

Distribution, Sources, and Potential Ecotoxicological Risk of Polycyclic Aromatic Hydrocarbons in Surface Sediments from Bahía Blanca Estuary, Argentina

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Abstract Thirty-four surface sediment samples were collected from Bahía Blanca Estuary, Argentina, to evaluate polycyclic aromatic hydrocarbon (PAH) contamination and ecotoxicity risk by applying sediment-quality guidelines (SQGs) and toxic equivalent factors (TEQ). Total concentrations of 17 parent PAHs, including the 16 United States Environmental Protection Agency priority PAHs, were measured using gas chromatography–mass spectrometry, and their levels ranged from 19.7 to 30,054.5 ng/g dry weight. The greatest values were found near the urban/industrial core and decreasing as the distance from that site increased. Molecular ratios determined mixed sources of PAHs with a slight imposition of pyrolytic over the petrogenic inputs. The ecotoxicological evaluation, based on the SQG model, showed that some of the individual PAHs were in excess of the effects range low (ERL) and the effects range median's threshold; then, predicted occasional (ERL) and frequent adverse effects over the surrounding biota at the area of study were determined. Total PAH levels were expressed as benzo-a-pyrene TEQ and compared with literature data.

Polycyclic aromatic hydrocarbons (PAHs) are a large group of compounds composed of multiple aromatic rings fused together. They are ubiquitous persistent environmental contaminants (Neff 1979), and due to their toxic, carcinogenic, and mutagenic characteristics, 16 PAHs have been included as priority pollutants by the United States Environmental Protection Agency (USEPA). Furthermore, the USEPA has classified as Group B2, i.e., probable human carcinogens, the following seven PAHs: benzo[a]anthracene, chrysene, benzo[b]-fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and dibenzo[a,h]anthracene (USEPA 2002).

Anthropogenic activities are generally considered the major source of PAH release into the environment, even though they may have natural origins. PAHs can be introduced into marine environments by different ways; for example, atmospheric deposition, urban runoff, wastewater discharge, emissions from watercraft and vehicles, industrial processes, and spillage of fossil fuels. Once in the aquatic environment, they tend to be associated with organic matter and finally are deposited in sediments, which represent the most important reservoir of PAHs in the marine environment (Culotta et al. 2006).

The study of hydrocarbons in estuarine systems is important because these areas are highly productive and receive large amounts of pollutants from terrestrial drainage. Despite this, the Argentinian coast has not received much attention regarding PAH contamination; in fact, only a few studies have been performed over >6000 km of marine coast (Colombo et al. 1989, 2005, 2006; Esteves et al. 2006; Commendatore and Esteves 2007; Commendatore et al. 2012; Massara Paletto et al. 2008; Arias et al. 2009, 2010a, b; Amin et al. 2011). In particular, the estuary of Bahía Blanca (BBE) is a critical area that should be included in pollution-monitoring surveys because is

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affected by an intensive and increasing anthropogenic activity such as petrochemical industries, oil refineries, two commercial harbors, and a large city with >350,000 inhabitants, and without adequate treatment and purification, its effluents are directly introduced into the estuarine waters. Moreover, the area of study has been recently included into the International Union for Conservation of Nature World Conservation Congress recommendation priorities to be included into the Ramsar list for protection and conservation of water-producing ecosystems (World Conservation Congress 2012).

The objectives of this study were as follows: (1) to investigate PAH levels in surface sediments of the BBE; (2) to identify their possible sources; and to (3) determinate the potential ecotoxicological impact of PAHs due to the anthropogenic activity in this area.

Study Area

The BBE is a mesotidal coastal plain located between 38°45'–39°40'S and 61°45'–62°30'W on the southeastern coast of Buenos Aires province in Argentina (Fig. 1). It has an elongated form, directed northwest to southeast, approximately 80-km long within the main channel, with numerous streams that separate islands and tidal flats (Perillo and Piccolo 1991). It has a semidiurnal tidal regime, and the water surface at low tide is 400 km², whereas at high tide this area increases to nearly 1300 km².

