

Reconstruction of hydrocarbons accumulation in sediments affected by the oil refinery industry: the case of Tehuantepec Gulf (Mexico)

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Abstract The Isthmus of Tehuantepec corresponds to the shortest distance (~200 km) between the Gulf of Mexico and the Pacific Ocean in Southern Mexico, and the main economical activity of this region is oil extraction and refining. Polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPHs) were determined in a ^{210}Pb dated sediment core collected from the continental shelf of Tehuantepec Gulf, in the vicinity of the oil refinery of Salina Cruz, Oaxaca, the main oil refining facility of the country. The sediments were mostly of coarse nature and hence PAHs and TPHs concentrations throughout the core (61–404 $\mu\text{g g}^{-1}$ and 29–154 mg kg^{-1} , respectively) were

below international quality benchmarks. Depth profiles of both PAHs and TPHs concentrations showed increasing trends since the early 1900s but the higher values were found from the 1950s to present. PAH congener ratios showed that these contaminants had both petrogenic and pyrolytic sources, although the former has been predominant since the 1970s. The Salina Cruz refinery started operations in 1978 but the oil industry activities in the Tehuantepec Isthmus go back to the beginning of the twentieth century with the operation of Minatitlan refinery in the Gulf of Mexico, and the Gulf of Tehuantepec being the main conduit for oil distribution in the Pacific coast. The observed changes in contaminant distributions described well the oil industry development in the area.

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Introduction

Petroleum hydrocarbons (PHCs) are widely used in everyday life, mostly as energy sources (heating, transportation) and as starting products for the chemical industry. They are found in the environment as by-products from commercial or private uses, routine shipboard operations, as well as a result of oil spill accidents. Contamination caused by petroleum products contain a wide variety of hydrocarbons (ranging from light, volatile, short-chained organic compounds to heavy, long-chained, branched compounds). The approximate carbon numbers for individual hydrocarbon products present in petroleum products are as follows: gasoline (C6–C12), diesel (C8–C26), kerosene (C8–C18), fuel oil (C17–C26) and lubricating oils (C21–C50) (George 1994). Because there are so many

compounds, it is usually impractical to measure all of them and, instead, screening methods are used to show that petroleum hydrocarbons are present in the sampled media (ATSDR 1999).

The term total petroleum hydrocarbons (TPHs) is used to describe a broad family of several hundred of chemical compounds that originally come from crude oil (including petroleum hydrocarbons in the range of C1 to beyond C35), present in the environment in a measurable amount (Speight 2005). The amount of TPH found in a sample is useful as a general indicator of petroleum contamination at that site, although it does not provide information on the composition (i.e., individual constituents of the hydrocarbon mixture) (ATSDR 1999). Conventional TPH analytical methods have been widely used to investigate sites that may be contaminated with petroleum hydrocarbon products (Andrade et al. 2004; Ferraro et al. 2009; Vega et al. 2009; EPA 2009, 2010). Studies of animal exposure to TPHs show effects on the lungs, central nervous system, liver, kidney, developing foetus and reproductive system (ATSDR 1999); however, certain TPH compounds, such as some mineral oils, are not very toxic. The main hazards from elevated concentrations of TPHs are typically related to the content of polycyclic aromatic hydrocarbons (PAHs; e.g., benzo(a)pyrene) or other harmful compounds such as benzene, toluene and xylene, which are present in gasoline.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous and persistent contaminants. Sixteen of them, known to have mutagenic and carcinogenic properties (e.g., Conney 1982; Nielsen et al. 1995; Connell et al. 1997) are considered by the US Environmental Protection Agency as priority micropollutants (EPA 1982). Several natural and anthropogenic processes can lead to the formation of PAHs. Anthropogenic sources include combustion of fossil fuels, coal gasification and liquification processes, petroleum cracking, waste incineration and production of coke, carbon black, coal tar pitch and asphalt (McCready et al. 2000). Another common anthropogenic source of PAHs is spillage of unrefined and refined fossil fuels (e.g., Ke et al. 2002). High molecular weight (HMW) polyaromatic compounds are introduced to shallow environments through forest fires and natural coking of crude oil (Abrajano et al. 2005 and references therein), and certain compounds (perylene and retene) are thought to be diagenetically produced (Wakeham et al. 1980). Because of their hydrophobic nature, both PAHs and oil hydrocarbons in the aquatic environment are easily adsorbed onto settling particles and eventually accumulate in sediments. This adsorption–settling process is continuous over time and, therefore, sediments can act as recorders of contaminant inputs as well as of general environmental change over time (Kannan et al. 2005; Giuliani et al. 2008; Sanchez-Cabeza and Druffel 2009). Therefore, the study of sediment

records can provide information on levels, history and trends of pollutants in aquatic environments.

The use of sediment cores to reconstruct contaminant records has been well documented in many studies (e.g., Heit et al. 1988; Latimer and Quinn 1996; Frignani et al. 2003; Wakeham et al. 2004; Lima et al. 2003; Quiroz et al. 2005). The age–depth relationships in sediment cores can be estimated by using ^{210}Pb ($T_{1/2} = 22.20 \pm 0.22$ years; DDEP 2010), a natural radionuclide of the ^{238}U decay chain, which is mainly supplied to the aquatic environment by atmospheric precipitation and in situ production from ^{226}Ra decay. ^{210}Pb is an ideal tracer for dating aquatic sediments deposited during the last 100–150 years (Krishnaswamy et al. 1971), a period of time during which important environmental changes have occurred. ^{210}Pb dating is often validated with ^{137}Cs profiles ($T_{1/2} = 30.14$ years) since the use of this artificial radionuclide produced by nuclear weapons testing, which peaked in 1963, provides an independent chronological marker (e.g., Robbins and Edgington 1975; McCall et al. 1984).

In spite of the presence of industrial activities with high contamination potential, the anthropogenic impact in the Gulf of Tehuantepec has been scarcely studied, except for some near shore environments. For instance, Botello et al. (1995, 1998) reported a decreasing gradient in total PAH concentrations from the surroundings of Salina Cruz Port and outer port areas ($90\text{--}317 \text{ ng g}^{-1}$) towards the ocean sites ($0.21\text{--}26 \text{ ng g}^{-1}$). González-Lozano et al. (2006) confirmed decreased PAH concentrations from Salina Cruz Port to the ocean, and also reported a seasonal variation, with maximum values of 754 mg kg^{-1} in the harbour area and 41 mg kg^{-1} offshore (dry season) in contrast to 142 mg kg^{-1} and $<0.5 \text{ mg kg}^{-1}$ correspondingly (rainy season). They also reported signs of pollution by Cd, Cu, Ni, Pb and Zn in the harbour and outer port areas (maximum concentrations of 5, 64, 25, 124 and 596 mg kg^{-1} , respectively). González-Macías et al. (2007) reported concentration of total aromatic hydrocarbons (TAH) in sediments of Salina Cruz Bay ($0.10\text{--}2,160 \text{ } \mu\text{g g}^{-1}$) and confirmed seasonal differences (mean values of 40 and $21 \text{ } \mu\text{g g}^{-1}$ for the dry and rainy season, respectively). Iturbe et al. (2007) described soil contamination caused by oil spills from the pipeline pumping stations of the Salina Cruz oil refinery, with TPH and total PAH concentrations up to 13,683 and 218 mg kg^{-1} , respectively. Ruiz-Fernández et al. (2004) reported moderate trace metal enrichment in ocean sediments, starting in the early 1980s, when the Salina Cruz oil refinery became operative (maximum concentrations of 26, 250 and $476 \text{ } \mu\text{g g}^{-1}$ for Cd, Cu and Pb, respectively).

The aim of this work was to reconstruct the historical trends of organic contamination in the Gulf of Tehuantepec,

in relation with the oil-industry development in the Tehuantepec Isthmus, through a high resolution study of a ²¹⁰Pb dated sediment core, collected offshore the Salina Cruz industrial area.

