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Sedimentary record of PAHs in the Barigui River and its relation to the socioeconomic development of Curitiba, Brazil

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HIGHLIGHTS

• The changing concentration and patterns of PAHs distribution over the past 150 years have been recorded.
• Sources of PAHs might be associated with several historical episodes.
• Indices of socio-economic development are positively correlated with PAH inputs to the sediments from 1855 to 1970.

Abstract

Concentrations of polycyclic aromatic hydrocarbons (PAHs) were determined in a sediment core collected from the Barigui River, in Curitiba, South Brazil. The USEPA's 16 priority PAH concentrations ranged from 39 ng g⁻¹ to 2350 ng g⁻¹ of dry sediment over a period that corresponds temporally to between ca. 1855 and 2011. The concentrations and patterns of PAH distribution changed over this time period and may be associated with several episodes in the Curitiba's history. Two major PAHs concentration peaks occurred in approximately 1910 and 1970, which might reflect population increases due to immigration programs in the 1890s and the sudden economic development that occurred in Brazil from 1960 to 1980, "The Economic Miracle Period", respectively. Isomeric ratios revealed that the PAHs had predominantly pyrolytic sources. The population, number of highways and electric energy consumption of Curitiba, as indices of socioeconomic development, were positively correlated with PAH deposition in the sediment core from 1855 to 1970, indicating the influence of socioeconomic development on the environmental load of sedimentary PAHs.

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1. Introduction

Sediments are very important in aquatic ecosystems, as they can store nutrients, organic matter and pollutants, sometimes returning these substances to the water column. Sediments can be used to reconstruct the past and in particular to identify the impact of human population growth and land settlement. For example, since the middle of the last century, it has been possible to identify numerous pollutants in lake sediments, which reflect the demand for hydrocarbon consumption and other anthropogenic chemicals in modern society (Souza et al., 2011; Froehner et al., 2009; Venturini et al., 2008; Chen et al., 2004).

The demand for fossil fuels and the settlement of land has led to an increase in PAH concentrations in soils and sediments. They are often used as chemical markers to identify potential sources of environmental pollution from crude oil, gasoline and diesel (Froehner et al., 2012; Liu et al., 2008; Lee et al., 2005; Savinov et al., 2003; Yunker et al., 1999). PAHs can enter into the environment from different sources, which are primarily pyrolytic or petrogenic; biogenic sources are also possible. PAHs of pyrolytic origin are attributed to the incomplete combustion of fossil organic matter at high temperatures (Yunker et al., 2002). By contrast, petrogenic PAHs are produced when organic matter is matured over geological time through a geothermal gradient (Wan et al., 2005). The contribution of PAHs derived by microbial activity is considered small and has not yet been fully described (Bzdusek et al., 2004; Opene et al., 2007; Soclo et al., 2000).

The thermodynamics of the pyrogenic and petrogenic formation of PAHs, lead to different abundances of isomers, and the ratios between

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these can be used to identify the predominant source. Following the ratios proposed by Yunker et al. (2002), it is possible to infer the main contributing sources of petrogenic or pyrolytic PAHs. Thermodynamically stable isomers usually derive from petrogenic sources, while less stable isomers are of pyrolytic origin (Budzinski et al., 1997; Yunker et al., 2002). Hence, the formation of PAHs depends on the reaction temperature. At relatively low temperatures (catagenesis), the distribution of PAHs is governed by thermodynamic properties, while at elevated temperatures (pyrolysis) the distribution of these compounds is dominated by kinetic characteristics (Yunker et al., 2002, 1999; Yunker and MacDonald, 1995). For example, high concentrations of PAHs with more than four aromatic rings are indicative of the formation of the compounds during the pyrolysis of fossil fuels (Gogou et al., 2000) while forest, grass and prairie fires have distinct isomeric PAH distributions (Yunker et al., 2002). PAHs can be degraded in the environment and under aerobic conditions of sedimentation, microbial degradation of PAHs has to be considered. However, this is largely limited to PAHs with 2–3 aromatic rings, while PAHs of higher molecular weight are more resistant to degradation (Cerniglia, 1992).

