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Presence, distribution, and origins of polycyclic aromatic hydrocarbons (PAHs) in sediments from Bahía Blanca estuary, Argentina

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Abstract This paper is the first comprehensive survey of polycyclic aromatic hydrocarbons (PAHs) in coastal sediments in Bahia Blanca, Argentina, and provides useful information on their levels of concentration, composition, and sources of these pollutants. The total concentrations of PAHs ranged from 15 to 10,260 ng g^{-1}. The highest contents (mean 3,315 ng g^{-1}) of total PAHs in marine sediments were found in the inner channels of the estuary, while the lower ones (204 ng g^{-1}) belong to samples collected far away from contamination sources. The global average recorded in this study (1,500 ng g^{-1}) indicates that the studied area lies within the referenced category of industrialized coastal zones under chronic pollution. The diagenetic PAH contribution was found to be negligible at all sampled locations; however, the calculation of molecular ratios determined an overimposition of pyrolitic PAHs over the petrogenic input. Further, the use of principal components analysis (PCA) clearly separated ring group compounds and enabled the determination of pyrolitic/combustion PAHs dominancy.

Keywords PAHs · Sediments · Bahía Blanca estuary · Molecular ratios · PCA

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants in the marine and coastal environments (Neff 1979). These have been studied with regard to their origin, distribution, and destination in the environment during the last few decades (Ponce-Vélez et al. 2006; Kucklick et al. 1997; Magi et al. 2002; Yunker et al. 1999, 2001, 2002; Lipiatou and Saliot 1991, and reference therein) and counted among the major groups of environmental pollutants due to their bioaccumulative potential, carcinogenicity, and high persistence. PAHs can be originated by various processes: combustion of organic matter (pyrolysis), slow maturation of organic matter under geothermical gradient (petroleum), and short degradation of biogenic precursors (diagenesis).

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Anthropogenic activities are generally recognized to be the most important source of PAHs release into the environment (Culotta et al. 2006). At coastal areas, anthropogenic polycyclic aromatic hydrocarbons are introduced via urban runoff (McCready et al. 2000), industrial processes (Simpson et al. 1996), vehicle exhausts, and spillage of fossil fuels (Pettersen et al. 1997; Wang et al. 1999). As the process of industrialization and urbanization are stepping rapidly in Argentina, the potential associated increase in PAHs input is a concern. There have been a few number of PAH investigations at Argentinean coastal areas (Colombo et al. 1989, 2005) and no reports of PAHs concentrations at Bahía Blanca estuary, where a dense population and industrial complexes are settled, have been made.

The major objectives of the current study were to determine the distribution of parental PAHs in surficial sediments, to use molecular indices and principal component analysis to gain information about the sources, process, and/or pathways involved in the observed distributions and, finally, to assess potential ecotoxicological impacts in the sediments of Bahía Blanca Estuary.

The Bahia Blanca Estuary (38°40′ S and 62°09′ W) has a total surface of 2,300 km^2, of which about 410 km^2 of islands and 1,150 km^2 of intertidal sector. It is a mesotidal system with very little fluvial input covered by extensive tidal flats and salt marshes (Piccolo and Perillo 1990).

On the one hand, it presents an intensive anthropogenic activity at the north shoreline: oil, chemical and plastic factories, two commercial harbors and a big industrial city with more than 350,000 inhabitants; on the other hand, the inner part of the estuary presents low urbanized/rural lands, a tourist area, and a fishing/recreational port.

Sampling and methods

Sampling

Twenty-four sediment samples were collected between April 2004 and November 2005 over six selected areas named from S1 to S6 "sampling stations," on board of the "Buen día Señor" oceanographic vessel (Fig. 1). A total of 500 g of surface sediment were collected from each site using a grab sampler. The samples were immediately refrigerated on board, stored on solvent-cleaned glass containers avoiding exposure to light, and then rapidly transported to the laboratory to be deep frozen prior to analysis.