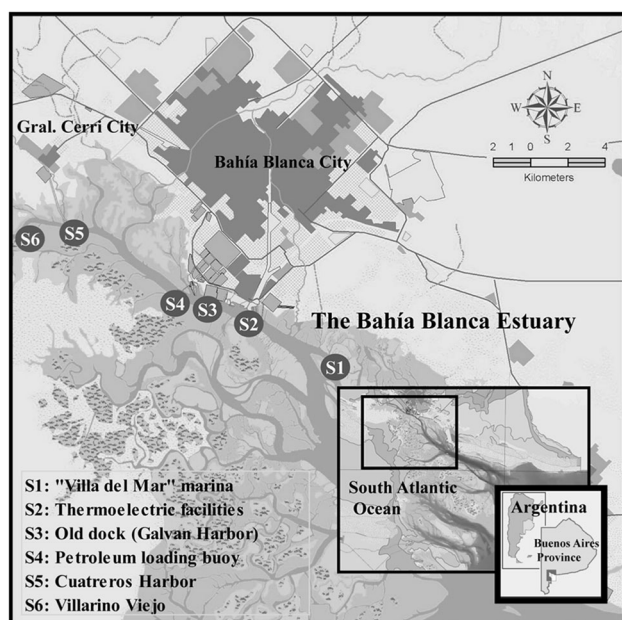


Fig. 1 Location of samples sites in the Bahía Blanca Estuary, Argentina

Two commercial harbors, towns (>350,000 inhabitants) and a large industrial park are located at the northern boundaries of the estuary. In addition, several streams discharge into the area; most of them are affected by anthropogenic activities (Fernández Severini et al. 2009). The main navigation channel is extensively used by fishing boats, oil tankers, and cargo vessels and thus requires regular dredging. As a consequence, this coastal marine system receives contaminant inputs from municipal wastewater; direct industrial discharges; harbor-related operations; runoff water, which carries contaminants from land-development areas; and aerial fallout from atmospheric pollutants (Marcovecchio and Ferrer 2005).

Materials and Methods

Sampling

Considering the high environmental variability described in the previous paragraph and to set an actual PAH level at the area, a periodical sampling was scheduled. Sediment samples were collected every 3 months between October 2011 and February 2013 from six sampling stations with different anthropogenic influence (Fig. 1). Sampling station 1 (S1) is located in the proximity of a coastal town (Villa del Mar) at the middle-outer reach of the Main Navigation Channel of the estuary, which sustains a marina with a small fishing fleet. S2 is located in the proximity of the Luis Piedra Buena thermoelectric facilities, which generates electric power by gas and/or fuel oil combustion. S3 and S4 are located at the highly industrialized area of the BBE within the Galvan Harbor. Although S3 is situated in an abandoned dock, S4 is located in the proximity of a petroleum and oil derivative-loading buoy. Next to them, S5 is located in a small recreational/fishing harbor (Cuatros Harbor) in the inner part of the estuary and close to the town of General Cerri. Finally, S6 is close to the head of the estuary in the vicinity of rural lands (Villarino Viejo).

Thirty-four sediment samples were obtained on board the IADO VI research vessel. Approximately 500 g of surface sediments (0–5 cm) were manually collected with a stainless steel spoon in solvent-cleaned glass container, refrigerated on board, and immediately transported to the laboratory and stored at –20 °C before analysis.

Laboratory Methods and Sample Processing

Ten g of wet sediment were dried using Na₂SO₄ and then Soxhlet-extracted with an acetone–hexane mixture (1:1 ratio) for 12 h (USEPA method 3540C). Before extraction, 100 µl of the mixture of four perdeuterated PAHs

(naphthalene-d8, acepnaphthene-d10, phenanthrene-d10, crysene d-12) was added as surrogate standards. The extracts were concentrated close to 5 mL in a rotary evaporator with a low-temperature thermostatic bath and further reduced to 1.5 mL under a gentle high-purity nitrogen flow. A silica–alumina (2:1 ratio) gel column was implemented to clean up the extracts. PAHs were eluted with 70 mL of hexane and dichloromethane (9:1 ratio) and then concentrated up to 5 mL by rotary evaporator and further to 1.5 mL under nitrogen flow. Finally, just before the gas chromatography (GC)–mass spectrometry (MS) injection, 100 μ L of deuterated internal standard were added to extract vials to recovery asses.

PAHs were quantified on an Agilent 7890 B (Santa Clara, USA) gas chromatograph coupled with an Agilent 5977A mass spectrometer (Santa Clara, USA). The GC column was an HP-5MS fused silica column (30 m; 0.25-mm i.d.; 0.25- μ m film thickness), and helium was used as a carrier gas. The samples were injected in the splitless mode at 250 °C, and the temperature program used was as follows: initial temperature 70 °C for 2 min; heated to 150 °C at 30 °C min⁻¹ then to 310 °C at 4 °C min⁻¹; and held for 10 min. The mass spectrometer was operated in selected ion–monitoring mode and electron-impact mode (70 eV).

Seventeen primary PAHs were analyzed: naphthalene (NA), 2-methyl-naphthalene (2-M-NA), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FL), phenanthrene (PHE), anthracene (AN), fluoranthene (FLU), pyrene (PY), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]-fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), dibenzo[a,h]anthracene (DBA), and benzo[ghi]perylene (BPE). Each individual PAH compound was confirmed by the retention time and the abundance of quantification/confirmation ions with respect to authentic PAHs standards. Quantification of individual compounds was based on the ratios of analyte peak areas/surrogate standards areas (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, internal standard method) using the corresponding calibration curves. Quality control for the PAHs analyses was performed by monitoring the recovery of the internal standard (benzo-[a]-anthracene-d12) spiked just before GC injection; recoveries ranged from 74 to 105 %.

Blanks were prepared according to the same procedure without adding a sediment sample. The protocol was validated by the use of reference material (SRM-NIST 1944). All of the results were expressed on a dry-weight basis. The laboratory detection limits (LDs) of the method for individual PAH ranged from 0.4 to 1.1 ng/g dw. The LD was set at five times the detected amount in the procedural blank.