Regardless of the source of PAHs in the environment, these compounds can be extremely valuable in the historical reconstruction of pollutants release into the environment (Guo et al., 2011; Itoh et al., 2010; Kannan et al., 2005). Consequently, it is possible to assess the influence of historical anthropogenic activity on local ecosystems (Liu et al., 2012). The settlement of areas near rivers contributes to the deposition of pollutants associated with population growth and industrial processes (Mitra et al., 1999; Huntley et al., 1995). However there have been few studies reporting PAHs in river sediments. Hence, the goals of our study were: (a) to reconstruct a history of PAH contamination in the Barigui River, Curitiba by exploring the relative influence of past pollution events and the management policies implemented in this area over the last 150 years and (b) to establish the relationship between socioeconomic development and the PAH burden of the sediments.

2. Materials and methods

2.1. Study area and sampling

The study area is the watershed of the Barigui River located on the First Parana Plateau, in the metropolitan region of Curitiba, Brazil, between 25°13′24″ and 25°38′23″ South and 49°15′00″ and 49°22′29″ West, oriented in the north–south direction toward the cities of Almirante Tamandare, Curitiba, and Araucaria (Fig. 1). The Barigui River is 67 km long, draining a watershed of 279 km², with 120 km² of drainage located

Fig. 1. Map of the Barigui Basin and sampling site.
in the municipality of Almirante Tamandare, 144 km² in the municipality of Curitiba, and 15 km² in the municipality of Araucaria. The pattern of drainage is predominantly dendritic (Froehner and Martins, 2008). The sampling station was located at latitude 25°23′55.81″ and longitude 37°35′33.84″, inside Tingui Park. Currently, the study area is surrounded by roads with intense and heavy traffic. Settlement is largely urban with residential use; the main economic activities are trade and services.

The site for sampling was selected according to previous monitoring campaigns, which define this area as reliable for collection and encompass the most significant data (Dombroski et al., 2012; Froehner and Martins, 2008). The selected site has been strongly influenced by urbanization. The Barigui River flows from north to south through the City of Curitiba. The sediment core sample was collected in November 2011 using a small gravity corer with a 6-cm diameter core barrel. The core sample was transported to riverside, extruded and sectioned at 2 cm intervals to a depth of 40 cm. Below 40 cm, the core was sectioned every 4 cm to 60 cm and then every 10 cm to 100 cm. The core sections were stored at 4 °C during transport to the laboratory, where they were frozen (−20 °C) and lyophilized prior to analysis. The core sections were characterized according to granulometric composition, age (chronology) and PAH content and distributions.

**Fig. 2.** Vertical profiles of $^{210}$Pb and $^{137}$Cs, in Bq kg$^{-1}$, the location of the $^{137}$Cs peak from fallout of 1963 is indicated by a dotted line (2A). Vertical profiles of the mass flux and sedimentation rate in the core from Barigui River (2B).
2.2. Granulometric composition

The sand, silt and clay content analyses were carried out at the Laboratory of Mineral and Rock Analysis (LAMIR-UFPR) using an integrated technique (sieving and laser diffraction). Briefly, samples were passed through a set of sieves with standardized mesh screens (mesh sizes 8, 14, 42, 80, 170, 250, 400, 500 and 635). The classification in sand, silt and clay was carried out according the Wentworth granulometric scale.

Fig. 3. Temporal changes in concentrations of PAHs in sediment core from Barigui River.
(Besler and Ritter, 2010). The fine grains were collected and analyzed with a laser analyzer that measures the grain size by detecting the diffraction angle from a bunch of light after it had passed through the sample in an optical cell (Froehner and Martins, 2008).