All chemicals used were of analytical and chromatographic grade with high purity. PAHs Standard mixtures and perdeuterated internal standards were from Ultra-Scientific Analytical Standards and Absolute Standards Inc.

Extraction and clean-up of PAHs from sediment samples

Wet sediment, 50–100 g, were chemically dried (Na_2SO_4) and extracted. Prior to extraction, 100 μl of perdeuterated PAHs as subrogate standards were added (naphthalene-d12, acenaphthene-d10, phenanthrene-d10, chrysene-d12). Soxhlet extraction apparatus was assembled and refluxed with hexane–acetone mixture for about 2 h for each batch of samples. After that, the dried samples were Soxhlet extracted for 12 hs, using a hexane–acetone 1:1 solvent mixture (EPA 3540C method). The extracts were concentrated close to 10 mL in a rotary evaporator with a low temperature thermostatic bath and further concentrated up to 2 mL under a gentle high purity nitrogen flow. For elimination of polar components, the extracts were passed through a 5% H_2O deactivated alumina/silica gel column (1 cm i.d./15 cm), and PAHs were eluted with 50 mL hexane/methylene chloride (8:1, *v*/*v*). Before the extract was loaded, 1–2 g of Na_2SO_4 was added to the top. Eluates were evaporated down close to 10 mL in a rotary evaporator, and further concentration was achieved drying the extracts under Nitrogen flow at room temperature up to 1 mL. Then, 100 μL of deuterated internal standard were added to extract vials for recovery test, giving a final concentration of about 2,000 ng mL^{-1}.

GC-MS analysis

PAHs were quantified using a gas chromatograph (Hewlett-Packard HP68906C) coupled with a quadrupole mass spectrometer (Hewlett-Packard