Study site

Geographical setting

The Gulf of Tehuantepec (Fig. 1; 14°30'–16°12' N, 92°00'–96°00' W) is the Southern oceanic boundary of the Mexican Exclusive Economic Zone on the Pacific coast

(Fig. 1). It has a continental shelf about 120 km wide and an approximate radial extension of 200 km (Lavin et al. 1992). The region is tropical warm with a mean annual temperature of 27°C, showing small variations during the year (García 1981); however, there is a well-defined rainy season from May to September and dry conditions from October to April; the coastal zone of the Gulf of Tehuantepec is considered as the driest area of the region (López et al. 2009). High energy conditions prevail in the Gulf of Tehuantepec due to intermittent forcing by an intense, offshore wind jet during the winter months (Barton et al. 1993) which causes an efficient dispersal of inputs (Trasviña and Barton 1997). Strong seasonal Northern

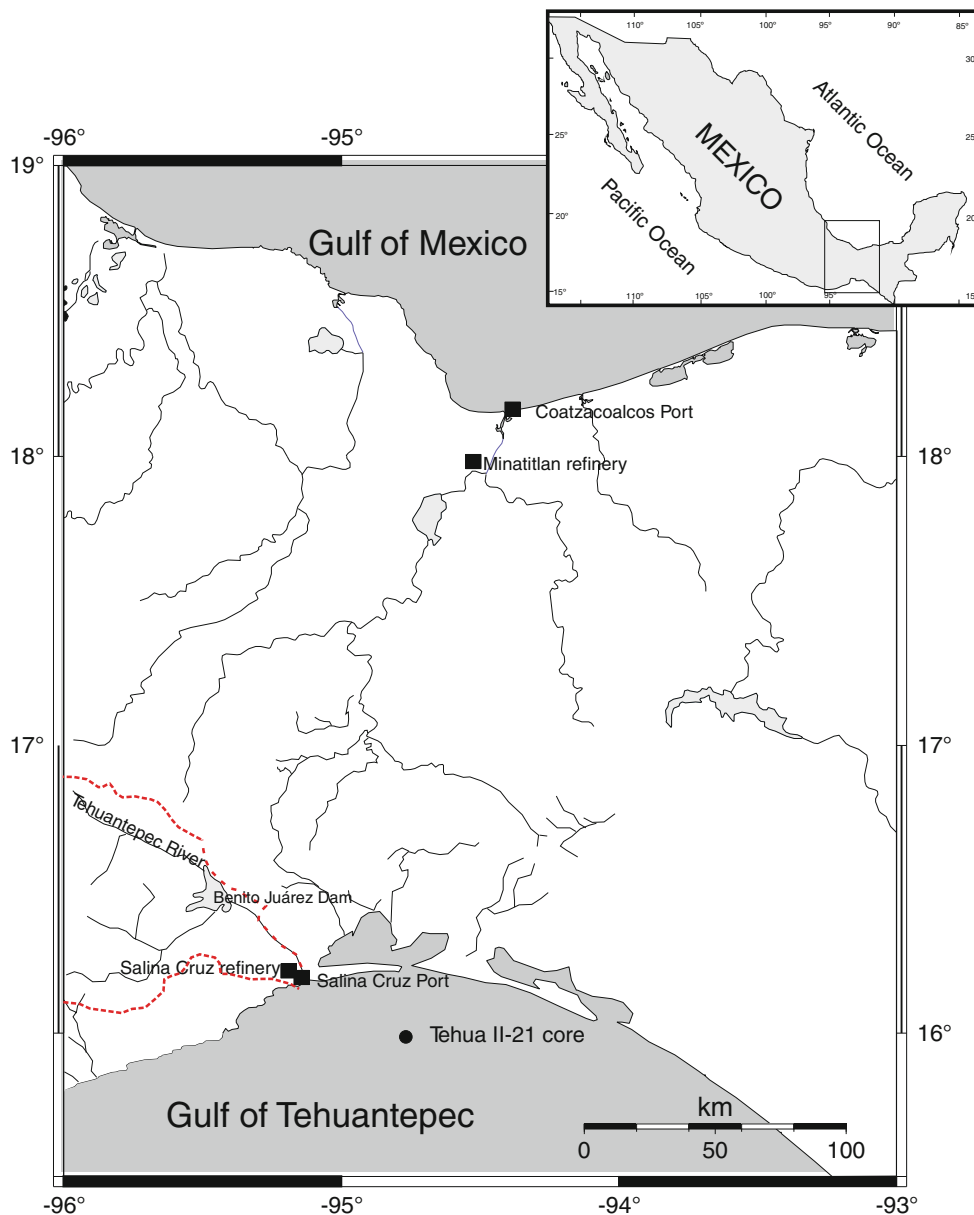


Fig. 1 Map of the study area showing the sampling point in the Gulf of Tehuantepec (~45 km distance from the refinery of Salina Cruz); the catchment area of Tehuantepec River (dashed lines) and the Benito Juárez dam

winds (regionally known as “Tehuano”) cross the Isthmus of Tehuantepec through the Gulf of Mexico, reaching the coastal area of the Gulf of Tehuantepec at speeds of 10–30 m s⁻¹.

The coastal plain of Oaxaca is composed by Mesozoic sedimentary rocks (limestone, sandstone and lutite) and Quaternary alluvial soils (INEGI 2011a) resulting from intense hydric erosion and the aridization of the central part of Oaxaca State (García-Mendoza et al. 2004). The predominant soil type in Oaxaca State is regosol (formed by hydric and aeolian erosion, enhanced due to deforestation and land use changes; SEMARNAT 2000) and cambisol in the coastal zone (INEGI 2011b) mostly composed by arenosol (aeolic sediments) and fluvisol derived from the fluvial valleys in Oaxaca State (García-Mendoza et al. 2004).

Industrial development

At the narrowest point of the Isthmus of Tehuantepec, only 200 km separate the Pacific Ocean from the Gulf of Mexico (Atlantic Ocean). Two main factors triggered its economic development since the end of the nineteenth century: its potential as a commercial bridge between the two oceans and the development of the oil industry in the corridor Minatitlán-Salina Cruz, in the Gulf of Tehuantepec (Fig. 1). The oil industry in Mexico initiated with the discovery of oil fields in the south of the Veracruz State (Gulf of Mexico) at the beginning of the 1900s. The first oil refinery was built in 1906 in Minatitlán (in Veracruz State) which nowadays has a current production capacity of 185 thousand barrels per day (SIE 2010). The refined oil used to be distributed by the railroad system that communicated Coatzacoalcos Port (in the Gulf of Mexico) with Salina Cruz Port (in the Gulf of Tehuantepec). Salina Cruz Port was closed due to infilling in 1933, reopened in 1938 and, in 1939, the Minatitlán refinery and Salina Cruz Port were connected through a pipeline transporting crude oil to storage tanks. Since then, it became the main Mexican oil export port in the Pacific coast (Martínez-Laguna et al. 2002). During the 1940s and 1950s there was an important development in the area, including the establishment of several factories (cement, limestone and pop-soda), the construction of the Panamerican (1942–1947) and Transisthmus (1946–1958) roads and the impoundment of Tehuantepec River in 1955, with the purpose to irrigate vast extensions of agriculture fields (Ruiz-Fernández et al. 2009 and references therein). The oil refinery of Salina Cruz (the main refining facility of Mexico) became operative in 1978 and was further expanded (in 1981 and 1983) to increase the original production capacity of 170,000 barrels per day to the current capacity of 330,000 barrels per day, which accounts for 22% of the Mexican refined products (SIE 2010).