2.3. Extraction, separation and analysis of PAHs

The procedure described by Hofmann et al. (2011) was followed, with minor modifications. Bulk sediment (5 g) was extracted using an accelerated solvent extractor (ASE; Dionex) in 5-minute static cycles (100 °C; 4 MPa) with dichloromethane (DCM) and acetone (1:1). Any elemental sulfur was removed from the extracts using activated copper, which was added directly after the extraction. The PAH fraction was isolated using columns (7 mm i.d.) filled with silica gel (approx. 1.3 g), first eluted with hexane (3 × 4 mL; Fraction 1) and then DCM (3 × 4 mL; Fraction 2). The latter contained the PAHs and was reduced in volume to approximately 0.5 mL prior to addition of a standard. It was then completely dried with nitrogen prior to dissolution in 200 μL of hexane, for analysis. A solution with 16 PAHs USEPA priority pollutants (AccuStandard PAH Mix Z-014G) was used as a standard solution to obtain a calibration curve for quantification. The mixture was composed of anthracene (ANT), acenaphthylene (ANP), acenaphthene (AEN), phenanthrene (PHE), fluorene (FLU), pyrene (PYR), indeno[1,2,3-cd]pyrene (ICP), benzo[a]pyrene (BaP), benzo[k]fluoranthene (BkF), benzo[b]fluoranthene (BbF), chrysene (CHR), dibenz[a,h]anthracene (DhA), benzo[g,h,i]perylene (Bgp), benzo[a]anthracene (BaA), fluoranthene (FLA), and naphthalene (NAP). Immediately before analysis, a deuterated PAH (fluroine-d10) was added to each sample as a standard, while acenaphthen-d8 was added before the extraction as to monitor the efficiency of the analytical procedure. The recovery rates were higher than 75% in most of PAHs. All solvents were HPLC grade; silica gel was extracted with DCM (24 h) and activated in an oven (400 °C; 4 h).

2.4. Analysis of PAHs by gas chromatography/mass spectrometry (GC/MS)

PAHs were identified and quantified by GC–MS using a Varian 450 gas chromatograph (GC) coupled to a Varian 320 Quadrupole mass spectrometer with electron-impact ionization. The GC was equipped with a Factor Four VF 5MS fused silica capillary column (60 m, 0.25 mm i.d., 0.25 μm film thickness) and helium as a carrier gas with a constant flow of 1.2 mL min⁻¹. The GC oven was programmed from 40 °C to 200 °C (at 5 °C min⁻¹), with an initial hold of 1 min at 200 °C and a final hold of 16 min at 280 °C. Both a full scan and a selected ion monitoring (SIM) modes were applied. PAHs were identified by comparing retention time with those of the appropriate authentic standards and published spectra. Quantitative analysis was performed using internal and external calibration methods, and the limit of detection was 10 ng g⁻¹.

2.5. Gamma spectrometry analysis

For the radionuclide measurements, approximately 20 g of sediment was transferred into air-sealed cylindrical polyethylene containers (base circular area of 21.7 cm², height of 1.1 cm and volume of 23.9 cm³) for gamma counting in an EG&G ORTEC® low-background gamma spectrometer (hyper-pure Ge, model GMX25190P). This equipment is characterized by a mean resolution of 1.97 keV for the 1332.35 keV 60Co photopeak and is coupled to an EG&G ORTEC® buffer type system (SPECTRUM MASTER, model 919) and a computer (IBM-PC 486). The analysis of the gamma spectra was performed using EG&G ORTEC® software (MAESTRO, version 5). The method, which was previously described by Figueira (2000), consists of detector calibration, background radiation detection, detector counting efficiency assessment and sample counting for 50,000 s.

The self-absorption correction of the samples was performed for gamma lines of energy inferior to 100 keV (e.g., 46.52 keV photopeak of 210Pb). The correction was made by comparing the areas of the 59.54 keV peak of the 241Am of the background container coupled to a 241Am (59.54 keV) source and the sample coupled to a 241Am source, according to Figueira (2000), resulting in self-absorption correction factors between 103 and 118%.

The determination of the minimum detectable activities (MDAs) of the elements of interest (the lowest activity that can be determined with 95% certainty) was performed according to Neves et al. (2014), resulting in MDAs of 1.47 Bq kg⁻¹ for 210Pb, 1.66 Bq kg⁻¹ for 226Ra and 0.28 Bq kg⁻¹ for 137Cs. All results obtained for the samples were above the MDAs of the studied radionuclides. Two models were used to calculate the sedimentation rate: CIC (Concentration Initial Concentration of unsupported 210Pb) (Robbins and Edgington, 1975) and CRS (Constant Rate of Supply of unsupported 210Pb) (Appleby and Oldfield, 1978) models according to Neves et al. (2014). From sedimentation rate the dating of samples was established, considering the core length and the time of collection. Moreover, the precision and accuracy of the methodology were evaluated through the determination of the radionuclides of interest (210Pb, 226Ra and 137Cs) in three certified reference materials: IAEA-326 (soil), IAEA-327 (soil) and IAEA-385 (marine sediment). Precision was checked using relative standard deviation (RSD), and accuracy was assessed using the relative error (RE) of the data generated from these measurements. The activity concentrations obtained for the certified radionuclide were close to the reported values with mean deviations and errors not exceeding 6%.

