C-CS02, C-CS03 and C-CS05 by AccuStandard Inc., New Haven, USA), for a total of 122 congeners.

Only those peaks with heights equivalent to at least three times the background value were considered for identification and subsequent quantification. GC-MS detection limits were 1 pg for all congeners, whereas at 0.6 pg level, 80% of them were detectable. Thirty-six chromatographic peaks, with reference to 49 PCB congeners (25 as single congeners) were analysed: 11 trichlorobiphenyls (PCBs 18, 17, 16 + 32, 26, 25, 28 + 31, 20 + 33, 22), 17 tetrachlorobiphenyls (PCBs 52, 49, 47 + 48, 44, 42 + 59, 41 + 64 + 71, 40, 74, 70, 66, 56 + 60, 77), 14 pentachlorobiphenyls (PCBs 93 + 95, 91, 84 + 90 + 101, 99, 97, 87 + 115, 85, 110, 118, 105), 6 hexachlorobiphenyls (PCBs 136, 151, 149, 153, 138 + 164), and one heptachlorobiphenyl (PCB 176).

Accuracy was checked at the time of analysis using a reference material (NIST, Standard Reference Material SRM[®]1941b) and the observed concentrations were in the 95% confidence intervals reported. Repeatability, based on two analyses of the same reference material ranged in the interval 0–9% for the single congeners, and was 4% for their sum.

4. RESULTS AND DISCUSSION

4.1. Sediment characterization

Most geochemical analyses (Fig. 2A–L) showed that Las Matas sediment core was composed of two distinct sediment types, separated by a discontinuity at 19 cm depth. The uppermost sediments (segment I) showed increasing sand content towards the core surface (from 20% to 53%), almost constant magnetic susceptibility ($3\text{--}4 \times 10^{-6}$ SI) and significantly lower values of organic carbon (C_{org} : 3–9%), total nitrogen (N_{tot} : 0.2–0.5%), C/N ratios (17–19), $\delta^{13}\text{C}$ (–25% to –26%) and reference metals (Al: ~4%, Li: 2–6 $\mu\text{g g}^{-1}$, Fe: 5–7%) than the underlying sections. Sediments in segment II were characterized by the prevalence of silt ($93 \pm 3\%$) with almost constant C_{org} ($16.5 \pm 0.8\%$), N_{tot} (0.8–0.9%), C/N (21–23), $\delta^{13}\text{C}$ (–24‰) and reference metals (Al: 7–8%, Li: 9–14 $\mu\text{g g}^{-1}$, Fe: 13–14%), and lower magnetic susceptibility ($2\text{--}3 \times 10^{-6}$ SI). CaCO_3 concentrations (not shown) ranged from 1% to 35% and presented an erratic profile with several subsurface maxima (not shown). Mn showed nearly constant values in segment II (72–73 $\mu\text{g g}^{-1}$), but an

increasing trend to the surface was observed in segment I (92–148 $\mu\text{g g}^{-1}$).

Magnetic susceptibility of sediments is related to sediment mineralogy (possible variation in sediment sources), grain size and shape; it can also vary with ferromagnetic content and can reflect climatically induced changes in vegetation, erosion and deposition (Thompson and Oldfield, 1986; Verosub and Roberts, 1995). The magnetic susceptibility profile from Las Matas core showed slightly higher values in segment I than in segment II, and was significantly correlated to the clay content of the core ($P < 0.05$, $r = 0.8$).

Al and Li concentrations are used as tracers to identify variations of terrigenous contributions to the aquatic environment. Al is a proxy for the aluminosilicate fraction (particularly clay minerals) and Li is a proxy for micas and/or clay minerals (Loring and Rantala, 1992). Al and Li concentrations in Las Matas core showed similar trends and correlated significantly with each other ($P < 0.05$, $r \geq 0.88$), as well as with the silt content along the core. These observations show that, in relation with the older sediments of segment II, segment I recorded an important reduction of terrigenous input to the site, associated with a decrease of fine particles content.

OC and N_{tot} concentrations were significantly correlated along the core ($r = 0.99$, $P < 0.05$) suggesting that N_{tot} content is mostly organic. C/N ratios from bulk organic matter have been used in many studies to distinguish between phytoplankton (4–10) and land-plant sources (>20) (Meyers, 1994, 2009). Sediments from Las Matas core showed intermediate C/N values, reflecting mixing of terrestrial and aquatic organic matter; although C/N ratios in segment II were higher than in segment I, indicating a higher proportion of terrestrial organic matter in the past. Although the $\delta^{13}\text{C}$ differences between segments I and II are small (only 1–2‰), they are consistent with a change in the predominant source of C_{org} to the site as indicated by the C/N ratio profile. From Cloern et al. (2002), $\delta^{13}\text{C}$ values for freshwater phytoplankton would vary between –32‰ and –26‰, whereas the range for terrestrial plants would be –32‰ to –20‰; therefore, the lighter $\delta^{13}\text{C}$ values found in segment I are most likely due to a higher contribution of aquatic C_{org} . As previously shown for Al, Li and silt content profiles, C/N and $\delta^{13}\text{C}$ data confirm that segment II has a larger terrestrial signature, which we attribute to larger stream discharges and finer sediment loads before the Las Matas Lagoon lost connection with the Calzadas River.

Fe and Mn are natural products of the continental weathering of silicate rocks and are subsequently transported by rivers as dissolved weathering products. Both of them are diagenetically mobile in aquatic systems depending on the redox conditions. Under anoxic or suboxic conditions, the reduced species dissolve in the pore-water and can either precipitate with sulfides or migrate to the sediment surface where they reoxidize and precipitate as oxyhydroxides, resulting in higher concentrations of Fe and Mn at the sediment–water interface (Cochran et al., 1998). Fe and Mn profiles in Las Matas core are contrasting (Fig. 2G and H). The Fe profile showed a decreasing trend towards the core surface and a strong correlation with Al, Li and silt contents ($P < 0.05$, $r \geq 0.91$) indicating that

Fe has a detrital origin and that its distribution is controlled by grain size variations; whereas the Mn concentration profile presents increasing values towards the surface of the core, and no significant correlation was found with the terrigenous reference metals.

There are two possible explanations for the divergent pattern of Fe and Mn: (a) the Mn concentrations found

in Las Matas core are not only the result of the absorption of Mn onto the sediment particles, but there are also higher Mn concentrations in the mineral lattice of the sandy sediments accumulated in the upper segment of the core; or (b) the Mn profile has been influenced by suboxic or mildly reducing conditions through the core, and an oxic at the sediment–water interface. The impact of the potential