Materials and methods

Sampling

The sediment core Tehua II-21 (15°59.99'N, 94°48.47'W, 67-m depth) was collected from the Gulf of Tehuantepec coastal zone in October 2004, on board of the O/V El Puma during the cruise Tehua II (Fig. 1) by introducing a PVC liner (inner diameter 10 cm) in the sediment collected with a Reineck-type box corer. Neither laminations nor evidences of sediment disruption (such as infauna excavation activity, sediment cracks, gas bubbles) were observed in the core. The sediment core, 18 cm long, was sliced every 0.3 cm from surface down to 10 cm depth, and every 1 cm for the rest of the core. The samples were freeze-dried and ground with a porcelain mortar and pestle before analyses (excepting for grain size analysis).

Analyses

The methods used for geochemical characterisation and radiometric dating were reported in detail in Ruiz-Fernández et al. (2009). Briefly, grain size distribution was obtained by the standard methods of wet sieving and pipette analysis according to Folk (1974) and the organic matter (OM) content was determined by using chromic acid wet combustion (Walkley and Black 1934); results are expressed as percent by weight (% w/w). ²¹⁰Pb activities were determined through its daughter ²¹⁰Po in equilibrium by alpha spectrometry (Schell and Nevissi 1983); the extraction of ²¹⁰Po and ²⁰⁹Po (used as yield tracer) was done according to Flynn (1968). ¹³⁷Cs and ²²⁶Ra were measured by γ -ray spectrometry in an HPGe well-detector at GEOTOP-UQAM facilities. Replicate analyses ($n = 12$) of the standard reference material IAEA-300 (Radionuclides in Baltic sea sediment) confirmed good agreement for ²¹⁰Pb and ¹³⁷Cs.

Mineralogical assemblages were determined by X-ray diffraction (XRD) at GEOTOP-UQAM. About 2 cm³ of sediment sample was scattered in deionised water and sieved on a 63- μ m mesh. The <63 μ m fraction was decalcified in 0.1 N HCl and the excess acid removed by repeated washings in deionised water and centrifugations. The <2 μ m fraction (clay particles) was separated by using the Millipore filter transfer method and oriented mounts were made using the “glass slide method” (Moore and Reynolds 1989). The samples were then analysed on a Siemens X-ray diffractometer with CoK α radiation. Each slide was scanned three times: (1) under dry air conditions (scan from 2° to 45° 2 θ), (2) under ethylene-glycol solvation (during 24 h, scan from 2° to 30° 2 θ) and (3) after heating (at 500°C for 4 h, scan from 2° to 30° 2 θ). Semi-quantitative estimations ($\pm 5\%$) were based on the area of

three main diffraction peaks measured after ethylene–glycol solvation (Peak-height ratio method, Biscaye 1965). The heights of the diffraction peaks of smectite (17 Å), illite (10 Å) and chlorite + kaolinite (7 Å) were multiplied by the width at half height and the peak areas were summed to represent 100%. The results are reported as weighted peak area percentages of the clay minerals (%). In addition, the sand and silt sample fractions were ground, the powder was packed (back-loading sample preparation, Klug and Alexander 1974) in plastic holders and analysed as randomly oriented mounts. The samples were scanned between 2° and 70° 2 θ . Semiquantitative calculations followed the method of Cook et al. (1975).

The infrared spectrophotometric method ISO/TR 11046 (ISO 2005) was used to quantify the Total Recoverable Petroleum Hydrocarbons (TRPH) that correspond to the high molecular weight ($12 < C < 40$) fraction of TPHs, also known as the diesel range organics (DRO) that do not include gasoline and the biodegradable animal greases and vegetable oils. This method is considered as a screening technique for the identification of petroleum products and for remediation of sites (ATSDR 1999; Rauckyte et al. 2010). The lighter congeners can be more dangerous but, being more volatile, are less particle reactive. Two grams of sediment was accelerate solvent extracted (ASE 200) using a hexane/isooctane (1:1 v/v) mixture. The extracts were purified by elution through a Florisil (5 g) column using 30 ml of hexane/isooctane (1:1 v/v). Elutions were dissolved in carbon tetrachloride and finally analysed with a Thermo Nicolet FT-IR with narrow band mercury cadmium telluride (MCT) detector in the range 2,925–2,958 cm^{-1} . Detection limit was circa 0.5 $\mu\text{g g}^{-1}$ and the repeatability, based on six analyses of the same sample, was better than 10%.

PAHs analysis considered the 16 USEPA priority pollutant PAHs, 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. Total PAHs (ΣPAHs) represent the sum of the 16 USEPA priority congeners. On the basis of the number of aromatic rings, individual PAHs were grouped into low molecular weight PAHs (LMW, $<200 \text{ g mol}^{-1}$, 2–3 benzene rings) including Na, Acy, Ace, Fl, Phe and An; and high molecular weight (HMW, $>200 \text{ g mol}^{-1}$, 3–6 benzene rings) including Flt, Py, BaAn, Ch, BbFlt, BkFlt, BaPy, BghiPe, Ipy and DahAn (Nagpal 1993).

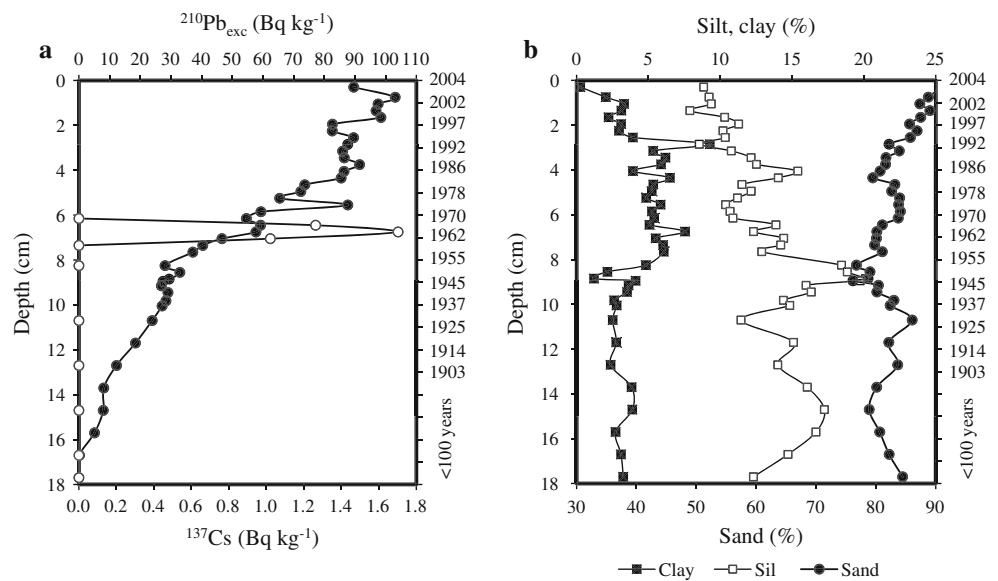
PAHs were extracted from circa 2 g of freeze-dried sediment by means of accelerate solvent extraction (DIONEX ASE 200) using hexane/acetone (80:20 v/v). For quantification, a solution of six deuterated PAHs (Ace d-10; Flt d-10; Phe d-10; BaAn d-12; BaPy d-12; DahAn d-12) was added to the samples as internal standards before extraction. The extracts, concentrated and re-dissolved with 0.5 mL cyclohexane, were purified by column chromatography using a solid phase extraction cartridge containing 2 g silica and eluted first with 10 mL of n-hexane and then with a 20 mL cyclohexane:acetone (70:30) mixture. Final extracts were concentrated and re-dissolved with 400 μL solution of two deuterated PAHs (acenaphthylene d-8 and chrysene d-12) and then analysed by capillary column gas chromatography and mass spectrometric detection. All the gas–mass analyses were carried out by a Thermo Fisher DSQ-Trace GC–MS. An analytical column (95% dimethyl, 5% phenyl–polysiloxane) 30 mm \times 0.25 mm \times 0.25 μm was used to separate PAH molecules. The temperature program was the following: 80°C maintained for 1.5 min, to 200°C at a 15°C/min, then to 305°C at a 7°C/min and isothermal for 10 min. The injection volume was 1 μL in splitless mode. Operative conditions were: ion source 280°C, inlet 250°C and He as carrier gas (1.2 mL/min). PAH molecules were identified by their GC-retention time in comparison with reference compounds and literature data. However, for more reliable identification, data were complemented with mass spectral data obtained from the MS NIST library. The mass spectrometer operated at an EI of 70 eV. After identification of PAH molecules, mass spectrometer operated in selective ion monitoring (SIM) mode to enhance the sensibility and accuracy of the instrument. Laboratory quality control procedures included analyses of blanks and reference material BCR-535. Instrument stability and reproducibility was checked using NIST standard solutions. Estimated recovery for each compound ranged between 94% and 107%. Accuracy was better than 90% for each single molecule. Repeatability, estimated on triplicate samples, was $\geq 90\%$. The limit of detection was estimated at $\geq 5 \text{ ng/g}$ for each PAH. All results were calculated with respect to dry weight.