To confirm the results provided by the CIC and CRS models, the vertical profile of 137Cs activity was determined, verifying the location of the 137Cs peak of 1963, which corresponds to the global maximum.
fallout from a past nuclear test, and the profile was compared to the results from CIC and CRS models.

2.6. Statistical analysis

Pearson correlation tests ($P < 0.05$) were carried out using GraphPad Prism version 5.00 for Windows (GraphPad Software, San Diego, CA) in order to assess the linear interdependence among variables in the data matrix.

3. Results and discussion

3.1. Dating results

Fig. 2A shows the vertical profiles of $^{210}$Pb and $^{137}$Cs in Bq kg$^{-1}$. The location of the $^{137}$Cs peak of 1963, corresponding to the global maximum fallout from a past nuclear explosion and was used to compare and endorse the dating results presented in this study. Fig. 2B presents the vertical mass flux and sedimentation rate in the various subsamples of the core from Barigui River.

3.2. PAH distributions

The individual concentrations of PAHs ranged from 39 to 2350 ng g$^{-1}$, while the $\Sigma16$ PAHs varied from 1766 ng g$^{-1}$ to 14,924 ng g$^{-1}$ from 1855 to 2011 (Fig. 3). The distribution of PAHs was dominated by pyrene and phenanthrene in all samples. Indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene were found only in two time intervals, 1910–1920 and the 1985 sediment horizon, ranging in concentration from 100 to 780 ng g$^{-1}$.

The distribution of PAHs in the surficial sediment sample (0 to 2 cm) was similar to those reported in other studies conducted in Brazil (Santanna et al., 2010; Nishigima et al., 2001; Zanardi et al., 1999). This is the first report to our knowledge of the temporal distribution of the PAHs in Curitiba, although their distribution in surface sediments of the Barigui River has been described (Froehner et al., 2012).
The main concern about the presence of PAHs in sediments is their toxicological impact on the ecosystem, which is dependent on their concentration. Hence, sediments can be classified as moderately contaminated when the PAH concentration is between 200 and 3000 ng g\(^{-1}\), whereas a concentration higher than 3000 ng g\(^{-1}\) labels sediments as highly contaminated (Benlahcen et al., 1997).

In this study, most of the core samples can be classified as moderately contaminated; however, the sub-samples from 0 to 10 cm have higher concentrations of PAHs than those from the deepest section.

Levels of PAHs depend on the potential sources of emission. Particular sources may be responsible for the simultaneous emission of several PAHs. The sedimentary concentrations of all PAHs apart from fluorene are significantly correlated (R > 0.6, P < 0.01), suggesting that the PAH contamination in the Barigui River originated from the similar sources during the period studied or were influenced by a similar deposition process. The PAH concentrations in the surface sediments (2011) are similar to those sediments corresponding to 2000, suggesting that regional and local sources may be the primary contributors in this period. Local sources could include municipal storm water runoff, wastewater treatment plants, vehicular emissions, and asphalt dust.

### 3.2.1. Temporal distributions of PAHs

Based on the sediment chronology, changes in \(\Sigma 16\) PAH concentrations and those of the individual PAHs were determined (Fig. 3). \(\Sigma 16\) PAH concentrations increased between approximately 1855 and 1910 (1996 ng g\(^{-1}\) to 7176 ng g\(^{-1}\)), decreased and then increased dramatically to 1766 ng g\(^{-1}\) in 1940. During this period, high molecular weight PAHs concentrations (>202) were dominant, mainly pyrene and fluorene. The \(\Sigma 16\) PAHs increased in concentration again after 1940, and the maximum was observed in 1971 (14,924 ng g\(^{-1}\)); the concentration then gradually decreased to 5142 ng g\(^{-1}\) in 2011. After 1940, low molecular weight PAHs (<202) dominate, mainly naphthalene and phenanthrene (Fig. 3).