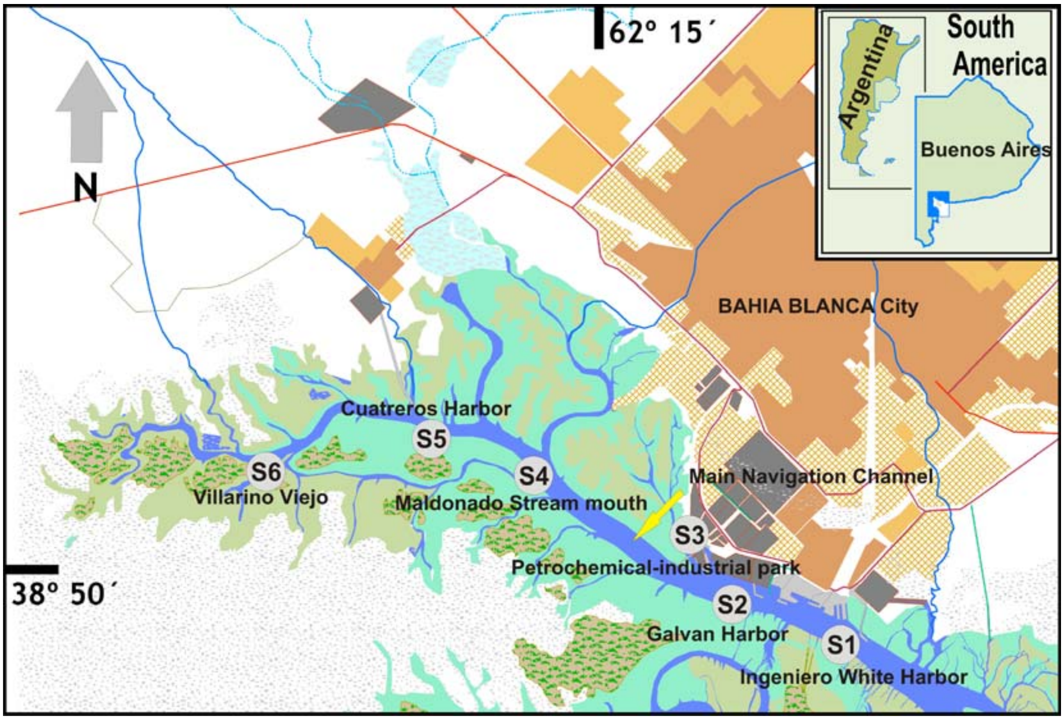

Fig. 1 Sampling sites map in the Bahia Blanca estuary, Argentina

HP5972). The GC column was an HP-5MS fused silica column (30 m; 0.25 mm i.d.; 0.25 μm film thickness), and helium was used as a carrier gas. The mass spectrometer was operated in the electron impact mode (70 eV). The samples were injected in the splitless mode at 250°C. 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. PAHs were monitored in selected ion monitoring mode (SIM).

The studied parent PAHs ranged from the di-aromatics to the hexa-aromatics: naphthalene (Naph), 2-methyl-naphthalene (2-M-Naph), acenaphthylene (Aceph), 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), perylene (Per), benzo[*a*]pyrene (BaP), indeno [*1,2,3-cd*]Pyrene (IP), dibenzo[*ah*]anthracene (DBA), benzo[*g*, *h*, *i*]perylene (BPE).

Each individual PAH compound was confirmed by the retention time and the abundance of quantification ions/confirmation ions with respect to authentic PAHs standards, except for Perylene; this compound was identified by comparing its elution sequence and retention times as described in literature and by spectrum match using the MS spectrum library of the HP68906C. Perylene contribution was evaluated by the percent area of the Total PAHs area.

All values reported for the sediments are on a dry weight basis. Quality control for the PAHs analyses was carried out by monitoring the recovery of the internal standard (Benzo-[*a*]-pyrene-d12) spiked just before GC injection. Quantification of individual compounds was based on comparison of peak areas with internal standards and recoveries ranged from 75% to 105%. Method blanks were run with every batch of eight samples. The quantification limit for individual PAHs species was set following IOC UNESCO N° 45 (1982), and was set in average at

10 ng ml^{-1}. Protocol was validated by the use of reference material (SRM-NIST 1944).

Sediment physicochemical parameters analysis

Total organic carbon, water content, and particle size distribution were also analyzed.

The total organic matter was estimated using a gravimetric method by ignition loss. First, a subsample of the wet sediment was weighed into a tared capsule, dried at 105°C until a constant weight was achieved. Secondly, dried sediments were calcined in muffle oven at 450°C during 4 hs to obtain ignition loss of the samples. It is assumed that the ignition loss at 450°C is approximately the organic matter content in the samples (Commendatore and Esteves 2004). Then, total organic carbon (TOC) was calculated from this measure using a constant factor quotient (Margalef 1979). Water Content was determined by the sediment subsample weight loss at 100 ± 2°C. For grain size analysis, sediment was dried in oven and sifted in an automatic equipment with 2 mm and 63 μm mesh sieves. As a result, three fractions were obtained: gravel (particle sizes > 2 mm), sand (particle sizes between 0.063 and 2 mm), and silt-clay (particle sizes < 0.063 mm).

Data analysis techniques

Principal component analysis was carried out using a statistical package software; this allowed the summarized data to be further analyzed and plotted. Data submitted for the analysis were arranged in matrix where each column corresponded to one PAH compound, and each row represented a sampling site case.

Results and discussion

Sediment PAHs levels and composition

PAHs concentrations

All sediments samples ($n = 24$) from Bahia Blanca estuary contained detectable amount of PAHs. A wide range of PAHs concentrations was

Table 1 Concentration of PAHs in sediments from Bahia Blanca Estuary (ng g^{-1}, dry weight)