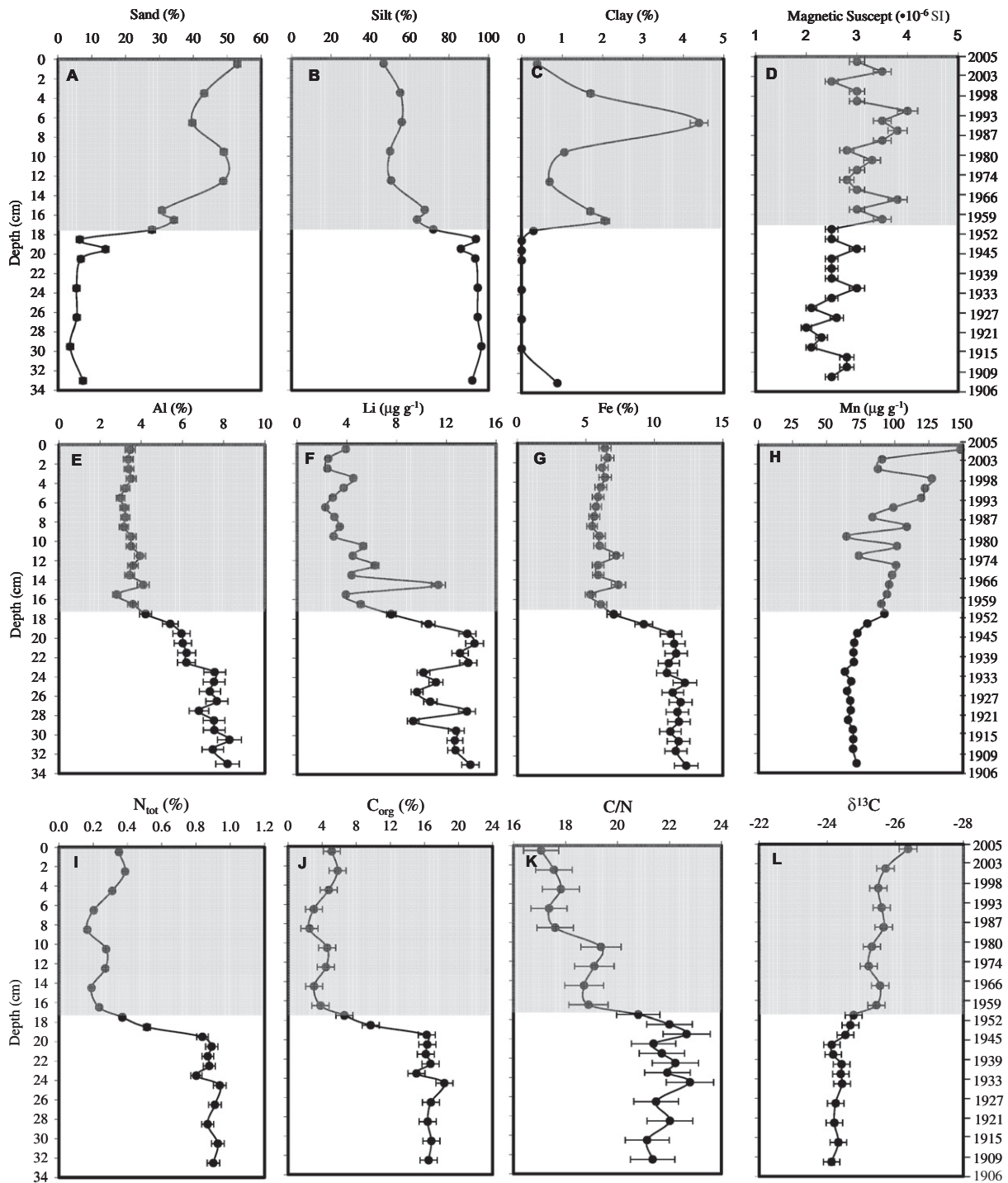


Fig. 2. Depth profiles of grain size distribution (sand = A, silt = B and clay = C), magnetic susceptibility (D), metals (Al = E, Li = F, Fe = G and Mn = H), nutrients (N_{tot} = I and C_{org} = J), C/N ratio (K) and $\delta^{13}\text{C}$ (L) in Las Matas core.

changing redox conditions on Fe and Mn profiles would not be the same because Mn oxides are more susceptible to dissolution than Fe oxides: the former begin to reduce at values slightly below 250–300 mV, whereas Fe oxides can only be reduced below +100 mV (Presley and Trefry, 1980).

There are no data on the mineral composition of the sediments or redox potential measurements to support any of the hypotheses. However, a change in redox conditions is plausible. Indeed, as Las Matas Lagoon is drying out, nutrient concentrations may increase causing eutrophication blooms (Mungall and McLaren, 1991), leading to recurrent hypoxic episodes in the water body, which finally could affect the redox conditions in the lagoon.

4.2. Radioisotope dating

Total ^{210}Pb activities ($^{210}\text{Pb}_{\text{tot}}$) ranged from 11.3 ± 0.6 to $56.8 \pm 1.7 \text{ Bq kg}^{-1}$. Supported ^{210}Pb ($^{210}\text{Pb}_{\text{sup}}$) was calculated as the average $^{210}\text{Pb}_{\text{tot}}$ concentrations between 29 and 34 cm depth ($13.3 \pm 0.7 \text{ Bq kg}^{-1}$), and was in agreement with gamma-derived ^{226}Ra activities determined in three samples of the core. The $^{210}\text{Pb}_{\text{tot}}$ profile (Fig. 3) showed a slight depart from the expected exponential decay between 10 and 19 cm depth (5 and 11 g cm^{-2}) at the bottom of segment I. To compensate the effects of compositional changes, $^{210}\text{Pb}_{\text{sup}}$ activities were normalized by using Al concentrations according to Kolker et al. (2009) and Ruiz-Fernández et al. (2009). Excess ^{210}Pb activities ($^{210}\text{Pb}_{\text{exc}}$) were calculated as $^{210}\text{Pb}_{\text{exc}} = ^{210}\text{Pb}_{\text{tot}} - (\text{Al}^{*210}\text{Pb}_{\text{sup}}/\text{Al}_{\text{bckg}})$.

^{210}Pb dates were obtained by using the constant flux-constant sedimentation (CFCS) model (Krishnaswamy et al., 1971; Smith and Walton, 1980) with two basic assumptions: ^{210}Pb atmospheric deposition is constant, and the mass accumulation rate is constant. When both assumptions are valid, a significant linear correlation between the logarithm of $^{210}\text{Pb}_{\text{xs}}$ concentrations and mass depth (g cm^{-2}) is found. The mass accumulation rate

(r , $\text{g cm}^{-2} \text{ year}^{-1}$) can be obtained from the slope (b) of the regression line as $r = -\lambda/b$, where λ is the ^{210}Pb radioactive decay constant. Irrespective of the sediment composition changes observed in the core (discussed in Section 4.1) and little variability observed in the 10–19 cm segment of the $^{210}\text{Pb}_{\text{tot}}$ profile, the highly significant correlation found between the $\ln ^{210}\text{Pb}_{\text{xs}}$ values and the mass depth in Las Matas core ($r = 0.94$, $P < 0.05$) confirmed that the CFCS hypotheses were valid.

The average sediment and mass accumulation rates obtained were $0.32 \pm 0.02 \text{ cm year}^{-1}$ and $0.20 \pm 0.01 \text{ g cm}^{-2} \text{ year}^{-1}$, respectively; and these rates were used to estimate calendar ages until the core bottom. The total core formation time was 99 ± 7 years, within the validity range of the ^{210}Pb dating technique.

^{137}Cs concentrations were very low (3.0 ± 0.03 to $3.7 \pm 0.04 \text{ Bq kg}^{-1}$), no subsurface maxima were observed, and thus could not be used to validate the ^{210}Pb -derived dates. This limitation has also been observed in sediments from other coastal Mexican aquatic systems (Páez-Osuna and Mandelli, 1985; Rosales-Hoz et al., 2003; Ruiz-Fernández et al., 2002, 2004, 2007).

The sediment characteristics changes observed above 19 cm are most likely related to the construction of the road connecting the Gulf of Mexico with the Gulf of Tehuantepec, across the Isthmus of Tehuantepec. This road was built through the former Las Matas wetland and the construction works started in 1946 (Ortiz Wadgymar, 1971; Martínez-Laguna et al., 2002). The wetland fragmentation interrupted the water exchange between Las Matas Lagoon and the Calzadas River (Fig. 1). The confinement of the remnant part caused an important alteration of the natural pattern of water fluxes (Toledo et al., 1987) that is reflected in the conspicuous changes of the sedimentary material characteristics, such as grain size, C_{org} and reference metals concentrations (as described in Section 4.1). This date is in excellent agreement with the ^{210}Pb derived age of the 19 cm level, namely 1947 ± 4 , and we concluded that this was a solid validation of the age model.