The peaks in \(\Sigma 16\) PAH concentrations coincide with particular historical events during the development and settlement of the Curitiba region. For example, the first peak in concentration, which occurred around 1910, may reflect population growth due to immigration programs of the 1890s. From 1960 to 1980, Brazil experienced a sudden economic development, the “Economic Miracle” (Azevedo and Barcellos, 2011), and this could account for the highest PAHs concentrations, which apparently occurred in the 1970s.

The concentration of sedimentary PAHs is dependent on the sedimentation rates and grain size, chemical stability and emission factors (Yunker et al., 2002). The sedimentation rate in the Barigui River has been relatively constant over time (0.44 g cm\(^{-2}\) yr\(^{-1}\), ± 0.09), suggesting no influence on the PAHs concentrations e.g. by sediment dilution.

The core has significant variation in its granulometric composition according to Fig. 4. In general, sand (63–2000 μm) and silt (4–63 μm) size fractions dominated most samples, while the clay content (<4 μm) was minor. Usually, hydrophobic compounds such as PAHs are sorbed by fine particles (silt and clay), and modern sediments with high silt and clay contents have high PAHs concentrations. However, there is no significant correlation between the PAHs and fine sediment particles in the Barigui core, indicating that concentration does not depend exclusively on sediment grain size (Santanna et al., 2010). Hence, the controlling factors of the PAHs concentrations might be outside the sedimentary environment, such as the pathway between the source and the sediment, often under influence of diagenetic processes and changes in the hydrologic conditions in the watershed (Gelinas et al., 2001).

The chemical stability of PAHs is another factor that plays an important role in their preservation and therefore, sedimentary concentrations. Biomass and fossil fuel combustion produce aerosols with very different particle sizes and physical properties (Schmidt and Noack, 2000). These differences may affect both the dispersion pathways in the environment and the physical protection afforded to the PAHs (Gelinas et al., 2001). The black carbon of wood soot consists of large,
dark and refractory particles that provide a solid matrix that traps and stabilizes PAHs (Schmidt and Noack, 2000). This protection is greater for high molecular weight PAHs than for those with low molecular weight (Yunker et al., 2002). Thus, the predominance of high molecular weight PAHs (HMW) concentrations (≈200) until 1940 and low molecular weight (≈200) PAHs after 1940 (Fig. 3) may reveal influences of the source; alternatively, it may be related to the physical protection level of PAHs produced by grass and wood combustion. In addition, low molecular weight PAHs are more susceptible to degradation in the atmosphere and water column, as they are more volatile and soluble.

### 3.2.2. Sources of PAHs

Assessments of PAHs distributions and diagnostic ratios have been widely used for apportioning their sources in environmental samples. Different PAH sources may provide specific patterns or signatures, which can be used to identify the sources (Liu et al., 2012; Liu et al., 2005). According to Yunker et al. (1999), PAHs can be grouped in two subsets on the basis of their stability. The first is composed of less stable PAHs formed during combustion processes; the second includes more thermodynamically stable compounds. Considering the isomers formed by different processes, the relative ratio of a given molecular mass can be used to identify the possible source of PAHs (Yunker et al., 2002). Such ratios are useful to identify the possible contribution of PAHs in the environment (Table 2).

The presence of PAHs in sediments with a ratio of FLA/(FLA + PYR) lower than 0.4 suggests a source typically from petroleum contamination (Yunker et al., 2002, 1999); a FLA/(FLA + PYR) ratio higher than 0.5 indicates that the PAHs are mainly from the combustion of grass, wood, and coal; 0.4 < FLA/(FLA + PYR) < 0.5 indicates the combustion of petroleum (Yunker et al., 2002). In Bariguí core, the ratio of FLA/(FLA + PYR) was 0.53 to 0.68 (≈0.50, Fig. 5) between 1855 and 1920, indicating a predominance of pyrogenic sources, mostly wood combustion (0.51 ± 0.06), grass combustion (0.58 ± 0.04) and bush fires (0.61; Table 2). The maximum observed concentration of ΣPAHs in approximately 1910 (Fig. 5) could be associated with the sudden increase of the population of Curitiba by 102% in the 1900s (IPPUC, 2009), leading to the removal of the vegetation in large areas (bush fire, wood, and grass combustion). A FLA/(FLA + PYR) ratio of 0.62 is consistent with the fluorescent and pyrene content in creosote used as wood preservative; such a signal post-1885 could reflect the period when the railway line was installed in Curitiba City.