Results

Core chronology

A full description of the core ^{210}Pb chronology is published in detail elsewhere (Ruiz-Fernández et al. 2009). Briefly, the ^{210}Pb -derived geochronology was obtained by using the Constant Flux model (or CRS model: Appleby and Oldfield 1992) that assumes a constant flux of ^{210}Pb to the sediment.

Fig. 2 **a** ^{210}Pb and ^{137}Cs data for sediment core Tehua II-21; the ^{210}Pb -derived chronology was obtained by using the CRS model; **b** grain size depth distribution. The figures are based on data published in Ruiz-Fernández et al. (2009)



The Tehua II-21 core provided a record of ~ 100 years from surface to 13-cm depth (1906–2004, Fig. 2a) and the age model was validated by the presence of the ^{137}Cs peak in 1963 at 6.75-cm depth. Sediment accumulation rates ranged from 0.03 to 0.21 cm year^{-1} , corresponding to mass accumulation rates of 0.05–0.29 $\text{g cm}^{-2} \text{year}^{-1}$.

Sediment characterisation

Grain size and organic matter content

The sediments in core Tehua II-21 were characterised by low content of organic matter (0.5–1.6%) (data not shown) and high presence of fine sand (76–89%; Fig. 2b). The abundances of silt and clay were usually <10 and $<20\%$, respectively, and their depth distribution profiles showed a significant decreasing trend from 8.5-cm depth (corresponding to the early 1950s) towards the core top.

XRD-mineralogy and sediment provenance

The temporal variation of mineral assemblages in the different grain size fractions of the sediments accumulated in the core was used to identify changes in the main particle sources. The stratigraphic variations of the mineral assemblages in marine sediments is commonly used to infer differences in sediment provenance, because the mineralogical composition can provide information on the source areas (Middleton 2003).

The mineral abundances (%) of the different sediment size fractions are presented in Table 1. Sand and silt fractions have K-feldspars and NaCa-plagioclase as the main constituents, respectively; and the abundance intervals

Table 1 Mineral composition (%) of the sand, silt and clay fractions in Tehua II-21 sediments

Mineral	Abundance (%)		Mineral	Abundance (%)
	Silt fraction	Sand fraction		
Plagioclase	20–53	7–76	Kaolinite	17–53
Feldspars	12–53	16–70	Smectite	16–49
Quartz	14–49	3–18	Illite	19–39
Calcite	3–14	1–18	Chlorite	2–5
Dolomite	0.6–6	0.1–5		
Amphiboles	0.5–4	0.2–6		
Micas	1–3	1–5		
Haematite	0.2–4	0.3–3		
Chlorite	<0.1 –0.5	0.2–3		
Magnetite	0.1–3	0.1–2		
Apatite	<0.1 –2	0.1–2		
Gypsum	<0.1 –0.7	<0.1		

of both detrital minerals were comparable at each grain size fraction. Quartz and calcite were also present in considerable amounts, together with small quantities of amphiboles, micas, dolomite, haematite, chlorite, magnetite, apatite and traces of gypsum. The abundance depth distribution of most of the major minerals in the sand and silt fractions was somewhat erratic (Fig. 3a, d). Most of the peak values of the amphiboles, K-feldspar and NaCa-plagioclase were observed upcore (above 9-cm depth, i.e., 1945). A significant ($P < 0.05$) inverse correlation was found between the abundances of K-feldspars and NaCa-plagioclase in both silt and sand fractions ($r = -0.55$ and -0.78 , respectively) which was explained on the basis of weathering susceptibility, since the plagioclase is much

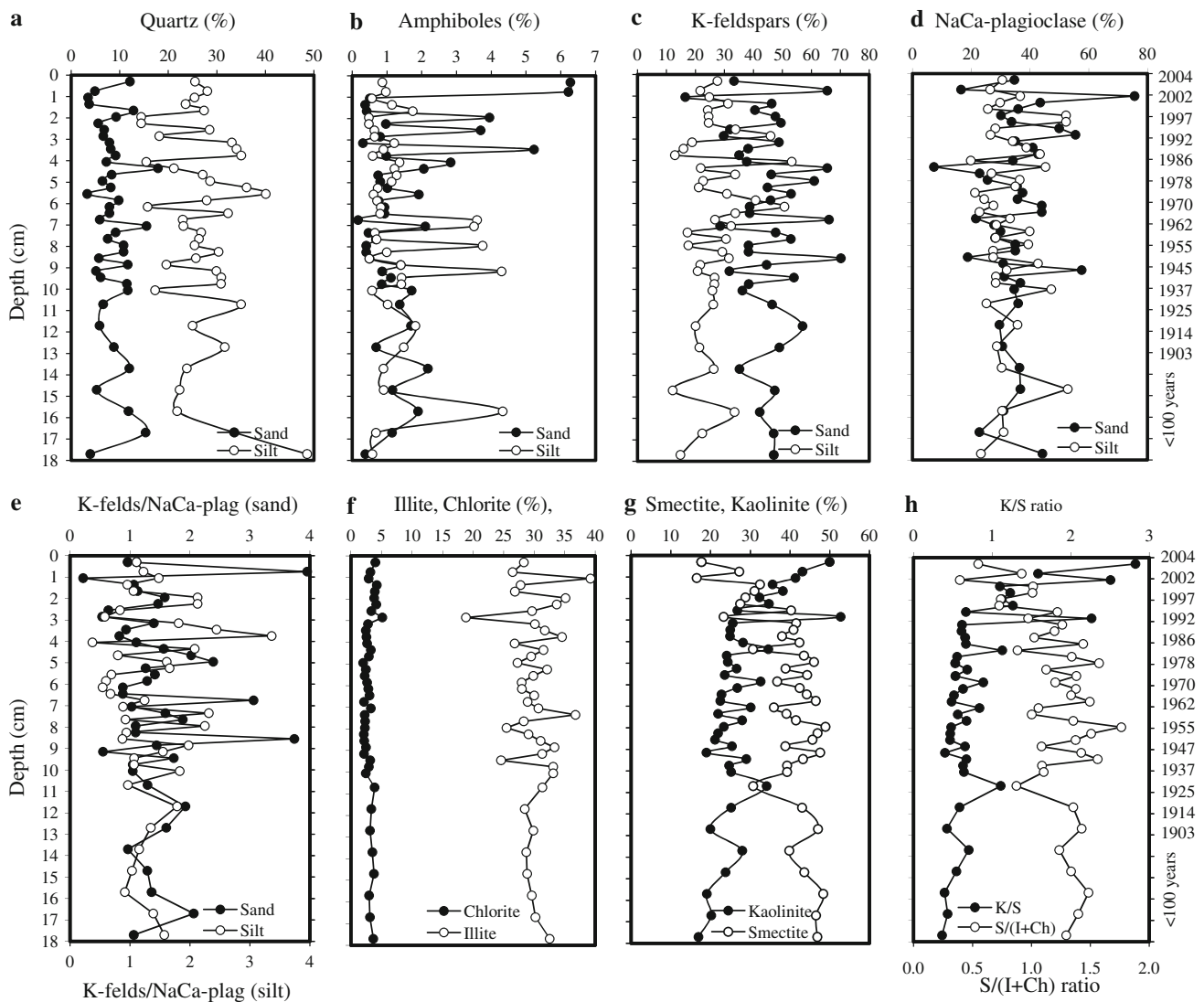


Fig. 3 Time dependent profiles of XRD-mineral abundances in Tehua II-21 sediments. Sand and silt fractions: **a** quartz, **b** amphibols, **c** K-feldspars, **d** NaCa-plagioclase and **e** K-feldspars/NaCa-plagioclase

ratio. Clay fraction: **f** illite and chlorite, **g** smectite and kaolinite, **h** kaolinite/smectite (K/S) ratio and smectite/(illite + chlorite) (S/(I + Ch)) ratio

less resistant to weathering than K-feldspars (Kendall and McDonnell 1998) thus, the peak values of K-feldspar/NaCa-plagioclase ratios in the most recent core layers (Fig. 3e) are indicative of higher chemically weathered sediments.