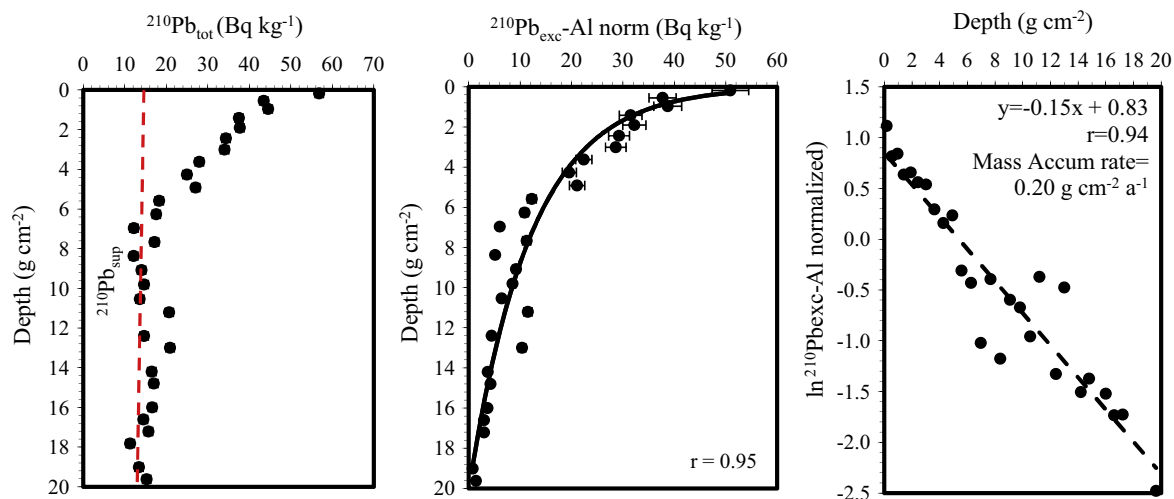


Fig. 3. Activity-depth profiles of total and excess ^{210}Pb in Las Matas core.

Table 1
Total concentrations (ng g⁻¹) of the 16 EPA-defined priority PAH in Las Matas core.

Depth	Na	Ace	Acy	Fl	Phe	An	Flt	Py	BaAn	Ch	BbFlt	BkFlt	Bapy	BghiPe	Ipy	DahAn	ΣPAHs
0.5	82.3	30.1	34.1	42.8	127.1	17.6	82.3	46.1	3.2	8.2	2.6	<d.l.	6.7	4.3	7.7	7.0	502
1.5	63.9	27.0	32.9	48.9	82.1	7.8	71.7	45.2	2.7	6.7	2.9	<d.l.	7.3	3.2	6.6	4.9	414
2.5	99.8	30.8	52.7	69.6	80.7	14.2	75.3	46.5	4.2	7.1	3.3	<d.l.	6.7	3.9	5.7	4.1	504
3.5	55.2	21.3	30.7	38.5	51.3	9.2	62.0	42.3	11.4	12.2	10.7	4.2	11.7	7.9	7.4	8.3	384
4.5	57.8	9.5	28.7	37.5	57.3	8.9	75.4	44.4	14.6	17.7	12.3	6.8	15.0	8.2	9.4	11.1	415
5.5	37.0	5.3	26.2	37.1	157.4	23.0	101.2	65.8	15.2	19.0	12.0	7.0	14.7	9.3	10.2	11.5	552
6.5	38.5	9.1	43.1	39.3	583.6	96.4	183.9	116.9	12.7	18.9	5.6	2.7	10.7	3.6	4.2	6.2	1176
7.5	45.1	8.1	31.4	25.1	77.5	8.4	54.4	34.5	3.3	6.7	4.9	<d.l.	8.1	4.0	3.7	4.6	320
8.5	60.7	14.5	25.6	30.3	64.2	7.3	74.9	40.7	6.2	9.5	7.4	2.2	11.6	5.2	5.6	3.8	370
9.5	67.2	24.9	34.4	37.2	81.8	11.8	91.1	48.3	3.2	9.2	3.6	<d.l.	6.9	2.3	3.0	5.1	430
10.5	54.0	9.1	29.7	20.6	65.3	5.4	66.1	35.7	2.4	5.9	4.9	<d.l.	7.1	3.4	3.6	5.3	319
11.5	41.0	7.0	22.3	12.4	51.4	10.3	96.0	57.9	6.1	9.1	7.2	3.2	12.0	6.5	6.4	5.2	354
12.5	41.8	7.5	21.2	22.0	83.3	14.8	168.3	86.0	5.4	12.6	9.1	3.1	13.1	3.7	4.5	6.8	503
13.5	103.6	52.0	74.9	13.3	137.0	23.2	134.2	84.0	38.7	37.7	23.0	10.7	21.2	24.2	22.0	13.0	813
14.5	40.2	14.3	22.9	27.0	53.6	9.1	115.5	58.0	3.1	7.3	5.5	<d.l.	7.4	4.2	4.3	4.0	376
15.5	58.0	11.7	36.8	14.4	98.9	27.5	98.8	46.8	4.8	14.6	4.7	<d.l.	9.1	4.3	4.2	3.0	437
16.5	34.9	9.4	21.3	22.3	79.0	16.1	154.7	81.1	9.2	14.2	14.0	6.1	16.5	11.1	8.6	6.3	505
17.5	38.7	11.4	22.5	20.2	66.3	13.1	138.3	65.2	3.4	8.9	7.1	2.2	8.3	3.8	4.3	4.5	418
18.5	87.5	34.1	51.6	30.0	88.1	16.0	245.6	101.5	6.6	15.4	12.1	2.9	14.5	7.4	4.3	10.2	728
19.5	29.1	8.5	24.0	15.6	51.2	2.8	69.8	42.2	1.0	3.7	<d.l.	<d.l.	5.6	<d.l.	1.4	3.9	259
20.5	44.9	38.2	35.3	10.2	79.7	16.0	235.0	95.9	7.2	17.6	11.0	4.3	13.0	4.8	4.5	10.6	628
21.5	38.6	24.0	40.5	45.0	51.9	15.8	149.4	78.0	4.3	13.7	7.7	2.4	10.7	6.2	3.9	5.3	497
22.5	25.9	25.5	26.4	38.3	49.2	13.4	182.9	88.9	5.5	14.3	8.8	3.2	10.7	6.0	4.7	4.8	508
23.5	69.5	33.8	37.2	59.9	72.0	18.1	212.8	101.1	6.7	18.7	12.1	3.8	18.6	5.7	4.3	8.2	682
24.5	34.9	23.3	50.3	31.5	94.3	26.5	210.6	99.3	8.1	20.7	13.5	3.9	18.9	8.8	6.5	6.3	657
25.5	28.0	5.1	19.2	15.2	89.7	24.3	235.4	122.0	8.5	22.0	18.0	5.9	19.0	7.2	8.9	5.7	634
26.5	24.9	13.5	41.6	16.1	79.8	12.9	161.5	69.1	6.2	17.8	9.1	3.5	15.6	6.9	6.6	6.3	491
27.5	69.7	27.0	67.0	68.2	89.8	26.2	191.6	81.8	6.9	19.4	10.5	3.3	17.7	5.5	5.6	7.6	698
28.5	62.7	14.5	35.3	34.9	60.8	14.1	138.7	69.3	6.6	14.2	11.5	3.1	17.8	4.2	4.4	6.3	498
29.5	33.7	13.9	34.9	46.0	65.7	13.2	131.5	64.7	6.1	16.3	10.8	3.4	15.9	7.2	6.2	7.3	477
30.5	34.8	15.6	36.8	36.4	67.8	19.5	166.5	78.7	7.5	19.3	13.2	4.1	15.9	6.7	5.4	7.0	535
31.5	93.0	34.1	50.0	70.9	65.2	17.1	123.0	59.4	6.3	14.9	10.1	2.9	15.2	7.0	5.9	7.5	582
33.0	74.2	35.7	50.9	43.4	60.1	15.4	152.5	66.5	6.9	16.5	12.1	4.2	16.6	6.5	5.2	4.4	571

<d.l. = below detection limit.