A PAH standard mixture of 17 PAHs, deuterated internal standard solutions, and benzoanthracene-d12 was obtained from Supelco (Bellefonte, Pennsylvania, USA).

All solvents used for sample processing and analyses (hexane, acetone, and dichloromethane) were of analytical and chromatographic grade from Merck (Darmstadt, Germany). A certified reference material sample was obtained from National Institute of Standards and Technology (NIST-SRM 1944). Merck silica gel 60 [70–230 mesh (American Society for Testing and Materials)] and aluminum oxide activated at 450 °C were heated at 120 °C for 12 h before use. Glassware was washed with nonionic detergent, rinsed with ultrapure water and a mixture of acetone and hexane, and dried at 120 °C before use.

Water content was determined by the sediment subsample weight loss at 105 \pm 2 °C.

Total organic carbon (TOC) in sediment was measured by a carbon analyzer (LECO CR-12, USA) after the carbonates were removed with concentrated HCl. The grain size of the sediment was analyzed using a laser particle-size analyzer (model, Malvern Mastersizer 2000, Worcestershire, UK). Before analysis samples were treated with hydrogen peroxide to eliminate organic materials.

Data Processing and Statistical Analyses

PAH ratios of FLU/FLU + PY, IP/IP + BPE, and abundance ratio of 2- to 3-ring PAHs to 4- to 6-rings PAHs (LMW/HMW) were used to identify PAH sources (Budzinski et al. 1997; Yunker et al. 1999, 2002). In addition, to deepen the analysis, principal component analysis (PCA) was performed using STATISTICA 7.0 (StatSoft, Tulsa, USA). Data submitted for the analysis were arranged in a matrix where each column corresponded to one PAH compound, and each row represented a sampling-site case. Before statistical analysis, data values less than the LD were assumed to be equal to half of the LD.

PAH carcinogenic potential was evaluated using the toxic equivalent of benz[a]pyrene (TEQ-BaP). TEQ-BaPs are generated by comparing the carcinogenic effects of the measured concentrations of various representatives of PAHs to that of BaP, one of the most toxic and well-investigated carcinogenic PAHs, and were calculated as $TEQ-BaP = \sum c_i \times TEF$, where c_i is the concentration of individual PAHs (ng/g), and TEF is the toxic equivalency factor of PAHs relative to BaP (USEPA 1993; Nisbet and Lagoy 1992).

Results and Discussion

Sediment Physicochemical Characteristics and Distribution of PAHs

The grain size (clay, silt, and sand) distribution and TOC content in sediment samples are listed in Table 1.

Regarding the grain size fractions, the totality of the sampling stations were classified as silty/clay sediments.

Several studies have found that concentration and distribution of PAHs in sediments are influenced by a number of physicochemical parameters including TOC content and particle-size distribution (Viguri et al. 2002; Culotta et al. 2006; Chen et al. 2013, He et al. 2014). Nevertheless, in this study, results did not show a significant correlation between TOC and PAH concentration ($r = 0.13$ $p < 0.050$). A probable rationale is that the high productivity of the BBE (Freije et al. 2008), which includes a plenty of benthic communities, contributed to the TOC levels, thus masking any relationship that may exist between PAHs and organic carbon (Guinan et al. 2001; Guzzella et al. 2005; Ünlü and Alpar 2006). In a similar manner, correlations for total PAH concentration and particle size were not significant [$r = 0.20$ for silt, $r = 0.54$ for clay, and $r = -0.54$ for sand ($p < 0.050$)]. This is probably due to a great variability in deposition dynamics of sediments caused by high sediment-transportation rates (Perillo and Piccolo 1991) and the periodic remobilization of sediments by artificial dredging.

Concentration of PAHs

The results of PAH concentrations in sediments are listed in Table 2. All of the samples contained detectable amount of PAHs. Total PAHs (summary of the 17 PAHs analyzed) varied from 19.7 to 30,054.5 ng/g dw with an overall mean of 1798.5 ng/g. The maximum levels of PAHs were found at S3, located within the Galvan harbor area, which has the most industrial activity and is surrounded by wastewater discharge pipelines, industrial vents, docks, shipsides, petroleum-transfer buoys, etc. In particular, this station showed the greatest range of total PAHs, i.e., from 190 to >30,000 ng/g. In contrast, the concentration of total PAHs at the other five stations were lower and appeared to decrease as the distance from the urban/industrial core (centered at S3) increased. This trend follows the globally observed increase in total PAHs as a function of anthropogenic impact (Lipiatou and Saliot 1991) and is in agreement with a previous baseline for the area (Arias et al. 2010a).

Regarding the PAH sediment levels in a global context, the concentrations found at the BBE were within the range of the most important harbors around the world such as Kaohsiung (Taiwan), Imam Khomeini (Iran), Barcelona (Spain), and Montevideo (Uruguay) (Table 3). According to Baumard et al. (1998), levels of sediment contamination by PAHs can be classified as low (10–100 ng/g), moderate (100–1000 ng/g), high (1000–5000 ng/g), and very high (>5000 ng/g). According to these criteria, the levels of PAH in sediments samples could be classified from moderate (S1, S2, and S4 through S6) to very high (S3).