In the clay size fraction, kaolinite, smectite and illite were present in comparable abundances and chlorite was lower than 5% (Table 1). The depth profiles of illite and chlorite were consistent along the core (Fig. 3e) whereas kaolinite and smectite contents varied significantly with depth ($P < 0.05$). Abundances of kaolinite and smectite started to increase and decrease, respectively, at 8-cm depth (ca. 1954) showing a significant inverse correlation to each other ($P < 0.05$, $r = -0.91$, Fig. 3f). Smectite abundances correlated significantly ($P < 0.05$) with sand

($r = -0.64$) and silt ($r = 0.61$) contents; both smectite abundance and silt content showed a conspicuous decreasing trend starting in the early 1950s (Fig. 2b). The smectite/(illite + chlorite) (Fig. 3h) also showed significant ($P < 0.05$) correlations with depth, with an inflexion point at 8-cm depth (i.e. 1954).

Clay minerals are mostly of terrigenous origin, resulting from the hydrolytic decomposition of primary minerals during terrestrial weathering, and erosion processes are responsible for their transport, by fluvial and/or aerial input, to the near-continent ocean environment (Rao and Rao 1995; Petschick et al. 1996). Illite and chlorite are considered primary minerals, inherited from parental rocks (heritage process) which reflect the direct rock erosion under cold and arid (dry) climatic conditions, when

physical weathering is dominant (Liu et al. 2004); both are considered indicative of weak weathering intensities (Singer 1984). Chlorite is relatively uniformly distributed on the continents, although it is destroyed by chemical weathering in the warm and humid climates of the tropical areas, and hence does not reach the ocean in significant amounts (Petschick et al. 1996). Smectite is formed at low precipitation rates (dry conditions) by moderate leaching under temperate conditions, and kaolinite forms at the highest leaching intensities (more humid and warmer conditions). Clay mineral assemblages have been widely used to reconstruct changes in terrestrial climate (Calvert and Pedersen 2008 and references therein). However, it has been also demonstrated that changes in marine clay mineral assemblages do not systematically reflect changes in weathering conditions in the continental source area, but rather changes in clay mineral source areas or transport media (Fagel 2007). The negative correlation between the abundances of kaolinite and smectite has been used to explain changes in environmental conditions that cause the replacement of the prevalent sediment source (Thomas and Murray 1989; Liu et al. 2005). The relatively higher kaolinite/smectite (K/S) ratios indicate strengthened chemical weathering (Liu et al. 2004) and identify warm and humid climate with enhanced terrestrial runoff (Wing et al. 2003). The changes in smectite/(illite + chlorite) i.e., S/(I + C) ratio have been used to evidence variations in the balance between chemical and physical erosion on land, and/or in source materials induced by fluvial and/or aeolian contributions (Liu et al. 2005).

There is no information on the mineralogy of the continental area surrounding the Gulf of Tehuantepec and, therefore, it is difficult to ascertain the definitive provenance of the sediments accumulated at the Tehua II-21 sampling site. However, our observations indicated a shift in the sediment source, starting in the 1950s, as indicated by significant ($P < 0.05$) inverse correlation between smectite and kaolinite. Since flood plain environments are particularly favourable for smectite development (Thiry 2000) we concluded that before the mid 1950s, smectite rich sediments were mostly derived from the alluvial soils that cover the coastal plain of Tehuantepec Gulf. The sporadic peak values of K-feldspar/NaCa plagioclase ratios observed in the sand and silt fractions in the younger section of the core (since the late 1940s) also indicate episodic contributions of more weathered sediments (Kendall and McDonnell 1998) which could originate from weathered soils. Smectite (and silt) started to decrease since the mid 1950s, when the Tehuantepec river was impounded (1955). It is reported that Tehuantepec river sediment discharge reduced from 5 to $1.5 \cdot 10^6 \text{ m}^3 \text{ year}^{-1}$ after being dammed (Carranza-Edwards 1980). Since then, the relatively higher K/S ratios suggest

a higher contribution of sediments derived from a source characterised by soils formed in a wet and warm environment, such as tropical humid zones (Fagel 2007). The transfer of soils into the sea initially requires physical erosion, with the intensity of deflation and abrasion essentially dependent on the vegetation cover (Zabel et al. 2001). Thus, the supply of terrigenous sediment increases with deforestation promoted by urbanisation and industrialisation of the region. Between 1950 and 1970 the coastal zone of Oaxaca had important transformations to sustain the economical development at the Tehuantepec Isthmus, including the impoundments of Tehuantepec River in 1955 for agriculture irrigation purposes and the construction of Transisthmus highway (1946–1958). The possible source of kaolinite enriched sediments might be the Zoque forest, the largest tract of tropical rainforest in Mexico, which is located between Oaxaca and Veracruz States. This area is reported to have high erosion rates as a consequence of intense deforestation (Arriaga et al. 2000). Winds are known to be an important agent for transporting significant amounts of terrestrial materials to the oceans (Windom 1975); as the study area is under the seasonal influence of the strong Northern winds, the aeolian transport could be a plausible mechanism of transport to the Gulf of Tehuantepec.

Petroleum hydrocarbons

Total petroleum hydrocarbons

The TPH concentrations ranged from 29 to 154 mg kg^{-1} (Fig. 4a; Table 2). These concentrations are above: (1) those reported for unpolluted sediments (typically below 10 mg kg^{-1} , Readman et al. 2002); (2) the limit suggested by Garcia et al. (1998) as indicative of contamination by fuel and oil residues (47 mg kg^{-1}) and (3) in most of the sediment layers, the value of 65 mg kg^{-1} , which is the TPH (DRO-derived) limit (LDEQ 2003) for screening studies on sediments affected by oil spills, e.g., the sediments deposited by receding flood waters after the hurricanes Katrina and Rita (EPA 2009) or the response programs for oil spills in the USA (FDEP 2010; EPA 2010).

The depth distribution profile of the TPH concentrations showed two distinctive segments, one between 9 and 12.7 cm (1906–1945) with a maximum value in 1914, and a second one (between 1945 and 2004) characterised by an increasing trend toward the surface of the core with the maximum values found between 1997 and 1998. No significant correlations were found between TPHs values and the grain size distribution or the organic matter content in the sediments, and therefore their relation with the TPHs depth profile was not further discussed.