4.3. PAH concentrations, sources and trends

The total concentrations of the 16 EPA-defined priority PAHs (Σ EPA-PAHs, Table 1) span the interval 259–1176 ng g⁻¹. Phe, Flt, Na and Py were the prevalent congeners, accounting for 10–50%, 16–37%, 3–20% and 9–19% of the total, respectively. These concentrations are very low in comparison to those previously reported for surface sediments in the region influenced by oil industry activities, such as the Coatzacoalcos River (56–1025 mg kg⁻¹, Vázquez Botello et al., 1997) and some coastal lagoons and bays in the Southern Gulf of Mexico (0.95–6.65 mg kg⁻¹, Gold Bouchot, 2003). The Σ EPA-PAHs concentration levels found in Las Matas core have a low probability of being toxic, since they are far below the LEL value (Lowest Effect Level) established by the NOAA sediment benchmarks (Buchman, 2008), which is the level of sediment contamination that can be tolerated by the majority of benthic organisms (4000 ng g⁻¹). However, the individual concentrations of Ace, Acy, Fl, Na, Phe in most sections core might be harmful, since they are above their corresponding Threshold Effects Level (TEL value; Buchman, 2008), the concentration above which adverse biological effects might occur.

PAHs downcore profiles are scattered (Fig. 4 for individual congeners and Fig. 5 for Σ EPA-PAHs), thus indicating rapid and short time-scale variations. Six congeners (Flt, Py, Ch, BaPy, BbFlt, BkFlt) show slightly lower values in sediments since the 1930s, three of them (Phe, An, BeP and BaPy) do not show any clear trend, and others first decrease with time and then increase again (Na, Acy, Ace, and Flt). No significant correlation was found between the Σ EPA-PAHs concentrations and the C_{org} and silt content of the sediments, which are considered to be the major carriers for these pollutants, suggesting that the distribution and concentration of PAHs in the sediment core are due to direct inputs, and not to sediments characteristics.

Sources of PAHs can be distinguished by the ratio of HMW/LMW congeners, or PAHs isomer ratios such as Phe/An, Flt/Py, BaAn/Ch, An/(An + Phe) or Ipy/Ipy + BghiPe. Pyrogenic (combustion) sources, in contrast to petrogenic, are characterized by low ratios of Phe/An (<15) and high values of Flt/Py (>1), HMW/LMW (>1) and BaAn/Ch (≥ 0.4) (Readman et al., 2002 and references therein). Furthermore, some PAH isomer ratios, such as An/(An + Phe) and Ipy/Ipy + BghiPe, might be useful to differentiate combustion sources: An/(An + Phe) values

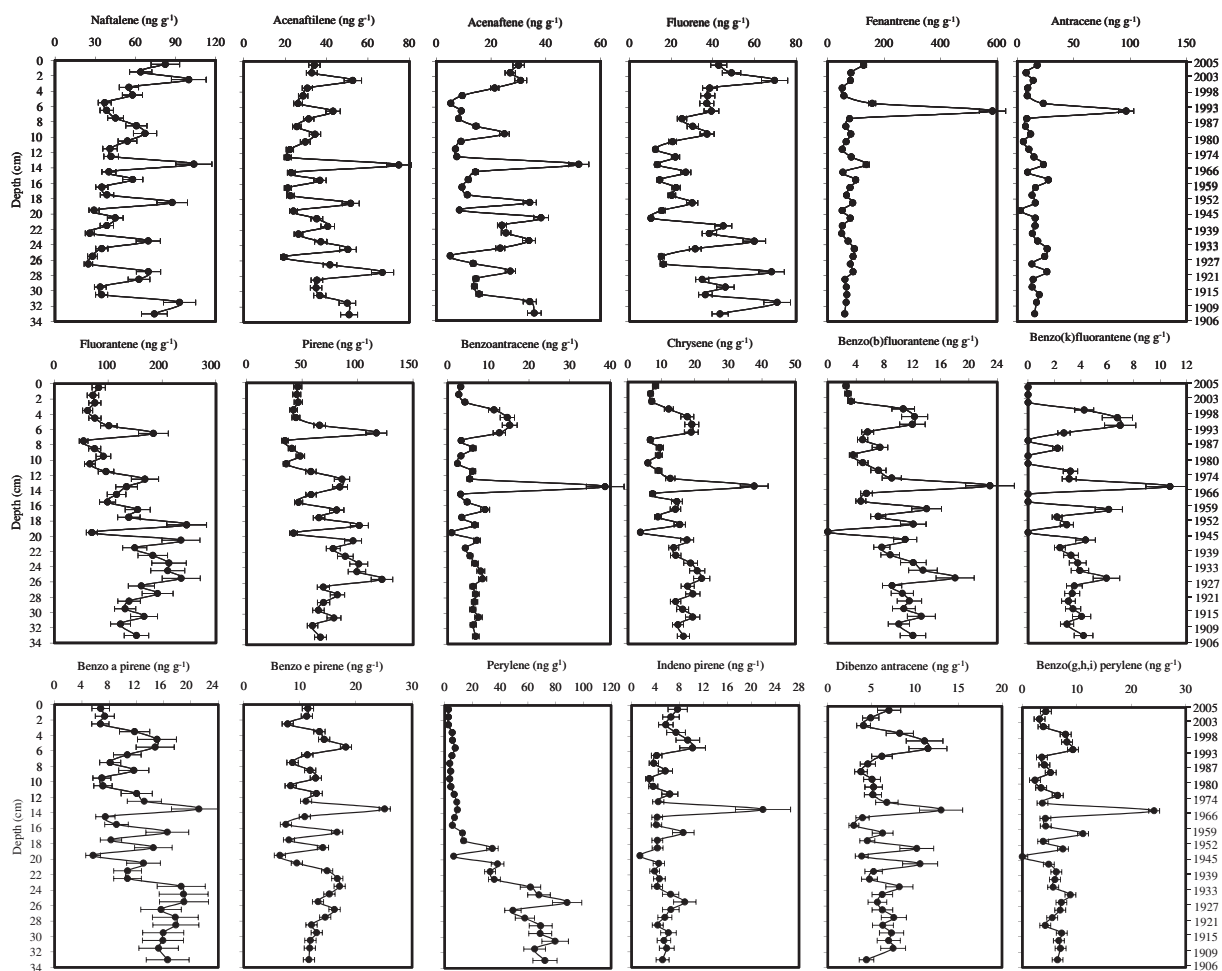


Fig. 4. Concentration-depth distributions of PAHs in Las Matas core.

<0.10 indicate petroleum combustion and >0.10 heavy fuel combustion (Budzinski et al., 1997); Ipy/Ipy + BghiPe values <0.2 indicate petroleum, 0.2–0.5 petroleum combustion, and >0.5 coal, grass and wood (Prah and Carpenter, 1983).

LMW-PAH species can originate from petroleum products (due to petroleum transportation, off-shore exploitation or natural oil seeps), incomplete combustion of fossil fuels and biomass at low to moderate temperature, and natural diagenesis. HMW-PAHs are generated by high temperature pyrogenic (pyrolytic) processes during the combustion of organic matter, anthropogenic industrial activity or natural fires. Some products, such as lubricating oil and asphalt, show intermediate profiles (Brown and Peake, 2006). Finally, some PAH compounds may have a diagenetic origin, such as perylene (Pe), which can be derived from biogenic precursors via short-term diagenetic processes.

The time dependent PAHs isomer ratios are presented in Fig. 6. Phe/An and Flt/Py profiles were fairly uniform along the core, indicating similar PAH sources, transport pathways and transformation mechanisms before and after

burial during the period studied (Mitra et al., 1999). Similarly, the highly significant correlation ($P < 0.05$, $r > 0.92$) found between Flt and Py (LMW-PAHs) and between BghiPe and Ipy (HMW-PAHs) indicate these PAHs have the same source(s). Phe/An ratios were generally <15 (excepting for a peak value of ~18 at 20 cm depth) and Flt/Py ratios were >1.