Composition and Sources of PAHs

The majority of PAHs in marine/estuarine sediments originate from pyrogenic or petrogenic sources (Zakaria et al. 2002; Chen et al. 2013). Pyrogenic PAHs are dominated by compounds with high molecular mass (4–6 rings) and are produced during incomplete combustion of carbon, fossil fuels, and wood. In contrast, petrogenic PAHs are dominated by compounds with 2–3 rings (Sanders et al. 2002; Dahle et al. 2003). Considering this, the ring percentage of PAHs at each sampling station is shown in Fig. 2. In general, the composition and relative abundance of individual PAH were homogeneous throughout the sampling stations suggesting a common PAH input pattern. The exception was marked by S3 where the abundance of 4 rings had the highest proportion, i.e., 50.1 % on average, which indicated a pyrogenic PAHs input at this location. In contrast, 3- and 4-ring PAHs were predominant at other stations with a general percentage mean of 36.8 and 30.2 %, respectively. The major compounds in terms of abundance were FLU, PY, and PHE (accounting for 16.52, 15.98, and 15.2 % of total PAHs, respectively), which are typical indicators of diesel combustion (Wang et al. 2009). In summary, these findings suggested a mixed sources origin (petrogenic and pyrogenic).

PAH ratios have been traditionally used to identify PAH sources (Budzinski et al. 1997; Yunker et al. 1999, 2002) based on the difference in thermodynamic stability observed in PAHs (Readman et al. 1987). The usual index of combustion and/or anthropogenic input is an increase in the proportion of the less stable and/or kinetically produced

Table 1 Average grain size (clay, silt, and sand) and TOC of sediments at each sampling station

| Sample | Latitude | Longitude | % Clay | % Silt | % Sand | % TOC |
|--------|--------------|--------------|--------|--------|--------|-------|
| S1 | 38°51'22.7" | 62°7'20.6' | 18.67 | 60.14 | 21.19 | 1.21 |
| S2 | 38°47'80.2" | 62°15' 48.8" | 12.07 | 56.76 | 31.17 | 1.10 |
| S3 | 38°47'13'.3" | 62°18' 00.0" | 29.56 | 58.06 | 12.38 | 1.73 |
| S4 | 38° 47'10.8" | 62° 18'22.1" | 18.68 | 55.58 | 25.74 | 0.96 |
| S5 | 38° 45'07.6" | 62° 22'80.3" | 30.59 | 52.4 | 17.01 | 1.02 |
| S6 | 38° 45'54.5" | 62° 26'18.5" | 27.64 | 49.43 | 22.93 | 1.05 |

Table 2 Range of PAH concentrations (ng/g dw) in sediments from BBE

| | S1 (<i>n</i> = 5) | S2 (<i>n</i> = 6) | S3 (<i>n</i> = 5) | S4 (<i>n</i> = 6) | S5 (<i>n</i> = 6) | S6 (<i>n</i> = 6) |
|--------------------|------------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| NA | <LD ¹ –40.3 | <LD–38.4 | 9.3–1451.2 | <LD –57.9 | <LD–57.3 | <LD–36.8 |
| 2-M-NA | <LD–10.8 | <LD–18.5 | <LD–848.2 | <LD–17.2 | <LD–24.6 | <LD–14.2 |
| ACY | <LD–1.3 | <LD | <LD–62.0 | <LD | <LD | <LD |
| ACE | <LD | <LD | <LD–2873.4 | <LD | <LD | <LD–38.8 |
| FL | <LD–29.5 | <LD–19.9 | <LD–1830.9 | 9.5–59.0 | <LD–41.2 | <LD–45.8 |
| PHE | <LD–62.0 | 7.1–78.7 | 50.7–4478.4 | 12.4–98.1 | 12.3–70.8 | 6.3–55.1 |
| AN | <LD–7.3 | <LD | <LD | <LD | <LD–8.3 | <LD |
| FLU | 4.7– 19.5 | <LD–28.8 | <LD–5164.6 | 8.4–57.2 | <LD–19.0 | <LD–23.4 |
| PY | 1.1–27.8 | 8.0–47.9 | 39.6–4776.0 | 13.3–98.2 | 12.3–55.4 | <LD–44.3 |
| BaA | <LD–9.6 | <LD–8.4 | <LD–1726.2 | <LD–107.8 | <LD | <LD |
| CHR | 2.5–14.9 | 5.8–16.8 | 17.4–3034.8 | <LD–117.6 | <LD–45.5 | 8.2–40.5 |
| BbF | <LD–10.2 | <LD–11.2 | 1.8–2224.6 | 0.7–147.9 | <LD–17.6 | 1.7–8.9 |
| BkF | <LD–6.0 | <LD–6.4 | 0.9–1632.8 | <LD–133.6 | <LD–14.4 | <LD–2.2 |
| BaP | <LD–11.5 | <LD–0.9 | <LD–1068.3 | <LD–193.0 | <LD–21.1 | <LD–3.5 |
| IP | 1.0–17.2 | <LD–17.1 | 1.7–951.3 | 0.5–758.6 | <LD–23.0 | 1.3–15.0 |
| DBA | <LD–13.2 | <LD–1.8 | <LD–192.2 | <LD–801.9 | <LD–40.3 | <LD–6.3 |
| BPE | 1.9–17.3 | <LD–32.5 | 3.1–736.8 | 0.8–737.5 | <LD–58.1 | <LD–14.7 |
| Total PAHs | 19.7–240.8 | 56.9–228.2 | 191.6–30,054.6 | 60.9–3323.3 | 109.1–347.2 | 54.1–243.0 |
| ∑LMW ^a | 3.4–142.0 | 27.0–138.8 | 109.44–10,410.18 | 28.38–169.98 | 44.6–164.6 | 16.0–137.5 |
| ∑HM ^b | 16.4–141.8 | 25.1–130.8 | 82.16–19,644.45 | 32.51–3153.32 | 49.3–252.4 | 37.6–142.7 |
| cPAHs ^c | 5.2–82.5 | 8.3–50.5 | 21.82–10,830.14 | 11.00–2260.48 | 10.2–138.9 | 13.8–63.6 |