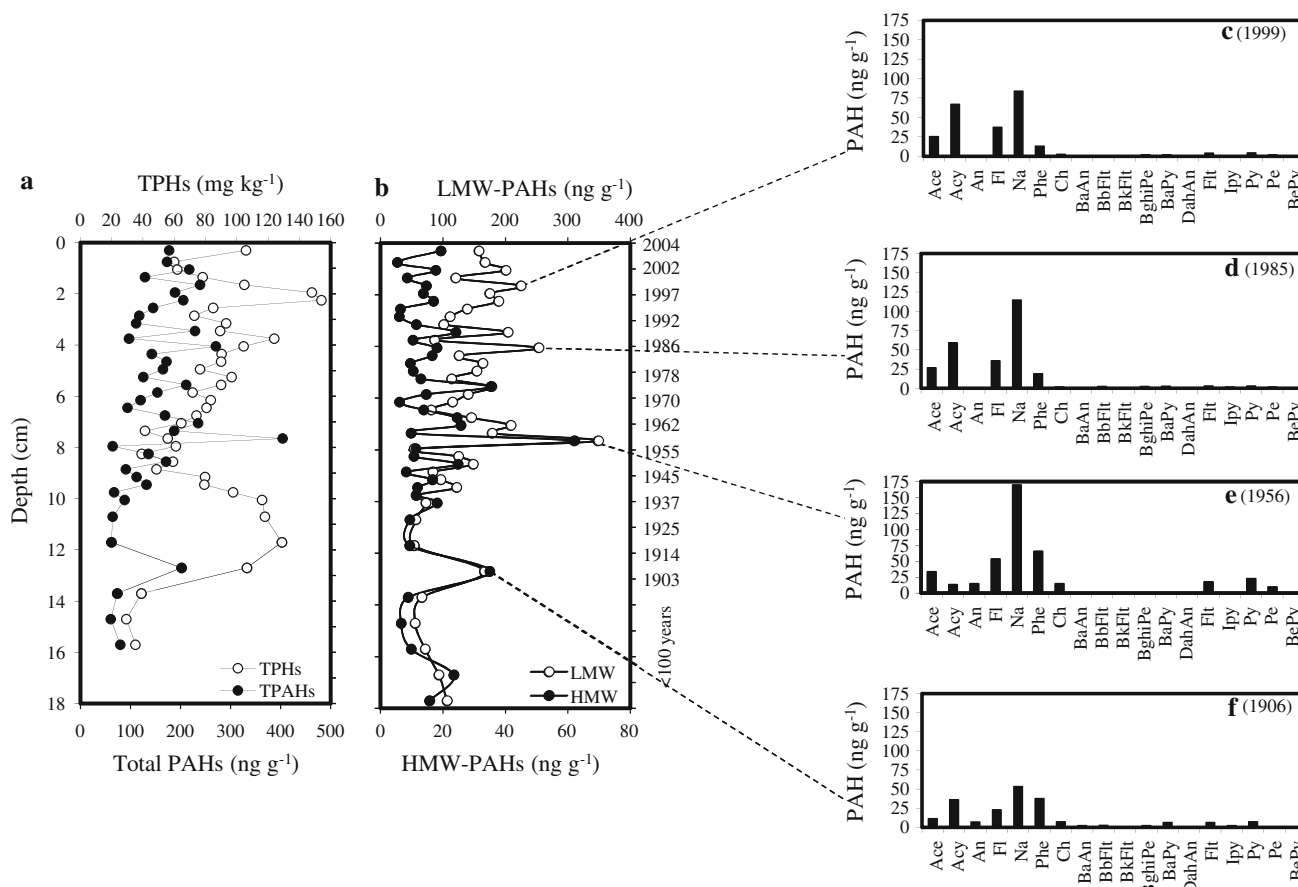


Fig. 4 Organic pollutants depth profiles in core Tehua II-21. **a** TPHs and total PAHs (as the sum of the 16 US Environmental Protection Agency priority congeners). **b** Low molecular weight and high

molecular weight PAHs. Individual PAHs concentrations (ng g⁻¹) in selected years: **c** 1999, **d** 1985, **e** 1956 and **f** 1906

PAH concentrations

Total PAH concentrations span the interval 61–404 ng g⁻¹ (Fig. 4; Table 2). These values were within the range reported by Botello et al. (1998) for oceanic surface sediments in the surroundings of Salina Cruz Bay (20–320 ng g⁻¹) but much lower (up to 3 orders of magnitude) than concentrations found in surface sediments collected from continental aquatic environments adjacent to the study site: 100–142,000 ng g⁻¹ (González-Lozano et al. 2006), 30–3,200 ng g⁻¹ (Botello et al. 1998) and 300–3,090 ng g⁻¹ (González-Macías et al. 2007). The total PAH concentrations were below the marine sediment screening benchmark of 2,900 ng g⁻¹ (EPA 2011) but were in the range of low polluted sediments (>100 ng g⁻¹; Tolosa et al. 2004 and references therein).

The low molecular weight (LMW) PAHs were predominant in Tehua II-21 sediments (Fig. 5) accounting for more than 80% of the total concentrations (Table 2). The prevalent congener was Na (between 10 and 50% of the LMW PAH concentrations) followed by Acy ≈ Phe > Fl > Ace > An. The high molecular weight PAHs were found in very low concentrations, Py being the prevalent

congener. At these levels, PAHs have a low probability of being toxic, since they were consistently below the Effects Range Low (ERL) benchmarks (the concentration of a contaminant above which harmful effects to biota may be expected to occur; Buchman 2008); although the peak values of some LMW-PAHs exceeded the ERL limits for single congeners (Table 2) and, therefore, could have been (or still be) unsafe for aquatic organisms (i.e., Na peak value in 1956, Ace values during 1950–1964, Acy during 1985–2004, and Fl values in 1906 and during 1940–2004).

Several PAHs, and especially their metabolic products, are known to be carcinogenic (Conney 1982; Connell et al. 1997). Total concentration of potentially carcinogenic PAHs (CPAHs, defined as the sum of BaPy, BaAn, BbFlt, BkFlt, Ch, DBahAn and Ipy) ranged from 0.8 to 19.9 ng g⁻¹ and accounted for 1–10% of total PAHs. Among all known CPAHs, BaPy is the only one for which toxicological data are sufficient for derivation of a carcinogenic potency factor (Peters et al. 1999). Toxicities of other PAHs can be quantified relative to BaPy, expressed as toxic equivalency factors (TEFs), which are used to

Table 2 Hydrocarbon concentrations in Tehua II-21 sediment core

	LMW PAHs (ng g ⁻¹)										HMW PAHs (ng g ⁻¹)					ΣPAH	TPH			
	Acc	Acy	An	Fl	Na	Phe	Flt	Py	BaAn	Ch	BbFlt	BkFlt	BaPy	BghiPe	Ipy			DahAn		
Min	1.7	9.0	1.2	2.3	9.8	9.8	2.5	1.6	ND	ND	ND	ND	ND	ND	ND	ND	54.1	4.5	60.7	29.4
Max	33.3	66.8	14.9	53.3	169	65.3	17.3	22.7	2.0	14.6	1.6	8.9	3.1	3.2	1.9	1.9	349.5	54.6	404.1	154.1
ERL	16	44	85.3	19	160	240	600	665	261	384	NA	430	NA	NA	NA	63.4	552	1,700	4,022 ^a	NA ^b

TPHs are in mg kg⁻¹, total PAHs (ΣPAH) and PAH congeners are in ng g⁻¹

ND no detectable (below minimal detectable concentration), NA not available, LMW low molecular weight PAHs, HMW high molecular weight PAHs, ERL effects range low (Buchman 2008)

^a The screening value for ecological risk assessment is 2,900 ng g⁻¹ (EPA 2011)

^b The screening level for management or evaluation is 65 mg kg⁻¹ (LDEQ 2003)

estimate BaPy-equivalent doses (BaPy_{eq}dose). According to the US Environmental Protection Agency (Schoeny and Poirier 1993), TEFs for BaPy, BaAn, BbFlt, BkFlt, Ch, DBahAn and Ipy were 1, 0.1, 0.1, 0.1, 0.01, 0.4 and 0.1, respectively. Total toxic BaPy equivalents (TEQs) of all these CPAHs range from 0.01 to 9.89 ngTEQ g⁻¹ in the core, which were considerably low values if compared with carcinogenic risk concentration for BaPy (100 ng g⁻¹; CalEPA 1994).