BaAn/Ch ratios showed consistent values (~0.4) before the 1950s, indicating similar PAH sources, transport pathways and transformation mechanisms for the isomers before and after burial. However, after the 1950s values are highly variable (0.3–1.0), which indicates either that (i) there is more than a single source of PAHs during this time period (pyrogenic and petrogenic), or (ii) isomers have experienced different degradation rates, presumably prior to deposition. An/(An + Phe) ratios, with values generally higher than 0.1, indicate that the prevalent source along the core was the combustion of heavy fuel, more conspicuously (values >0.2) in pre-1940s sections. Also Ipy/Ipy + BghiPe ratios (0.4–0.7) show that the HMW PAHs accumulated in the sediments are predominantly of petroleum combustion origin; although at certain depths the

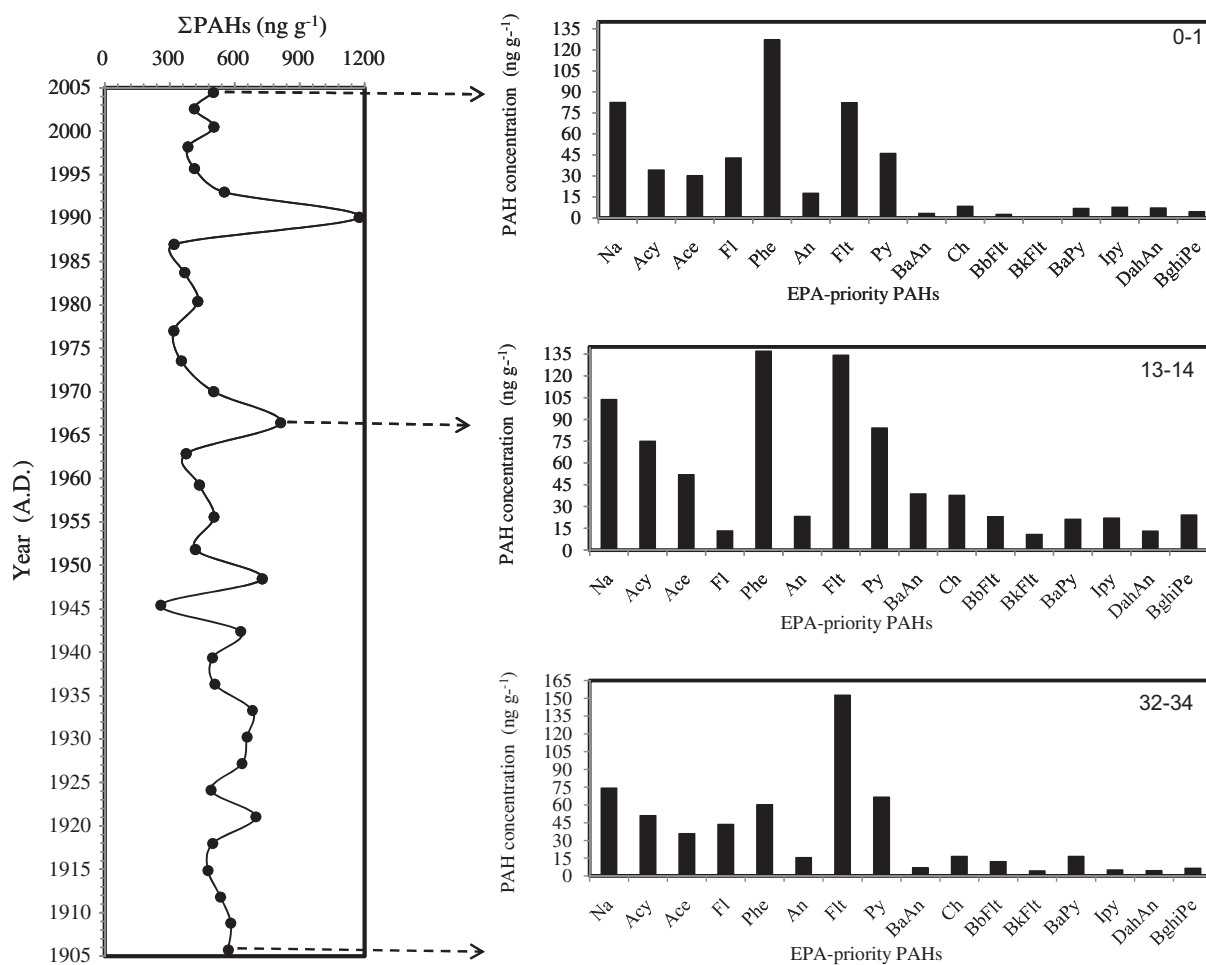


Fig. 5. Historical reconstruction of the 16 EPA-defined priority PAHs recorded in Las Matas core, showing the congener's composition at three depths: 0–1 cm, 13–14 cm and 32–34 cm.

values (>0.5) are compatible with coal or vegetation burning. Phe/An, Flt/Py and BaAn/Ch indices showed that PAHs accumulated at the site have a predominant pyrogenic origin; whereas An/(An + Phe) and Ipy/Ipy + Bghi suggested that these pyrogenic PAHs resulted from combustion of both vegetation and heavy fuels. HMW/LMW ratios corroborate these observations for sediments older than 1970s (values generally >1 below 10 cm depth), but also suggested the input of petrogenic PAHs in the most recent sediments. The pyrogenic origin of PAHs can be explained on the basis of (i) frequent wild fires that affect the grassland areas and swamps around Las Matas lagoon, during the warmer months of each year, and (ii) man-induced fires constantly set with urbanization purposes. The mixed signal (burning of vegetation and heavy fuels) might result from the burning of terrains reported to be contaminated by oil spills (Bozada Robles and Bejarano González, 2006) and the discharges of untreated wastes from the petrochemical facilities that neighbor the lagoon (PEMEX, 1991).

4.3.1. Perylene

Pe concentrations in Las Matas core represent a special case. Unlike the other PAHs, it follows the same pattern of terrigenous metals, silt and C/N decreasing dramatically from 85 ng g^{-1} at depth to $4\text{--}10 \text{ ng g}^{-1}$ towards the core surface. The origin of Pe has been attributed to diagenesis of biogenic precursors, such as allochthonous organic material from terrigenous plants and to autochthonous organic matter from algal production (Silliman et al., 1998), although relatively higher amounts of Pe are expected in reducing sediments that receive significant amounts of terrestrial organic matter (Venkatesan, 1988; Laflamme and Hites, 1979). Pe might also come from petroleum or pyrolytic processes (Soclo et al., 2000). Typically, for pyrogenic PAHs perylene represents about 1–4% of the total PAH concentration (Fang et al., 2003) and, according to Tolosa et al. (2004), it should be less than 20% of the total pentaromatic isomers ($\Sigma\text{penta-PAHs} = \text{PAHs with five rings, such as Pe, BaPy, BePy, DahAn, BbFlt and BkFlt}$). Pe/