LD lower than the laboratory detection limit

^a ∑LMW = sum of NA, 2-M-NA, ACY, ACE, FL, PHE, and AN^b ∑HMW = sum of FLU, PY, BaA, CHR, BbF, BkF, BaP, IP, DBA, and BPE^c cPAHs = sum of carcinogenic PAHs: BaA, CHR, BbF, BkF, BaP, IP, and DBA

parent PAH isomers relative to the thermodynamically stable isomers (Yunker et al. 2002). The literature reference values for the molecular ratios are listed in Table 4, whereas the cross-plots for sediment ratios are presented in Fig. 3a (IP/IP + BPE vs. FLU/FLU + PY). On the one side, sediment samples near the petrochemical industrial park wastewater-discharge zone (S3) showed mean FLU/FLU + PY and IP/IP + BPE ratios of 0.46 ± 0.1 ($n = 4$) and 0.82 ± 0.03 ($n = 5$), respectively, which outlined a mix of different combustion process at the area. On the other side, the rest of the stations (S1, S2, and S4 through S6) showed a wide range of PAH ratios and pointed to a mix of petroleum and combustion as PAH sources. Finally, LMW/HMW ratios were <1 for most of the samples (65 %), thus pointing to a slight imposition of pyrolytic inputs along the estuary (Fig. 3b). In summary, different PAHs origins were identified: Whereas combustion processes were the most important contribution at the estuary, a petrogenic footprint was also found. Fossil fuel-combustion sources could be possibly attributed to the intense anthropogenic activity at the industrial core zone and harbours, whereas the coal-combustion imprint could have both local and remote sources. In fact, as recent evidence

supports, the “coal sign” could be attributed to industrial vents (local sources) and city traffic emissions plus agriculture land fires [remote source (Arias et al. 2010c)].

PCA

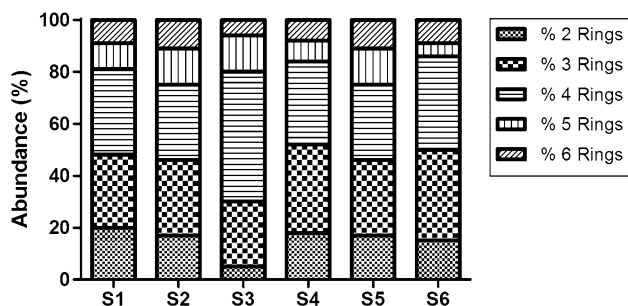
PCA identified two principal components (PC1 and PC2) accounting for 61.32 and 9.60 % of the total variance, respectively. PCA loading scores >0.60 were considered meaningful. Figure 4a shows the loadings for the individual PAHs at the PC plot. PC1 had strong correlations with PHE, FLU, PY, BaA, CHR, BbF, BkF, BaP, IP, DBA, and BPE. With the exception of PHE, all of these compounds include ≥ 4 rings in their structure and are strongly correlated with pyrolytic sources. Thus, PC1 could be interpreted as a pyrolytic source component. PC2 had significant positive loadings for LMW PAHs, namely, 2-M-NA, ACY, and ACE. As stated before, such PAHs are the result of crude oil or refined product inputs. Consequently, PC2 was defined as a petrogenic source component.