Over the period from 1920 to 2011, the ratio of FLA/(FLA + PYR) was 0.14–0.49 (≈0.5, Fig. 5), consistent with a mix of combustion and contaminant petroleum sources. The period between 1965 and 1985, when the ratio of FLA/(FLA + PYR) was slightly lower than 0.5 (0.4–0.5, Fig. 5), most likely reflects the increase in automobile traffic attributed to the rapid economic development of Brazil, the “Economic Miracle,” in 1960–1980 (Azevedo and Barcellos, 2011). Engine combustion and vehicle emissions are typical pyrogenic sources. While the ratio ANT/(ANT + PHE) can be used to identify sources of PAHs, the small difference in energy between pyrolysis and petrogenic process means that this ratio is less sensitive (Yunker et al., 2002). ANT/(ANT + PHE) values of >0.1 indicate or <0.10 can be interpreted as typical of pyrogenic and petroleum sources, respectively, but care should be taken due to the insensitivity of the ratio (Budzinski et al., 2011). On the other hand in samples representative of the period between 1855 and 1930, ANT/(ANT + PHE) ratios were significantly higher than 0.1 (0.26–0.42, Fig. 5), suggesting pyrogenic sources (>0.10, Fig. 5) and supporting the interpretation of the FLA/(FLA + PYR) ratios. After the 1930s, the ratios decreased (0.15–0.29), suggesting a mixture of combustion and contamination by petroleum sources such as used engine oil and gasoline vehicles (0.22), road dust (0.18), gasoline, diesel and crude oil combustion (0.11–0.27) and creosote (0.20) (Table 2).

The ANT/(ANT + PHE) ratio can also be influenced by the preferential degradation/removal of phenanthrene due its higher solubility (1.1 mg L⁻¹) when compared to anthracene (0.045 mg L⁻¹) (Netto et al., 2000), particularly post the 1930s, when the soil of wood and grass combustion contributions apparently decreased, also decreasing the physical protection of these PAHs. In consequence of decrease in physical protection, the PAHs became more exposed and those more soluble such as phenanthrene degrade easier.

PAHs with molecular weight of 228 (chrysene and benzo[a]anthracene) are used less frequently as indicators of contaminant sources. In addition, they are usually minor components in refined petroleum products (Gogou et al., 2000), although they are present in significant amounts in higher boiling point fractions including asphalt and, possibly bitumen or coal (Readman et al., 1987). A BaA/CHR ratio higher than 0.33 suggests typical combustion sources, whereas a BaA/CHR ratio between 0.20 and 0.35 indicates a mixture of combustion and petroleum sources; values lower than 0.20 indicate petroleum sources (Yunker et al., 2002). In the Curitiba samples, the BaA/CHR ratios show a Gaussian distribution over time that is most likely associated to heterogeneous sources (Fig. 4). According to Yunker et al. (2002) such behavior shows

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**Table 2**

PAHs ratios for petroleum, single-source combustion and environmental samples (Yunker et al., 2002).