The depth distribution of total PAHs and LMW PAHs (Fig. 4a, b) showed that, with exception of the peak values at 12.7-cm depth (1906), higher concentrations of these compounds were found in the upper core segment (above 9-cm depth, year 1945). Figure 4c to f show the relative importance of the individual PAHs at depths where total PAH peak values were significant. The PAHs congener content was not constant, and some LMW compounds (such as An and Phe) that were present in considerable amount in the older layer of the core (i.e., 1906 and 1956, Fig. 4e, f) were less important (Phe) or absent (An) in the youngest segments (1985 and 1999, Fig. 4c, d); in contrast, Acy concentrations showed the opposite tendency: lower values in 1906 and 1956, and higher values in 1985 and 1999.

Similarly to TPHs, no significant correlations ($P < 0.05$) were found between PAHs and organic matter concentration or any of the sediment grain size fractions. This lack of correlation suggested that the concentrations of TPHs and PAHs in the sediment core were driven by variations of the pollutant inputs, and not by changes in textural or chemical characteristics of the sediments.

PAH sources

Significant correlations ($r \geq 0.43$, $P < 0.05$) were found amongst some PAH congener concentrations, such as Na, Ace, Acy, Fl, Phe, Flt, Ch, Py and Pe, suggesting that they may have a common origin and behaviour. PAH congeners in marine sediments are generally derived from three main sources: petrogenic, pyrogenic and biogenic. The ratios between concentrations of PAH congeners or sums of congeners, e.g., LMW/HMW PAHs have been successfully used to assess the provenance of PAHs in the environment elsewhere (e.g., Prahl and Carpenter 1983; Canton and Grimalt 1992). Petrogenic sources are characterised by LMW/HMW >1, Phe/An >15, Ch/BaAn \geq 4 and Flt/Py <1 (Readman et al. 2002; Soclo et al. 2000). Furthermore, the PAH isomer ratios An/(An + Phe) and Ipy/(Ipy + BghiPe) might be useful to differentiate among combustion sources: An/(An + Phe) values <0.10 indicate that PAHs were formed by petroleum combustion and >0.10 suggest that the PAHs source was coal combustion (Fu et al. 2009 and references therein). In turn, Ipy/(Ipy + BghiPe) values <0.2 indicate petroleum, 0.2–0.5 petroleum combustion,

and >0.5 coal, grass and wood (Prahl and Carpenter 1983). The same series of information was provided by values <0.4, between 0.4 and 0.5, and >0.5 of the Flu/(Flu + Py) ratios (Li et al. 2006).

The predominance of LMW over HMW PAHs (LMW/HMW >1, Fig. 5a) indicative of petrogenic sources, i.e., direct discharges of crude or non-combusted oil, mainly of anthropogenic origin (Choudhary and Routh 2010 and references therein), was recorded in the sediment core since the beginning of the twentieth century, although the ratio increased considerably from the middle 1940s. This petrogenic origin was corroborated by the ratios Ch/BaAn (values ≥ 4 , Fig. 5b). Phe/An and Flt/Py ratios suggested

the presence also of pyrogenic PAHs along the core, though confirmed the prevalence of PAHs derived from petrogenic sources, especially in sediments above 5-cm depth (1978). Also Phe/An values <15 (off scale in Fig. 5c) and Flt/Py ratios >1 (Fig. 5d) indicated the influence of pyrogenic sources (mostly below 5-cm depth). Furthermore, both An/(An + Phe), Flt/(Flt + Py) and Ipy/(Ipy + BghiPe) ratios (Fig. 5e, f) traced the contribution of mixed pyrogenic sources (petroleum as well as coal, grass and wood combustion). Ipy/(Ipy + BghiPe) values <0.2 (Fig. 5g) evidenced the presence of PAHs derived from unburned petroleum above 5-cm depth (1978), in agreement with the Phe/An and Flt/Py ratios (Fig. 5c, d) but also

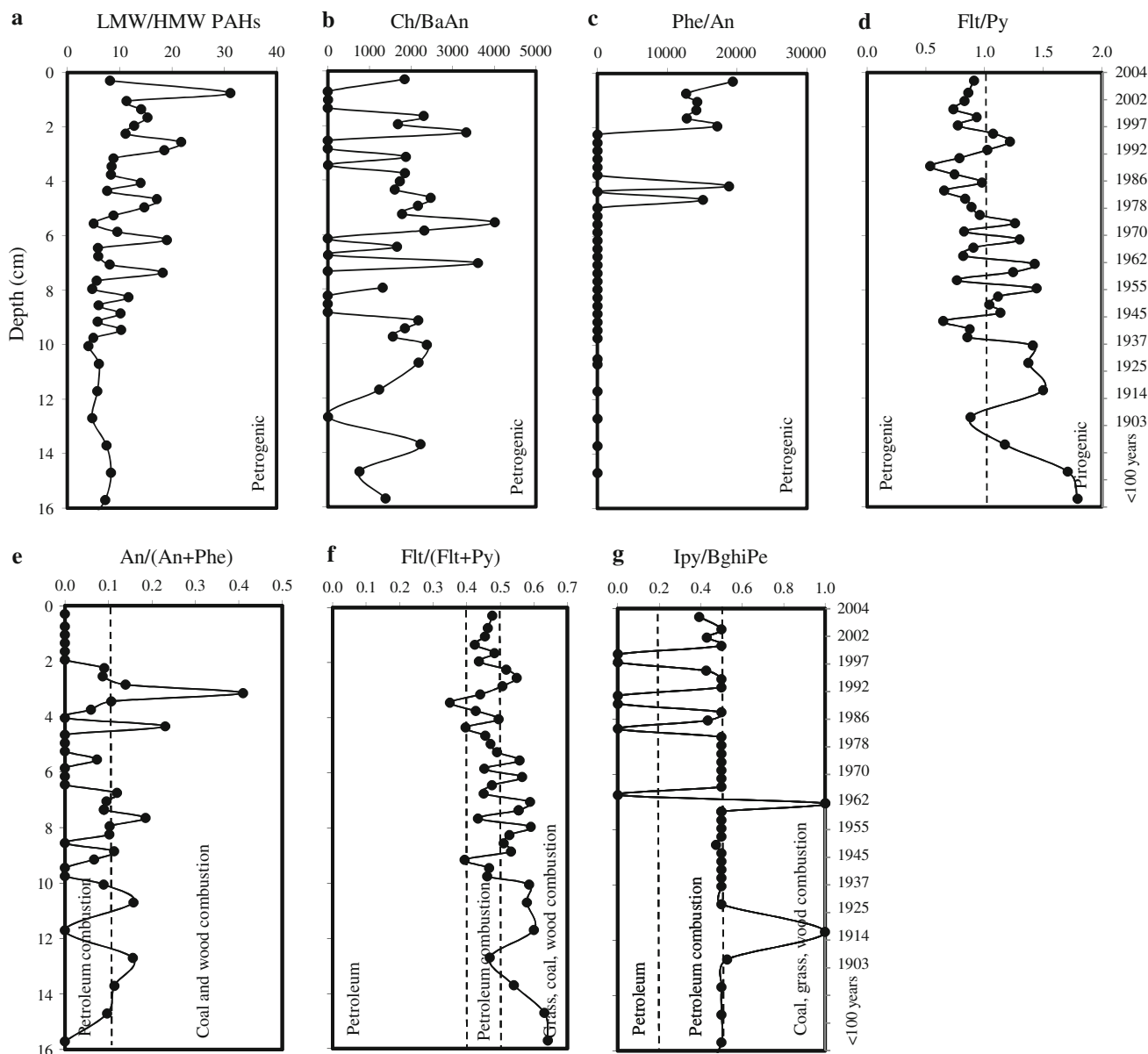


Fig. 5 PAH congener ratios in core Tehua II-21. The dashed lines indicate the limit to distinguish between sources indicated in the plots (see explanation in the text). a LMW/HMW PAHs, b Ch/BaAn, c Phe/An, d Flt/Py e An/(An + Phe), f Flt/(Flt + Py), g Ipy/BghiPe

showed a peak value at 6.8-cm depth (1964). The Ipy/(Ipy + BghiPe) peak values observed in sediments at 7- and 11.7-cm depth (1918 and 1961) clearly distinguished the presence of PAHs derived from the combustion of coal, grass and wood.