	Sampling station							
Compound	S1	S2	S3	S4	S5	S6	Average	Maximum
Naphthalene	54 ± 37	45 ± 42	213 ± 178	49 ± 30	61 ± 42	41 ± 46	77 ± 135	213
2-Methyl-naphthalene	35 ± 46	74 ± 53	403 ± 636	48 ± 37	54 ± 41	7 ± 3	104 ± 417	403
Acenaphthylene	32 ± 42	73 ± 64	366 ± 511	31 ± 41	22 ± 30	N.D.	88 ± 345	366
Acenaphthene	29 ± 28	N.D.	171 ± 132	N.D.	18 ± 20	N.D.	39 ± 111	171
Fluorene	30 ± 43	31 ± 45	142 ± 116	30 ± 43	33 ± 49	N.D.	45 ± 94	142
Phenanthrene	112 ± 83	126 ± 91	184 ± 72	74 ± 34	72 ± 30	48 ± 54	103 ± 80	184
Anthracene	29 ± 42	50 ± 40	160 ± 120	29 ± 41	32 ± 47	N.D.	51 ± 100	160
Fluoranthene	46 ± 38	79 ± 63	223 ± 211	48 ± 30	53 ± 35	32 ± 40	80 ± 154	223
Pyrene	38 ± 49	73 ± 53	311 ± 364	47 ± 42	50 ± 40	37 ± 50	93 ± 253	311
Benzo [a] anthracene	58 ± 89	63 ± 86	154 ± 61	7 ± 3	N.D.	N.D.	49 ± 84	154
Chrysene	56 ± 42	28 ± 40	202 ± 137	39 ± 31	51 ± 34	28 ± 36	67 ± 116	202
Benzo [*b*] fluoranthene	37 ± 48	35 ± 52	164 ± 60	57 ± 41	N.D.	7 ± 3	51 ± 81	164
Benzo [*k*] fluoranthene	23 ± 29	22 ± 30	134 ± 66	30 ± 26	N.D.	4 ± 1	37 ± 72	134
Perylene	0.2	0.5	1.8	1.1	0.8	0.5	–	–
Benzo [a] pyrene	29 ± 42	33 ± 48	164 ± 76	32 ± 46	32 ± 46	N.D.	49 ± 87	164
Indeno [*1,2,3-cd*] pyrene	41 ± 62	N.D.	115 ± 76	N.D.	25 ± 35	N.D.	33 ± 70	115
Dibenzo [*ah*] anthracene	40 ± 61	N.D.	73 ± 66	N.D.	N.D.	N.D.	22 ± 54	73
Benzo [g,h,i] perylene	41 ± 62	N.D.	142 ± 74	N.D.	24 ± 33	N.D.	37 ± 80	142
Total PAHs	641 ± 722	733 ± 506	3324 ± 2437	523 ± 417	529 ± 387	203 ± 224	1024 ± 1140	3322

Perylene concentrations are expressed in percent of Total PAHs concentrations. The data for the individual stations are averages and SDs

N.D. not detected

measured (Table 1); total PAHs (17 PAHs ranging from two to six condensed rings), ranged from less than 20 ng g^{-1} to more than 10,000 ng g^{-1}. The mean total PAHs concentration recorded at the present study (1,024 ± 1,140 ng g^{-1}, $n = 24$; Table 1) indicates that the study area lies within low to moderately polluted marine environments. It is generally accepted that concentrations lower than 100 ng g^{-1} indicate a low pollution level, similar to pollution levels found in several well-known unpolluted zones around the world (Table 2). The highest total PAHs level was recorded at S3 station. This station is a shallow channel area located in the proximity of a petrochemical–industrial park and is surrounded by wastewater discharge pipelines. The total PAHs levels ranged from 1,200 ng g^{-1} to more than 10,200 ng g^{-1}at this station, with an average concentration of 3,322 ± 2,437 ng g^{-1} ($n=9$; mean ± SD; samples = 9; Table 1). Discarding the maximum and minimum values, the average level computed was of 2,742 ± 700 ng g^{-1} ($n = 7$), showing a quite uniform spatial distribution of PAHs for this area. In addition, previous analysis of wastewater samples from the discharge streams have shown high PAHs levels at this site (Tombesi 2004). These facts determine the S3 sampling zone as a "hot spot" with localized contamination.