Figure 4b illustrates the score plot of the first two components, which allows for the characterization of the sampling stations according to the first and the second

Table 3 A comparison of PAH concentrations (ng/g dw) in sediments from worldwide locations and from this study

| Location | Range (ng/g dw) | No. of PAHs | Reference |
|--|-----------------|-------------|-----------------------------------|
| Zhanjiang Bay, China | 41.96–933.90 | 16 | Huang et al. (2012) |
| Yangtze Estuary, China | 84.6–620 | 16 | Hiu et al. (2009) |
| Daya Bay, China | 42.5–158.2 | 16 | Yan et al. (2009) |
| Kaohsiung Harbor, Taiwan | 34.0–16,700 | 17 | Chen et al. (2013) |
| Imam Khomeini Port, Iran | 2885.8–5482.23 | 16 | Abdollahi et al. (2013) |
| Estuary of Chao Phraya River, Thailand | 30–724 | 17 | Boonyatumanond et al. (2006) |
| Mersey Estuary, UK | 626–3766 | 15 | Vane et al. (2007) |
| Cienfuegos Bay, Cuba | 450–10,500 | 41 | Tolosa et al. (2009) |
| Narragansett Bay, USA | 569–216,000 | 44 | Hartmann et al. (2004) |
| Barcelona Harbor, Spain | 300–10,320 | 16 | Martínez-Lladó et al. (2007) |
| Veracruz, centre of Gulf of Mexico | 200–12,400 | 16 | Ponce-Vélez et al. (2006) |
| Montevideo Harbour, Uruguay | 1560–90,440 | 20 | Muniz et al. (2004) |
| Jobos Bay, Puerto Rico | 40.4–1912 | 16 | Aldarondo-Torres et al. (2010) |
| Patos Lagoon Estuary, Brazil | 37.7– 11779.9 | 23 | Medeiros et al. (2005) |
| Bahía Ushuaia, Patagonia, Argentina | ND–360 | 16 | Commendatore et al. (2012) |
| Rio de la Plata Estuary, Argentina | 3–2120 | | Colombo et al. (2006) |
| Bahía Blanca Estuary, Argentina | 15–10,260 | 17 | Arias et al. (Arias et al. 2010a) |
| Bahía Blanca Estuary, Argentina | 19.7–30054.5 | 17 | This study |

ND = not detected

**Fig. 2** The composition pattern of PAHs by ring size in surface sediments from Bahía Blanca Estuary**Table 4** Literature values of selected molecular ratios

| Source | FLU/(FLU + PY) ^a | IP/(IP + BPE) ^a | LMW/HMW ^b |
|------------|-----------------------------|----------------------------|----------------------|
| Pyrolytic | >0.4 | >0.2 | <1 |
| Petrogenic | <0.4 | <0.2 | >1 |

^a Yunker et al. (2002)^b Yuam et al. (2001)

component. As shown in Fig. 4b, the PCA pooled samples into two major groups. The first group was composed by samples located at the petrochemical industrial park wastewater-discharge zone (S3), which was the area with the highest values of total PAHs. These samples were well

differentiated by the significant scores on the first component. The other group contained the remaining samples and showed significant scores coordinating with the two components, thus indicating concomitant inputs from petrogenic/pyrolytic PAHs.

In conclusion, taking into account PAH levels, ratios, and PCA classification, the industrial core at S3 could be identified as point source of pyrogenic PAHs, whereas the rest of the stations appeared to function as receptors of multiple inputs (pyrolytic/petrogenic) from both local and remote sources.

Sediment Ecotoxicity and Potential Carcinogenicity

In recent years, data on chemical analyses on the contaminants and their effects on aquatic organisms and environments have been used to develop SQGs. SQGs have been shown to be useful tools for assessing the quality of estuarine and marine sediments (Long et al. 2006), thus becoming important for the protection and management of marine ecosystems.

Two guideline values, effects range-low (ERL) and effects range-median (ERM) (Long et al. 1995) have been extensively used (Qiao et al. 2006; Chen and Chen 2011; He et al. 2014). ERL and ERM were developed as non-regulatory guidelines and correspond to the 10th and 50th percentile, respectively, in a database of increasing

Fig. 3 PAH Cross Plot for the IP/(IP + DBA) versus FLU/(FLU + PY) cross plot ratios (a) and LMW/HMW ratios (b)