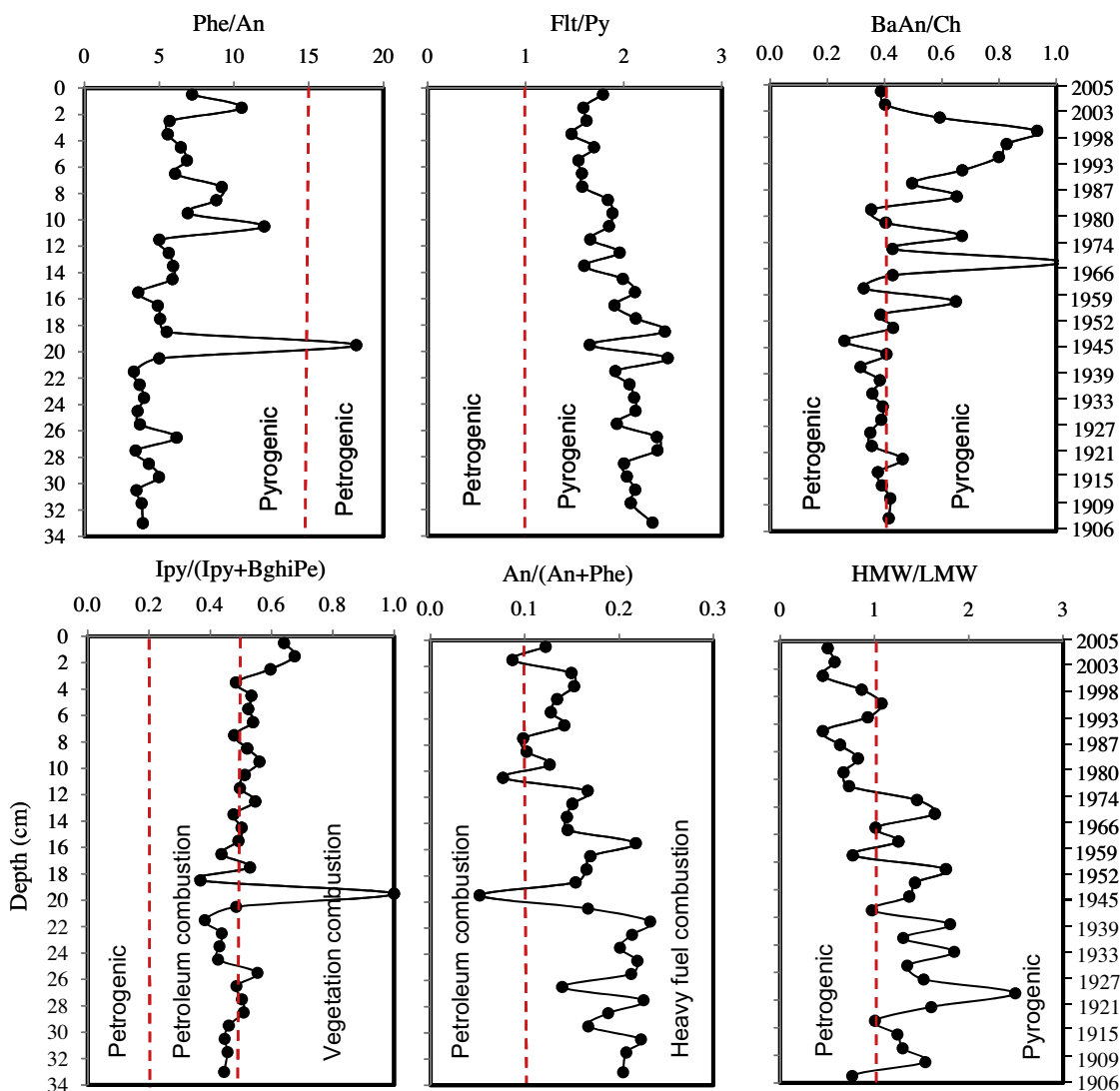


Fig. 6. Historical reconstruction of LMW/HMW and PAH isomer ratios recorded in Las Matas core.

Σ PAHs values in Las Matas core ranged from 6 to 13% and Pe/ Σ penta-PAHs from 28 to 58% indicating that Pe in sediments older than 1950 have most likely a biogenic origin, in contrast with the younger sediments that showed lower relative abundances (0.4–3.0 and 7–17, respectively), suggesting the contribution of pyrogenic sources.

Pe concentrations did not correlate with any of the other PAHs analysed in this sediment core, but showed a very significant correlation with C_{org} content in the sediments ($P < 0.05$, $r = 0.89$), especially if data from the strata corresponding to 20–22 cm depth are omitted ($P < 0.05$, $r > 0.97$). Also, significant correlations were observed with reference elements such Al, Li and Fe ($P < 0.05$, $r = 0.94$, 0.73 and 0.87, respectively), which are also strongly correlated with the fine sediments content. According to Jiang et al. (2000), the concentration of Pe in the sediments is proportional to the amount of terrestrial input, decreasing with distance from the source of land particles.

We have estimated the diagenetic production rates of Pe (Pe-DPR, $\text{ng Pe g}^{-1} C_{org} \text{ a}^{-1}$) in Las Matas core by using the reciprocal values of the linear regression slopes obtained from the time dependent profile of the Pe concentrations normalized with respect to C_{org} (Fig. 7). The Pe-DPR profile showed that the production rate of Pe in segment II (characterized by reduced conditions and higher amounts of terrestrial C_{org}) is considerably higher than in segment I (where oxic conditions and smaller concentrations of C_{org} prevail), in agreement with the observations of Laflamme and Hites (1979), Venkatesan (1988) and Jiang et al. (2000) who indicate that the major source of Pe in sediments is terrestrially dependent. Therefore, the lower relative abundances of Pe observed in the sediments deposited after 1950 might have been caused by the conspicuous reduction of terrigenous inputs to Las Matas Lagoon, caused by the cutoff of the connection between the former Las Matas wetland and the Calzadas River, due to the construction of the Minatitlán–Coatzacoalcos road.

4.4. PCB concentrations, sources and trends

Thirty-six PCB congeners with 3–7 Cl atoms were detected. Fig. 8 shows the results in terms of both total PCB (Σ PCBs) and some homologue concentrations for three selected depths. Σ PCBs ranged from 24 to 77 ng g^{-1} , with maxima (64–73 ng g^{-1}) found in sediments older than 1950s. The most recent Σ PCB concentrations are comparable to those found in lacustrine sediments from urban lakes in Wuhan, China (0.90–46.14 ng g^{-1} ; Yang et al., 2009), lake Erie, Canada (43 ng g^{-1} ; Marvin et al., 2004), Yukon river drainage basin (8–33 ng g^{-1} ; Rawn et al., 2001) and Rice Creek-lake Ontario (24.5 ng g^{-1} ; Chiarenzelli et al., 2001). Reports on Σ PCB sediment concentrations in Mexico are very scarce so far, and levels found in surface coastal sediments are rather low: $< 10 \text{ ng g}^{-1}$ for 42 surface samples from San Quintín Bay, Baja California (Gutiérrez-Galindo et al., 1996); and 1.2–9.3 ng g^{-1} in surface sediments of Chetumal Bay, Quintana Roo (Noreña-Barroso et al., 1998). Piazza et al. (2008) found concentrations in the interval 3–42 ng g^{-1} in surface sediments from four coastal areas in the States of Sinaloa, Sonora, Oaxaca and Veracruz, but

quite higher values in lacustrine sediments close to Mexico City (64–621 ng g^{-1}). It is important to emphasize that making detailed comparisons of regional differences is difficult, because frequently the data published in the specialized literature does not refer exactly to the same PCB congeners. Σ PCB values in the sections older than pre-1950s exceeded the TEL guidelines (Threshold Effect Limit: 34.1 ng g^{-1} ; Buchman, 2008) and, even if the most recent sediments have lower concentrations (24–32 ng g^{-1}), surface Σ PCB values are still close to this threshold.

Sediment samples are characterized by the constant prevalence of lower chlorinated species along the core. 3-CB and 4-CB content distribution with depth was very conservative along the core, with values ranging from 51 to 65%, and from 29% to 40%, respectively (Table 2). The sum of the seven indicator-PCBs (non-dioxin-like PCBs 28, 52, 101, 118, 138, 153 and 180) represented between 20% and 27% of the total PCBs along the entire core; and among the indicator-PCBs, also the 3-CBs PCB28 and PCB52 were the dominant species, with 69–77% and 13–16%, respectively. In addition, three WHO-TEF “dioxin like” PCBs (77, 105 and 118) were detected (Table 3), although in very low concentrations ($< 1\%$ of the total PCBs).