For the rest of the stations (S1, S2, S4, S5, and S6), total PAHs levels ranged from 15 to 1,550 ng g^{-1}. This group of stations are located over the estuarine Navigation Channel (5 to 14 mts. depth, Fig. 1). Apart from S3, sediments collected at stations S1 and S2 showed the highest mean concentrations for total PAHs, recording 730 ± 722 ($n = 3$) and 753 ± 506 ($n = 3$), respectively. They are both located at Ingeniero White National Harbour and Galván National Harbour entrance, respectively, two commercial harbors with high shipping activity. Industrial complexes are also settled within this area: oil, plastic polymers, byproduct derivative refineries, and a small commercial fishing fleet.

S4, S5, and S6 stations are located in the vicinity of low urbanized/rural lands and showed slight decreasing levels of Total PAHs, ranging from 544 to 248 ng g^{-1} (Table 1). Consequently, total PAHs levels appeared to decrease as the distance from urban/industrial centers increases. This trend has been globally observed and reported in previous works (Laflamme and Hites 1978; Cantillo et al. 1997; Miles and Delfino 1999).

In particular, Station S4 receives water inputs from Maldonado Stream, which runs through agriculture lands and across the entire city. At this station, the mean concentration of total PAHs was 544 ± 417 ng g^{-1}.

Table 2 Comparison of PAHs concentrations (ng g^{-1}, *d.w.*) in surface sediments of different worldwide locations and this study

Locations	Average PAHs concentration	Maximum PAHs concentration	References
Santa Ponza Bay, Balearic Islands	63	127	Baumard et al. (1998)
Barcelona Harbour, Spain	5,050	8400	Baumard et al. (1998)
Gironde estuary & Arcachon Bay, France	255	853	Soclo et al. (2000)
Todos los Santos Bay	96	813	Macías-Zamora et al. (2002)
Guba Pechenga, Barents Sea, Russia	76	208	Savinov et al. (2003)
Yalujiang Estuary, North China	443	1500	Wu et al. (2003)
Daya Bay, China	481	1134	Zhou and Maskaoui (2003)
Río de la Plata estuary, Argentina	400	1,300	Colombo et al. (2005)
Minjiang river estuary, China	433	887	Zhang et al. (2004)
Veracruz, Centro Golfo de México	3,300	12,400	Ponce-Vélez et al. (2006)
Tabasco, Sur Golfo de México	1,100	3,100	Ponce-Vélez et al. (2006)
Naples Harbour	3,142	31,774	Sprovieri et al. (2007)
Yellow River, China	1,415	2,621	Xu et al. (2007)
Daliao River watershed, China	6,471	13,448	Guo et al. (2007)
Bahia Blanca estuary, Argentina	1,024	10,261	This study

The lowest total PAHs concentration was found at S6 station, located at the inner extreme point of the estuary and surrounded by agriculture lands.

Sediment physicochemical parameters and PAHs distribution

It is generally stated that the environmental fate and behavior of hydrophobic organic compounds is ultimately determined by the physicochemical properties of each compound and sediments, namely, sediment organic matter content, size particle distribution, PAHs octanol–water partition coefficients (K_{ow}), and water salinity (Baker et al. 1991; Doong and Lin 2004). Then, in this work, the relationship between the concentrations of PAHs and some physicochemical parameters of samples has been studied.

On the one hand, total organic carbon (TOC) percent ranged from 0.77 to 1.46 along the sampled sites (Table 3), and the sedimentary water content was high (43–51%) at all the stations apart from S6. With regard to the grain size fractions, S1 to S5 stations were classified as silty/clay sediments while only S6 sediment was of sandy type.

Accordingly to several coastal sediments studies, a positive linear relationship between sediment's PAH concentration and TOC is commonly found (Wu et al. 2003; Culotta et al. 2006; Guo et al. 2007; Xu et al. 2007); however, our results show a low linear correlation between total PAHs concentration (ng g^{-1}, d.w.) vs TOC percent ($r = 0.26$, $p < 0.2700$). In addition, low correlations were also found for total PAHs concentration and the $< 63 - \mu$m sediment fraction percent ($r = 0.24$, $p < 0.2600$).