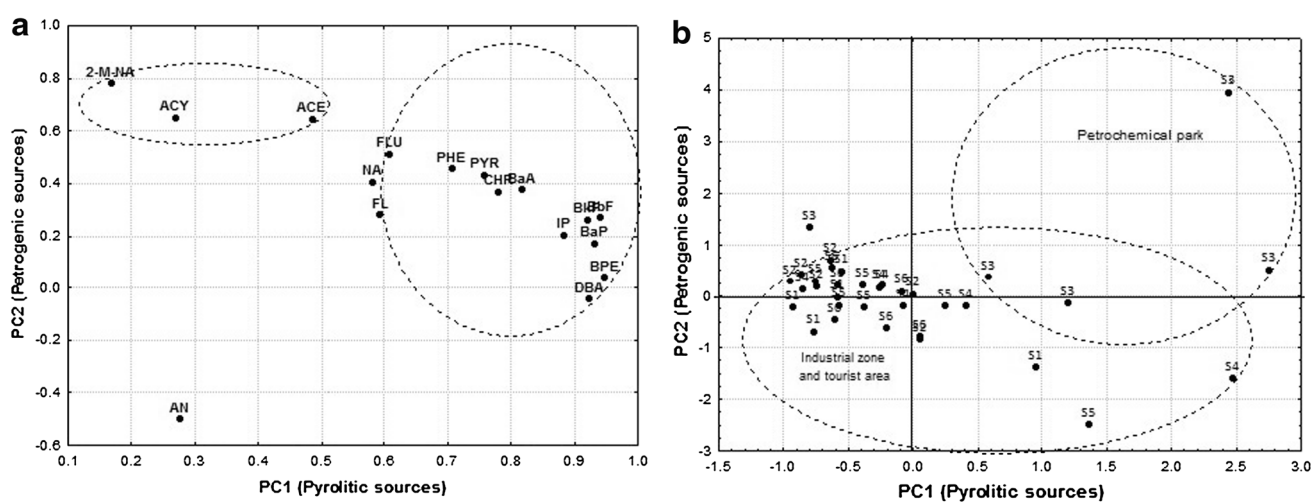
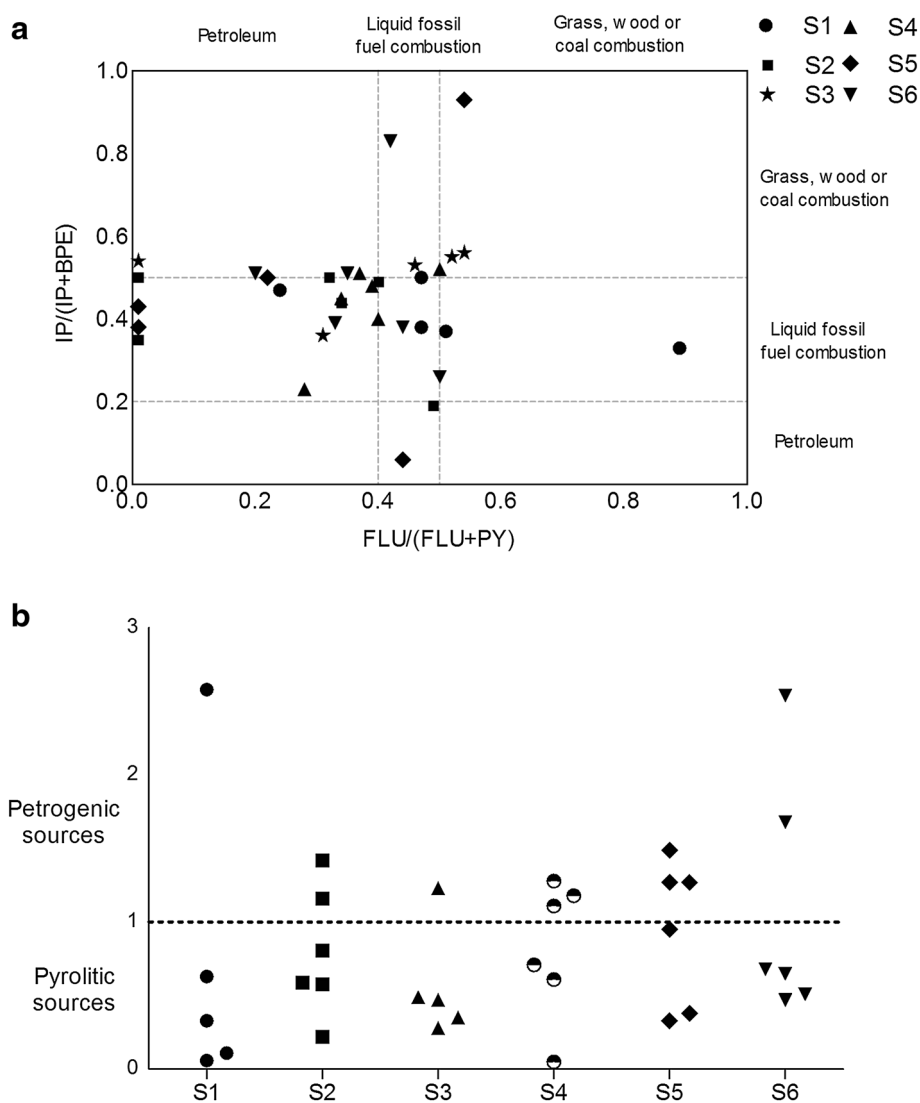


Fig. 4 **a** The PCA loading plot for individual PAHs. **b** PCA (PC1 and PC2) loading plots for the sampled areas