Perylene (Pe) is reported to be a diagenetic product of terrigenous (plant residues, peat deposits) and marine (phytoplankton, diatoms, foraminifera, etc.) organic matter (Venkatesan 1988; Yunker et al. 1993; Loring et al. 1995; Page et al. 1999). However, the organic matter at the site was low and Pe could be also produced from petroleum or pyrolytic processes (Soclo et al. 2000). In such cases Pe usually would represent between 1 and 4% of the total PAHs (Fang et al. 2003). Pe concentrations in Tehua II-21 sediments ranged from 1 to 9 ng g⁻¹, which account between 1 and 3.5% of total PAHs and therefore it may be most likely due to pyrogenic sources.

Discussion

The economical development in the Isthmus of Tehuantepec has been mostly based on the oil industry activities which started at the beginning of the twentieth century with the operation of Minatitlan refinery (in the Gulf of Mexico) and the Salina Cruz Port (in the Gulf of Tehuantepec), being the main conduit for oil exports. The sediment core Tehua II-21 provided a historical record of the environmental changes related with the development of the economical activities in the region in the period 1906–2004.

The record of TPHs and PAHs concentrations in Tehua II-21 sediments showed oil pollution since the beginning of the past century. The TPHs record showed a peak value in 1906 and an increasing trend between 1945 and 2004, whereas the PAHs depth distribution (Fig. 4a) showed higher values (above 100 ng g⁻¹) in 1906 and between 1943 and 2004. Nonetheless, no significant correlation ($P < 0.05$) was found between the two groups of organic pollutants. Similar findings reported by Readman et al. (2002) were attributed to diverse primary sources and/or differing transport processes for the two classes of compounds. For example, it was proposed that combustion derived PAHs would have aeolian components to their transport mechanisms, whereas petrogenic PAHs would be predominantly fluvial.

Congener concentration showed that PAHs accumulated in Tehua II-21 sediments had a mixed origin, both petrogenic and pyrogenic. The predominant abundance of LMW-PAHs and the high values of Ch/BaAn (≥ 4) indicate the prevalence of petroleum sources along the core, whereas Phe/An, Flt/Py and Ipy/BghiPe ratios showed that PAHs derived from the petroleum sources were more relevant in the sediments accumulated after 1976, but that

there were important contributions of pyrogenic PAHs in the precedent decades. These pyrogenic PAHs were also the result of mixed sources. The Flt/(Flt + Py) ratio showed the dominance of PAHs derived from combustion of grass, coal and wood in sediments between 1906 and 1940, a mixed signal from both sources between 1940 and 1978 and a predominant signature of petroleum combustion between 1976 and 2004.

The sediment records of TPHs, LMW-PAHs, as well as the PAH ratios LMW/HMW, Ch/(BaAn), Phe/An, Flt/Py, Flt/(Flt + Py) and Ipy/BghiPe were consistent with the historical development of the oil industry in the Isthmus of Tehuantepec. Sediments showed signs of oil pollution since the beginning of the past century, as evidenced by the pattern of TPH discussed above.

The TPH and total PAH depth profiles were not completely in agreement, but the presence of PAHs and the peak values of TPHs found between 1906 and the late 1930s (Fig. 4a) were most likely related with the activities of the Minatitlan refinery and the shipping operations in Salina Cruz harbour (e.g., oil spills, harbour ship scraping). The stop of shipping in the harbour in the middle 1930s decreased the overall release of hydrocarbons to the environment. Things changed with the onset of the industrialization period in the region starting in the 1940, which was reflected by the increasing trends in TPHs and the higher values of total PAHs observed since then. The prevalent petrogenic signature of PAHs observed since the late 1970s was most likely related with the oil production activities of the Salina Cruz refinery. Oil spills caused by pipeline damages are very frequent in the coastal zones of this region since 1980 (González-Lozano et al. 2006). González-Macías et al. (2007) have also found an increasing temporal trend of total aromatic hydrocarbons (TAHs) concentrations in Salina Cruz Bay analysing surface sediment samples collected during 20 years (between 1982 and 2002) and related such contamination with industrial activities, atmospheric input and domestic sewage contribution, all of them from continental runoff.

The provenance of the combustion derived products (mostly recorded from the beginning of the century until the late 1970s according to Flt/Py and Ipy/BghiPe ratios) remains uncertain. Possible sources include the recurrent wild forest fires across the Isthmus of Tehuantepec, particularly the dry forest in the coastal plain of Oaxaca (García-Mendoza et al. 2004), as well as the intentional burning of the tropical rain forests to build roads, to support new urban settlements and for agriculture and ranching purposes. Another potential source could be the atmospheric transfer of organic contaminants from the oil refinery of Minatitlán, carried by the strong northern winds that seasonally blow from the Atlantic to the Pacific Ocean through the Isthmus of Tehuantepec. According to

Simpson et al. (1996), hydrocarbons input by fluvial transport do not reach significant distances (>30 km) because of rapid particle removal from the water column along the way; however, it is feasible that a significant amount of particle-adsorbed PAHs is transferred by aeolian transport over distances of at least 100 km.

From the stratigraphic variations of the mineral assemblages in core Tehua II-21, a shift in provenance of the sediments accumulated in the core was observed since the 1940s (as suggested by the K-feldspar/NaCa plagioclase ratios in the sand and silt fractions) and the 1950s (as shown by the S/(I + Ch) ratios in the clay fraction). Before this period, sediments in the core were mostly derived from the alluvial soils surrounding the coastal plain of Tehuantepec Gulf, but since the middle 1950s, a higher contribution of more weathered sediments was evidenced, most likely derived from the erosion of soils following the tropical deforestation in the Northern part of the Isthmus of Tehuantepec. We considered that the most important factor influencing the change in sediment source was the damming of Tehuantepec River in 1955, and that the most weathered soils are transported across the Isthmus of Tehuantepec by the strong winds that occur in the region. This mechanism was probably the same that transported combustion derived products from Minatitlán to the Gulf of Tehuantepec since its operation at the beginning of the past century.

Conclusions

A sediment core, collected from the continental shelf of Tehuantepec Gulf, was analysed to reconstruct the historical trends of organic contamination in relation with the oil industry development in the Tehuantepec Isthmus. Despite the coarse sediment composition and the dynamic environment of the sampling area, the ^{210}Pb -derived age model agreed well with the history of the development of the oil industry in the region, told by changes in the time evolution of PAHs and TPHs concentrations, which also emphasise the impact of the oil refining industry and related harbour activities on the environmental conditions of the coastal zone. No evidence was found of harmful hydrocarbon pollution, either by total PAHs or TPHs, as most values were lower than international benchmarks. This was most likely a consequence of the strong coastal hydrodynamics in the Gulf of Tehuantepec, which disperses the contaminants and favour the accumulation of sandy particles. According to the PAHs congener ratios (LMW/HMW, Flt/Py, Phe/An; Ch/BaAn, Ipy/BghiPe) the composition of the mixtures accounts for a preponderant contribution from petrogenic sources since late 1970s, most likely resulting from the oil transport, refining and shipping in Salina Cruz.

There was also evidence of important contributions of pyrogenic derived PAHs and their probable origin was related with the forest fires in the region, as well as with the oil industry activities taking place in the industrial zone of Minatitlán in the Gulf of Mexico, most likely supplied by aeolic transport. Although the observations derived from this study are limited to a single core, it shows the usefulness of this strategy to reconstruct the impact of land-based activities on a marine environment where environmental data is relatively scarce.

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