Table 3 Characteristic values of selected molecular ratios for pyrolytic and petrogenic origins of PAHs

Location	Water content	TOC %	Grain size (< 63 µm fraction %)	Sediment classification
S1	49.62	1.08	69.10	Silty/clay
S2	50.26	1.46	82.50	Silty/clay
S3	50.69	1.13	82.50	Silty/clay
S4	45.54	0.92	67.10	Silty/clay
S5	43.41	1.17	96.30	Silty/clay
S6	25.39	0.77	60.90	Sandy

Simpson et al. (1996) concluded in their studies that the relationship between total PAHs and organic carbon in sediments was only significant for highly contaminated sites, where total PAHs were more than 2,000 ng g^{-1}. This relationship was also observed in our study at S3 sampling site, where total PAHs concentrations ranged from 1,247 to 10,260 ng g^{-1}, and the highest correlations between total PAHs vs TOC ($r = 0.56$, $p < 0.12$) were achieved.

Although PAHs and TOC correlated fairly well for highly contaminated sites (S3, $n = 9$), it cannot be assumed that the observed positive correlation represents preferential partitioning of PAHs onto sediment according to TOC percentages. Firstly, S3 station is located in the close vicinity of heavy industries (petrochemical–industrial park) and was defined as a hotspot (see above); hence, its PAHs loads are not the same from the remaining studied sites (inputs are not uniform). Secondly, there is a lack of correlation for the rest of the stations. Additionally, in another study (paper in preparation), a high correlation between water total PAHs and particulate organic matter is also found for the S3 sampling station in particular. For these reasons, we suggest that the correlation found at these sites is due to particulate emissions from the industries rather than active thermodynamically driven partitioning of PAHs into biogenic sediment organic carbon.

These preliminary results reveal a complex relationship between sediment's PAHs concentration and some physicochemical parameters of sediments at Bahia Blanca Estuary, thus, suggesting the occurrence of other factors such as site specificity and proximity to sources in the environmental fate and behavior of PAHs.

Composition of PAHs

According to the number of aromatic rings, the 17 PAHs were divided into three groups, representing (2 + 3) rings, (4) rings, (5 + 6) rings PAHs. Composition and relative abundance of each group is shown in Fig. 2a. It is well stated that in order to assess PAHs sources, pyrogenic PAHs present the dominance of high molecular mass (4–6) rings PAHs over those with low (2–3) rings molecular mass (Witt and Trost 1999; Sanders et al. 2002; Dahle et al. 2003 and reference therein).

The percent of high molecular weight PAHs (HMW = 4 to 6 rings) to Total PAHs ranged from 44 to 54.4% with a mean percent of 50.5 for all the sampled stations; on the other hand, the average percent of low molecular weight PAHs (LMW = 2 to 3 rings) ranged from 37% to 68% with a mean percent of 49.5. Then, there was no significant prevalence of any PAHs ring group (Fig. 2a). This preliminary evidence suggests that PAHs pollution over the sampling area might be originated from a "mixed" origin source (s). Additionally, the distribution of ring number groups was found to be homogeneous along the estuary, even though with significant differences in total PAHs concentrations (Fig. 2a, Table 1).

From another point of view, the correlation factors between the sediment concentrations of all the individual PAHs can give an idea whether they all originate from the same source (s) or not. As shown in Fig. 2b, PAHs concentrations were found to correlate linearly with high coefficients (all PAHs compounds mean correlation, $r^2 = 0.71$).