<table>
<thead>
<tr>
<th>Source</th>
<th>FLA/(FLA + PYR)</th>
<th>ANT/(ANT + PHE)</th>
<th>BaA/CHR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum</td>
<td>0.46</td>
<td>0.04</td>
<td>0.35</td>
</tr>
<tr>
<td>Kerosene</td>
<td>0.26 (±0.16)</td>
<td>0.09 (±0.05)</td>
<td>0.35 (±0.04)</td>
</tr>
<tr>
<td>Diesel oil</td>
<td>0.22 (±0.07)</td>
<td>0.07</td>
<td>0.12 (±0.06)</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>0.29 (0.17–0.30)</td>
<td>–</td>
<td>0.11–0.12</td>
</tr>
<tr>
<td>Asphalt</td>
<td>–</td>
<td>–</td>
<td>0.50</td>
</tr>
<tr>
<td>Combustion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood soot</td>
<td>0.50</td>
<td>0.26</td>
<td>0.43–0.49</td>
</tr>
<tr>
<td>Grasses</td>
<td>0.51 (±0.06)</td>
<td>0.14–0.29</td>
<td>0.40–0.52</td>
</tr>
<tr>
<td>Gasoline</td>
<td>0.44</td>
<td>0.13–0.26</td>
<td>0.46 (±0.02)</td>
</tr>
<tr>
<td>Kerosene</td>
<td>0.50</td>
<td>0.12–0.16</td>
<td>0.30–0.44</td>
</tr>
<tr>
<td>Diesel</td>
<td>0.39 (±0.11)</td>
<td>0.01–0.27</td>
<td>0.38 (±0.01)</td>
</tr>
<tr>
<td>Fuel oil</td>
<td>0.51</td>
<td>0.06</td>
<td>0.17 (±0.05)</td>
</tr>
<tr>
<td>Crude oil</td>
<td>0.44 (±0.02)</td>
<td>0.22–0.26</td>
<td>0.49 (±0.01)</td>
</tr>
<tr>
<td>Environmental samples</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bush fire</td>
<td>0.61</td>
<td>–</td>
<td>0.23</td>
</tr>
<tr>
<td>Road dust</td>
<td>0.42</td>
<td>0.18</td>
<td>0.11</td>
</tr>
<tr>
<td>Used engine oil, gasoline car</td>
<td>0.30</td>
<td>0.22</td>
<td>0.50</td>
</tr>
<tr>
<td>Used engine oil, diesel cars</td>
<td>0.37</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Creosote</td>
<td>0.62 (±0.01)</td>
<td>0.20 (±0.05)</td>
<td>0.50 (±0.03)</td>
</tr>
</tbody>
</table>
**Fig. 6.** Relationship between the $\Sigma_{16}$ PAH concentrations in the sediment core with the socioeconomic indicator data (population, number of highways and energy consumption) of Curitiba.
the low value of such ratios. In 1855, the BaA/CHR ratio of 0.23 is typical of bush fire (Table 2); this ratio increased progressively to 0.5 in 1940, which likely can be attributed to wood combustion (0.40–0.52) and creosote (0.50 ± 0.03). The peak (in approximately 1940) indicates the additional influence of gasoline and crude oil combustion (0.44–0.50) and asphalt (0.50 ± 0.03) (Table 2). In this period, there was almost one car per inhabitant of the city (IPPUC, 2008). From 1940 to the present, a slight decrease in the BaA/CHR ratios (Fig. 3), can most likely be attributed to the same sources as the Gaussian peak added to diesel combustion (0.38 ± 0.01), fuel oil combustion (0.17 ± 0.05) and contamination by petroleum sources such as kerosene (0.35), diesel oil (0.35 ± 0.04) and lubricating oil (0.11–0.12) (Table 2), which have likely reduced the BaA/CHR ratios (Fig. 4) through to present day.

The data presented are consistent with the ratio between low molecular weight PAHs (<202, LMW) and high molecular weight PAHs (>202, HMW). LMWs are the major constituents of petroleum, while HMWs are associated with pyrogenic sources. Ratios of LMW/HMW higher than 1 suggest petroleum sources, whereas ratios of LMW/HMW lower than 1 indicate pyrogenic sources (Silva et al., 2007). In the same was as the other ratios (FLA/PYR, ANT/(PHE + ANT), BaA/CHR), the ratio of LMW/HMW in this study showed an increase since 1940 (Fig. 5), suggesting petroleum sources. According to the history of the city, the petroleum sources are likely asphalt and engine oil associated with the increase in paved streets and cars, in addition to the petroleum contamination sources mentioned earlier. However, despite increased petroleum-based contributions after 1940, during all the periods studied, there is a predominance of pyrogenic sources, which is confirmed by the strong correlation between the total PAHs and benzo[a]pyrene (R = 0.93 P < 0.01, Table 1). Negligible concentrations of benzo[a]pyrene are found in petroleum sources, and thus, a significant amount in the environment indicates pyrogenic sources.

Overall, all ratios studied showed the predominance of wood and grass combustion sources between 1855 and 1920 (Fig. 5, Table 2). The period between 1920 and 1940 might be considered a transition period, with a mixture of biomass and petroleum combustion sources. Finally, after 1940 until present, petroleum derivative combustion and petroleum derivative contamination sources predominate.