Table 5 Mean PAH concentrations in sediments from BBE expressed in TEQ-BaP (ng TEQ-BaP/g dw)

| Compound | TEF | S1 | S2 | S3 | S4 | S5 | S6 |
|---------------|-------|-------|-------|---------|---------|--------|-------|
| NA | 0.001 | 0.014 | 0.014 | 0.340 | 0.025 | 0.024 | 0.017 |
| ACY | 0.001 | 0.000 | 0.000 | 0.023 | 0.000 | 0.000 | 0.000 |
| ACE | 0.001 | 0.000 | 0.000 | 0.581 | 0.000 | 0.000 | 0.006 |
| FL | 0.001 | 0.008 | 0.008 | 0.388 | 0.022 | 0.017 | 0.015 |
| PHE | 0.001 | 0.020 | 0.038 | 1.639 | 0.058 | 0.041 | 0.034 |
| AN | 0.01 | 0.015 | 0.000 | 0.000 | 0.000 | 0.016 | 0.000 |
| FLU | 0.001 | 0.012 | 0.012 | 1.943 | 0.024 | 0.007 | 0.012 |
| PY | 0.001 | 0.015 | 0.034 | 1.777 | 0.041 | 0.036 | 0.024 |
| BaA | 0.1 | 0.193 | 0.213 | 64.717 | 1.992 | 0.000 | 0.000 |
| CHR | 0.01 | 0.092 | 0.125 | 10.414 | 0.297 | 0.175 | 0.160 |
| BbF | 0.1 | 0.371 | 0.408 | 59.068 | 2.861 | 0.627 | 0.393 |
| BkF | 0.1 | 0.212 | 0.228 | 44.557 | 2.423 | 0.409 | 0.110 |
| BaP | 1 | 2.722 | 0.257 | 348.565 | 35.289 | 6.353 | 0.585 |
| IP | 0.1 | 0.485 | 0.458 | 36.306 | 13.226 | 0.459 | 0.594 |
| DBA | 1 | 3.196 | 0.302 | 62.813 | 137.081 | 9.857 | 2.081 |
| BPE | 0.01 | 0.056 | 0.074 | 2.924 | 1.302 | 0.157 | 0.072 |
| Σ PAHS | | 7.412 | 2.169 | 636.055 | 194.642 | 18.180 | 4.103 |
| cPAHs | | 7.272 | 1.990 | 626.440 | 193.169 | 17.881 | 3.923 |

concentrations associated with adverse biological effects (He et al. 2014). ERL and ERM delineate three concentration ranges for a particular chemical in where biological effects are rare (less than the ERL), occasional (between ERL and ERM), and frequent (greater than the ERM).

Under the above-mentioned criteria, total PAHs were lower than the ERL in 32 samples (94.1 %) and between ERL and ERM in two samples (5.9 %). Samples that exceeded the total PAHs ERL value were from S3. Considering the individual PAHs guidelines, 12 sediment samples (35.3 %) exceeded the ERL value, which indicates that biological effects would occasionally occur. FL exceeded the ERL value with the highest frequency; in fact, at least one sample exceeded the FL guideline value in every sampling site, indicating that adverse toxicological effects caused by this compound might occasionally occur.

Considering ERM values, guidelines for individual PAHs were exceeded on 10 occasions at S3 and once at S4 station. Compounds exceeding the ERM were 2-M-NA, ACY, FL, PHE, FLU, PY, BaA, CHR, and DBA suggesting that biological impairments could be frequently expected due to those compounds at those stations.

In terms of human health, the Σ of the seven carcinogenic PAHs (cPAHs) varied from 5.2 to 10,830.1 ng/g, with an average of 608.9 ng/g dw, and accounted for 6.8–68 % of total PAHs in sediments of the BBE. Table 5 lists PAH levels in sediments expressed in TEQ-BaP in the six sites under evaluation. Total TEQ-BaP calculated for samples varied from 0.221 to 1969.3 ng/g dw TEQ-BaP. The results obtained for the 16 PAHs and the 7 carcinogenic PAHs were

similar, and that could be explained because the TEFs for carcinogenic PAHs are high. The greatest levels of TEQ-BaP were found at S3 and S4 (industrial area). To make comparisons with other studies, we used the TEQ-BaP values obtained for the 7 cPAHs. Concentrations found in sediments of the BBE were similar to those in sediments from Kaohsiung Harbor (Chen et al. 2013), lower than those from Naples Harbor (Sprovieri et al. 2007), and greater than those from Meiliang Bay (Qiao et al. 2006).

Conclusion

Analyses of the 34 surface sediment samples from BBE showed PAH concentrations ranging from 19.7 to 30,054.5 ng/g. Concentrations of Total PAHs appeared to decrease as the distance from the urban/industrial core increased. This trend is in agreement with the globally observed increase of Total PAHs as a function of the anthropogenic impact level found at many coastal zones around the world.

PAH distribution showed that 3- and 4-ring PAHs were predominant in almost all of the samples. These facts point to mixed PAH sources (pyrogenic + petrogenic). Different PAH origins were identified: Whereas the combustion process appears to be the most important source in the BBE, a petrogenic footprint was also found. Fossil fuel-combustion sources could be attributed to the high anthropogenic activity in the industrial zone, whereas the coal-combustion imprint can have both local and remote

sources. The industrial core at S3 could be considered a point source of pyrogenic PAHs, whereas the rest of the stations were classified as receptors of mixed inputs (pyrolytic/petrogenic) from local and remote sources.

The result of the ecotoxicological impact showed that some of the individual PAHs exceeded the ERL as well as the ERM. Thus, adverse toxicological effects caused by PAHs would occasionally and frequently occur in the study area. In addition, levels of sediment TEQ-BaP were greater near the industrial area.

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