The depth distribution profiles of Σ PCBs, indicator-PCBs and all PCB congeners showed the same pattern, with higher concentrations in the pre-1950s segment of the core, in contrast to the most common temporal trends found in the literature. We found PCBs in sections older (early 1900s) than the onset of industrial PCB synthesis. The presence of PCBs in preproduction sediments has been reported before (Van Zoest and Van Eck, 1993; Kjeller and Rappe, 1995; Muir et al., 1996; Gevao et al., 1997, 2000; Yamashita

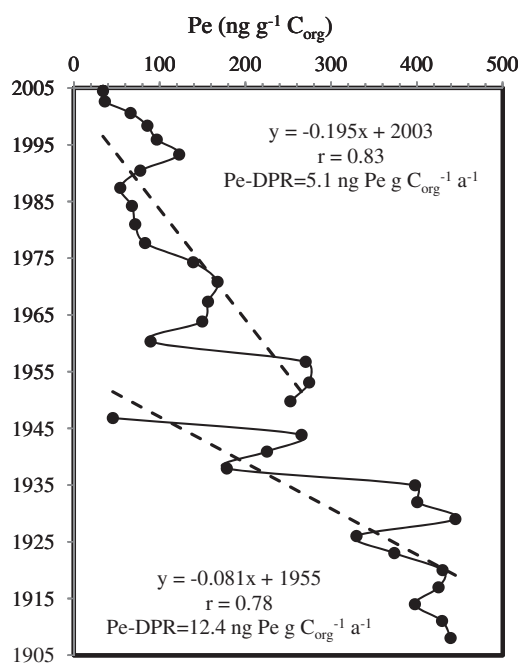


Fig. 7. Historical reconstruction of C_{org} -normalized perylene concentrations recorded in Las Matas core.

et al., 2000; Chiarenzelli et al., 2001; Malmquist et al., 2003; Yang et al., 2009) but their origin remains unclear. Possible explanations include (i) basic methodological aspects, (such as collection of mixed sediment; sample preparation and analysis); (ii) postdepositional mobility/percolation of low chlorinated (more water soluble) PCBs congeners (Yamashita et al., 2000; Malmquist et al., 2003; Yang et al., 2009); (iii) lateral flow or infiltration of groundwater (carrying dissolved-phase PCBs compounds) through previously deposited sediment (Chiarenzelli et al., 2001); and (iv) the combustion or

pyrolysis of natural organic matter (Pereira et al., 1980; Kjeller and Rappe, 1995; Pandelova et al., 2009).

We excluded sediment mixing because this would also have affected ^{210}Pb , which however, provided a validated chronology. Downcore smearing during sampling could not have created the observed ΣPCBs , indicator-PCBs and all PCB congeners profile patterns, which are very similar to the patterns of other variables measured in the core, such as C_{org} , Al, Li and Fe. Contamination during analysis is unlikely since all samples were analysed following the same method and under strict quality control checks.

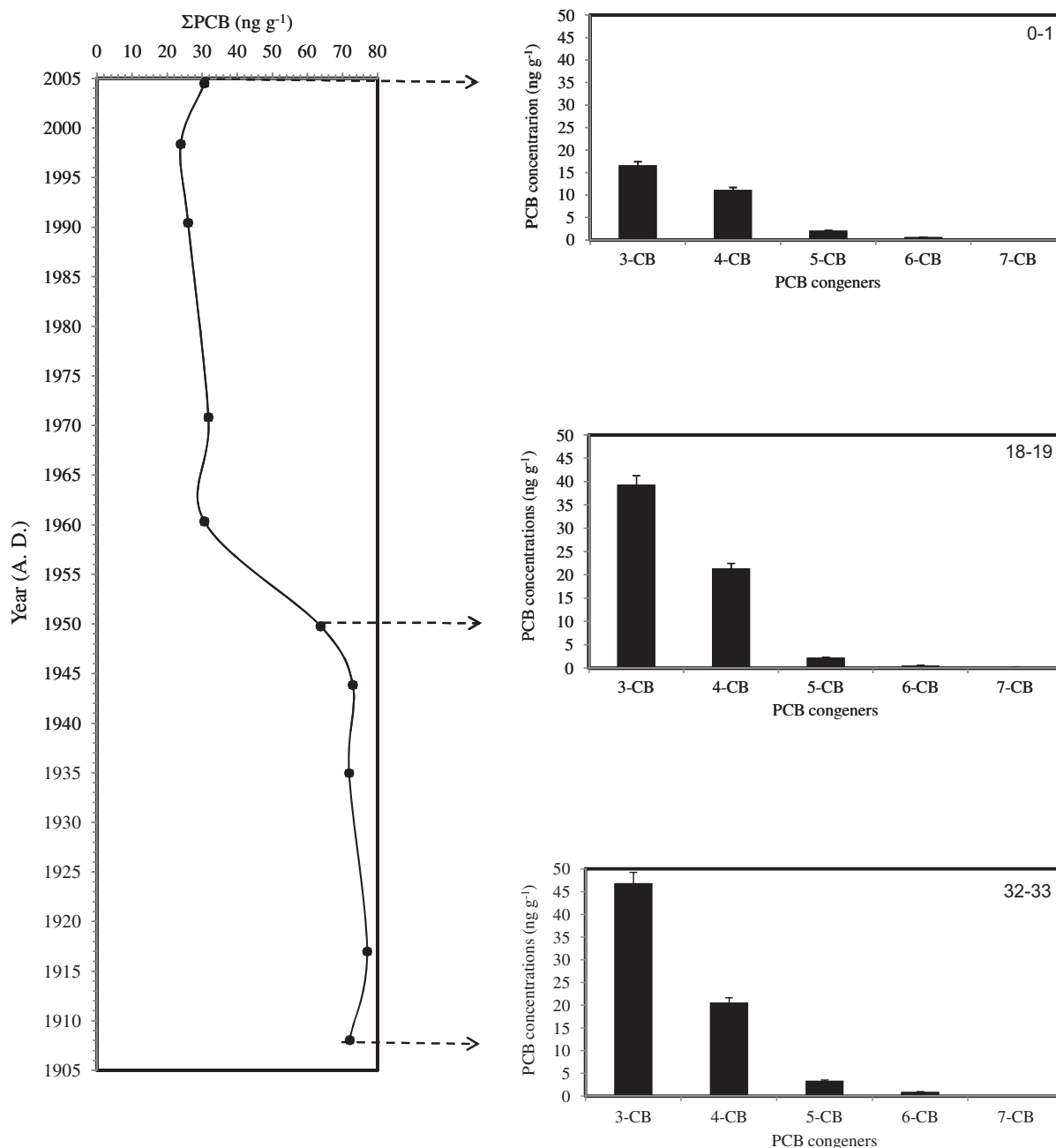


Fig. 8. Historical reconstruction of PCBs recorded in Las Matas core.

Table 2
Concentration of PCB (ng g⁻¹) congeners and percent content respecting the ΣPCB in Las Matas sediment core.

Depth (cm)	Year AD	PCB congeners										ΣPCB (ng g ⁻¹)
		3-CB		4-CB		5-CB		6-CB		7-CB		
		(ng g ⁻¹)	(%)	(ng g ⁻¹)	(%)	(ng g ⁻¹)	(%)	(ng g ⁻¹)	(%)	(ng g ⁻¹)	(%)	
0–1	2004	16.6	54.2	11.1	36.4	2.1	6.8	0.7	2.1	0.2	0.5	30.6
3–4	1998	12.1	50.8	9.5	40.0	1.6	6.9	0.4	1.8	0.1	0.5	23.8
6–7	1990	14.1	54.3	9.9	38.2	1.4	5.6	0.4	1.6	0.1	0.4	26.0
12–13	1971	17.7	55.7	11.1	34.8	2.3	7.3	0.6	1.9	0.1	0.3	31.8
15–16	1960	15.8	51.7	12.3	40.2	2.0	6.4	0.5	1.5	0.1	0.2	30.6
18–19	1950	39.3	61.7	21.4	33.6	2.3	3.5	0.6	0.9	0.2	0.3	63.8
20–21	1944	45.6	62.5	23.1	31.7	3.2	4.4	0.7	1.0	0.2	0.3	73.0
23–24	1935	40.2	55.9	27.9	38.8	3.1	4.3	0.6	0.9	0.1	0.1	71.9
29–30	1917	43.3	56.2	28.8	37.4	3.8	4.9	1.0	1.3	0.2	0.2	77.0
32–34	1906	46.9	65.1	20.6	28.6	3.4	4.7	1.0	1.3	0.1	0.2	72.0

Table 3
Concentration (ng g⁻¹) of PCB indicators and WHO-TEF assigned dioxin-like PCBs in Las Matas sediment core.