3.3. Relationship between historic regional socioeconomic data and PAHs

PAHs are produced mainly from the incomplete combustion of coal, petroleum and biomass materials and are used as a proxy to trace the impact of anthropogenic activities (Liu et al., 2012; Liu et al., 2005). Curitiba is one of the most important cities in Brazil and has undergone significant social and economic development since its founding. Previous studies have reported that the concentrations of PAHs in the environment are strongly influenced by the local human population (Zhang et al., 2013; Li et al., 2008), industrialization activities (Kumar et al., 2008), the number of vehicles (Liu et al., 2005), the length of highways and energy consumption (Liu et al., 2012).

Hence, the relationship from the 1850s to the present between PAHs concentrations and local historic socioeconomic data was evaluated to examine the influence of economic development on the local environment. In particular, we focused on the population and number of highways, and from the 1950s on electric energy consumption. The socioeconomic indices and historical records of the sedimentary PAHs are illustrated in Fig. 6 and Table 1. Pearson’s correlation coefficient (R) was used to assess their relationship.

A significant correlation among the socioeconomic data and the total PAHs concentrations in the sediment core during all the periods studied (1855–2011) (Table 1) was not found. However, a strongly significant positive correlation was observed among these data between 1855 and 1970 (Pop. R: 0.83, p: 0.0002; E.C. R: 0.97, p: 0.007; N.H. R: 0.72, p: 0.003, 1855–1970). After 1970, there is an opposite trend among the PAHs concentrations and socioeconomic data. While the PAHs concentrations decreased, the socioeconomic data continued to increase from 1970 until the present.

The population and the number of highways rose sharply from the 1960s to the present, largely due to the rapid local socioeconomic development (Fig. 6). It should be emphasized that the consumption of electric energy has sharply increased since 1970, consistent with a rise in industrialization and urbanization in Curitiba (Parigot de Souza, 1996).

In contrast, the total concentration of PAHs declined after 1970. This decrease may be related to two historic events in the city. The first is the remarkable change in the road system in 1970 (IPPUC, 2009), which shifted away the flow of heavy vehicles traveling from the north to the south of the country. In this period, there was a predominance of petroleum combustion and contamination sources that include vehicle emissions, most likely one of the major contributors to PAHs. The second historic event is the implementation in 1986 of a vehicular emission control program, which imposed 2.1 g km−1 as the limit for hydrocarbons (CONAMA, 1986). A considerable reduction in the atmospheric pollution has been reported in Curitiba in the few last decades (IPEA, 2011), despite the increase in the number of vehicles over the years, confirming the results obtained in this study (Fig. 3). Overall, the sedimentary record of PAHs contamination in the Barigui River effectively archives the history of development in Curitiba.

4. Conclusions

The record of environmental pollution in Curitiba during the last 150 years was assessed using PAHs distribution as well as isomer ratios. The highest concentration levels of PAHs occurred in approximately 1970, corresponding to the sudden economic development of Brazil between 1960 and 1980, which resulted in more fossil fuel consumption and increased combustion of petroleum derivatives. A peak with a lower concentration was detected in approximately 1910, which may reflect the increase in population due to immigration programs in the 1890s.

The strong and positive correlations indicate that most PAHs derive from the same sources or were controlled by similar deposition process. The PAHs isomer ratios showed a variation of PAHs sources, suggesting three historical periods of contamination: i) the predominance of wood and grass combustion sources (1855–1920), ii) a mixture of biomass and petroleum combustions sources, considered a transition period (1920–1940) and iii) the predominance of petroleum derivative combustion and contamination sources (1940–2011). The influence of the history of Curitiba on the PAHs sources was also apparent: increases in the population, the installation of railways, increases in the car fleet and paved streets. Although contamination from petroleum derivatives was observed, there was a predominance of pyrogenic sources, confirmed by the strong correlation between the Σ PAHs and benzo[a]pyrene.

Finally, the results provide insight into the historical input of PAHs from local and long-range sources to Curitiba and indicate an anthropogenic environmental influence, which shows that even low-level human settlement is responsible for detectable environmental changes.

Conflict of interest

We hereby state that we do not have any conflict of interest with regard to submission of this manuscript.

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