Depth (cm)	Year AD	PCB indicators							Dioxin-like PCBs	
		CB-028	CB-052	CB-101	CB-118**	CB-138	CB-153	ΣPCB-ind/ΣPCB (%)	CB-77	CB-105
0–1	2004	6.1	1.0	0.5	0.3	0.1	0.2	27	0.1	0.1
3–4	1998	4.7	1.0	0.5	0.2	0.1	0.1	27	0.0	<d.l.
6–7	1990	5.1	0.9	0.4	0.2	0.1	0.2	26	0.1	<d.l.
12–13	1971	4.8	1.1	0.6	0.3	0.1	0.2	22	0.1	<d.l.
15–16	1960	5.4	1.2	0.4	0.3	0.1	0.2	25	0.1	0.2
18–19	1950	11.9	2.2	0.6	0.4	0.2	0.2	24	0.1	<d.l.
20–21	1944	11.8	2.4	0.8	0.5	0.2	0.2	22	0.2	0.2
23–24	1935	13.4	2.9	0.8	0.4	0.1	0.2	25	0.2	0.1
29–30	1917	14.2	3.0	1.0	0.5	0.2	0.4	25	0.2	0.2
32–34	1906	10.0	2.2	0.9	0.5	0.2	0.3	20	0.1	0.0

*WHO = World Health Organization. International Programme on Chemical Safety (IPCS). **CB-118 belongs to both categories; <d.l. = below detection limit.

Post-depositional mobility was dismissed, first of all, because it would have also affected other organic compounds (such as PAHs) and would have changed the PCB congener distribution (which is quite constant along the core for all of them); and finally, lateral migration was also excluded because the ΣPCB concentrations showed highly significant correlations ($P < 0.05$) with the concentrations of terrigenous metals (Al, Li, Fe; $r \geq 0.94$), C_{org} and Pe ($r > 0.97$) and the silt content ($r = 0.96$) in the sediments. If lateral transport had occurred, the strong associations with all these terrigenous-indicators would not have been so evident. Therefore, taking into account that (1) PAHs isomer ratios denoted a dominant pyrogenic source of PAHs along the sedimentary record, and (2) there is a strong correlation between PCBs and C_{org} concentrations, it might be possible that PCBs in old samples were produced by the combustion or pyrolysis of natural organic matter (like coal, wood and peat) as hypothesized by Pereira et al. (1980), Kjeller and Rappe (1995), Rose and Rippey (2002), Rose et al. (2004) and Pandelova et al. (2009). Although it is difficult to prove this hypothesis with only 3 samples in the preproduction segment, we cannot neglect that results are consistent during the time period elapsed (1908–1935).

Based on the strong correlation observed between the ΣPCBs and the C_{org} and silt content, we confirmed that

the ΣPCBs and PCB congener profiles (showing higher concentrations in pre-1950 sediments) are controlled by the content of fine particles and C_{org} , which are known to be important carriers for the transport of PCBs (Zhang et al., 2007). According to Kuzyk et al. (2010), C_{org} availability dictates the PCB transport and fate, including entry into food webs or burial in sediments, and therefore changes in the organic system (terrestrial or aquatic) implies changes in the contaminant pathways. Additionally, many authors have reported an inverse relationship between particle size and PCB sediment concentrations (Pierard et al., 1996; Alkhatib and Weigand 2002; Zhang et al., 2007; Kuzyk et al., 2010; Nehyba et al., 2010) which is attributed to the fact that the greater surface area of the smaller particles also provides a larger area for the adsorption of C_{org} (Zhang et al., 2007).

Las Matas core showed considerable changes in grain size distribution and C_{org} content along the core; and even in the scenario of a constant PCB flux to the sediments, the increment in sand content and reduction in C_{org} concentrations affected the retention capacity of the sediments, resulting in a decreasing PCBs accumulation trend after 1950s. Furthermore, as riverine waters and runoff are one of the most important sources of PCBs to coastal areas (Van Metre et al., 1997; Konat and Kowalewska, 2001), the loss

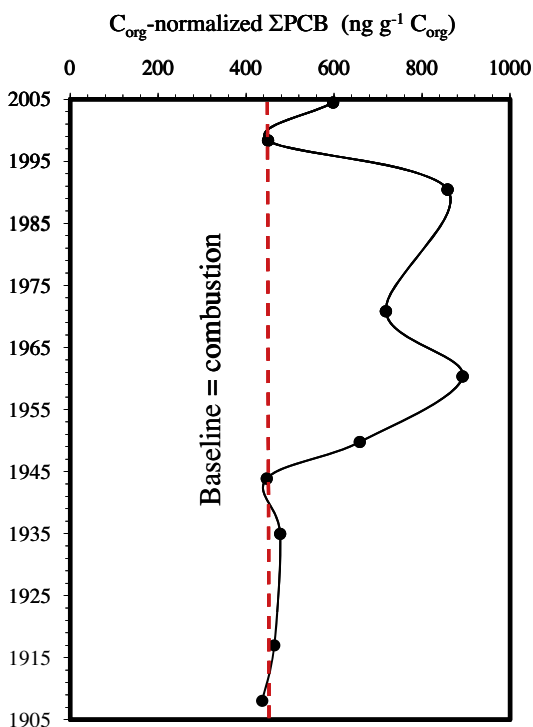


Fig. 9. Historical reconstruction of C_{org} -normalized PCBs concentrations recorded in Las Matas core.

of connection between Las Matas Lagoon and the Calzadas River, caused by the construction of the Trans-Isthmus road in 1946, would also have cut down the riverine flux of PCBs to the lagoon.

The profile of Σ PCB concentrations normalized to C_{org} contents (Fig. 9) showed a low constant value in the older sections, and a rapid increment after the 1950s, most likely related to the use of synthetic PCBs. We therefore concluded that normalization of Σ PCB concentrations to C_{org} allows to discriminate the background (pyrogenic) and industrial contributions of PCBs. Anthropogenic PCBs decreased after 1990s, most likely because of more strict environmental legislation, but still show levels twice higher than the baseline.

5. CONCLUSIONS

Las Matas core constitutes a striking example of environmental changes due to urbanization and industrial development. A major change in both sedimentological and geochemical features, recorded at 19 cm depth, corresponds to the beginning of the construction of the Trans-Isthmus road at the end of the 1940s. This date is in excellent agreement with the $^{210}\text{Pb}_{ex}$ sediment chronology. Despite the changing environment, the core has retained a good record of the events spanning the last century; therefore, a reliable history of the environment, its characteristics and evolution was reconstructed. PAH concentrations are scattered throughout the core, with peaks that account for episodic input variations. A significant component of

the PAH mixture is made of pyrogenic congeners, originated from the combustion of waste hydrocarbons and swamp vegetation (either by natural or man-induced fires to obtain usable terrain) that are transferred to the lagoon by atmospheric deposition. Downcore distribution of PCB concentrations is controlled by particle size and organic matter concentrations. Their occurrence in sediments deposited before industrial production dates are most likely originated by the combustion of natural organic matter. Considering that Las Matas Lagoon sustains small scale fishery cooperatives, and that some PAHs congeners and the total PCBs concentrations are close to the TEL-NOAA benchmark, further investigations on organic contamination of food and human exposure levels are strongly recommended.

ACKNOWLEDGMENTS

This research has been funded through the grants SEMAR-NAT-CONACYT-2004-C01-32 and PAPIIT-UNAM IN105009. CONACYT-CNR 2005 bilateral program for academic exchange provided mobility grants for ACRF, MS, MF and LGB; travel support for ACRF was also granted by UNAM-CIC and ISMAR-CNR. Thanks are due to B. Ghaleb from GEOTOP-UQAM for gamma spectrometry measurements; E. Marsella and G. Rizzato for PAH and PCB analyses; H. Bojórquez-Leyva, C. Ramírez-Jáuregui, G. Ramírez-Reséndiz, V. Montes-Montes, P. Mellado-Vázquez and S. Bojórquez-Sánchez for their technical assistance. C. Mugnai and S. Albertazzi provided useful data interpretation. This is contribution No. 1714 from the CNR-ISMAR, Bologna, Italy.

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Associate editor: Martin Novak