Taking this into account, it can be first stated that there exists a uniform group of sources loading PAHs to the sampled locations. These sources possibly include "mixed" contributors, all present in the area, such as, industrial wastewater discharges, shipping oil spills, land runoff, riverine inputs (Maldonado Stream), city sewage drainage discharges, and diffuse atmospheric fallout. Secondly, levels were found to decrease

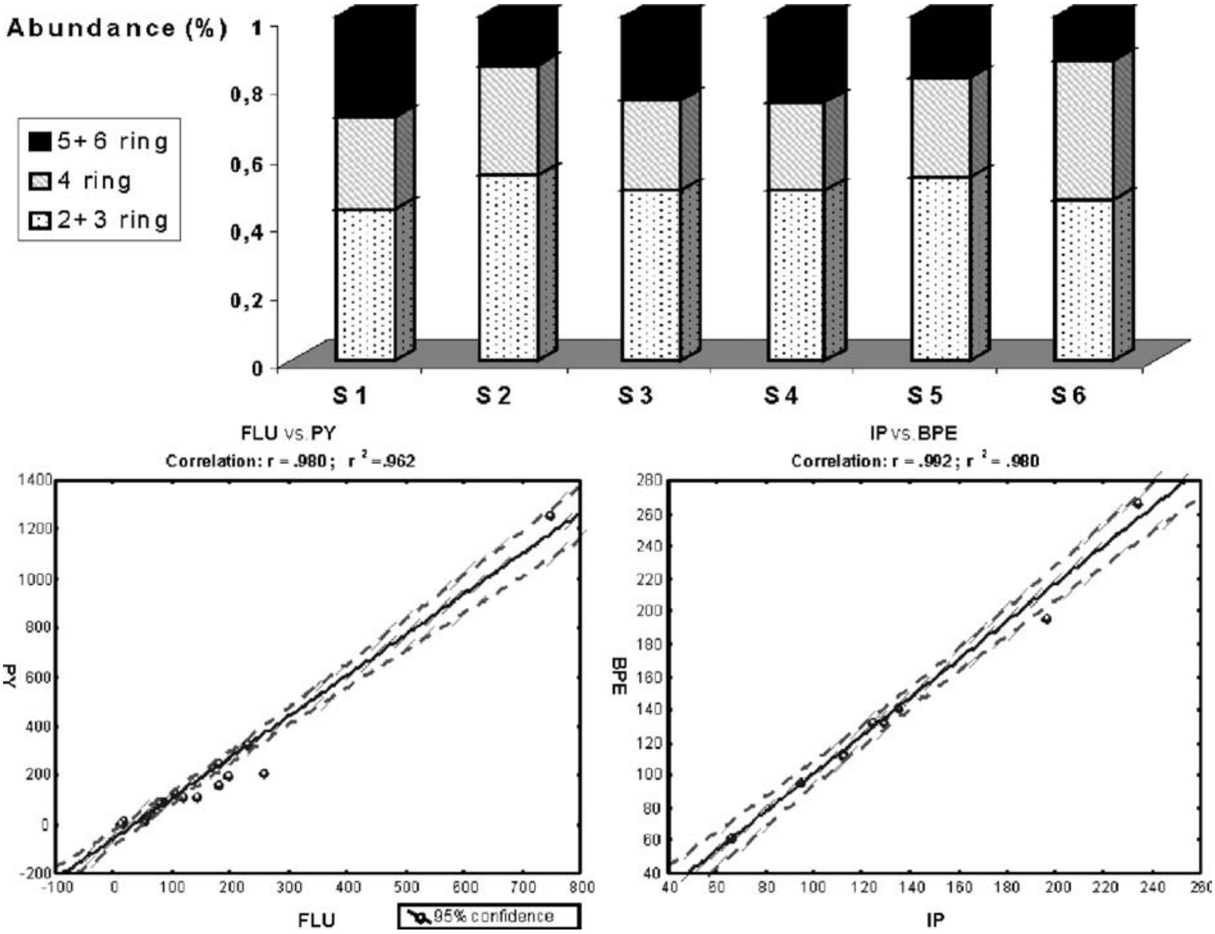

Fig. 2 **a** Contribution of (2 + 3), 4, and (5 + 6) ring groups to Total PAHs; **b** Correlation analysis between estuarine levels of Flu vs Py, IP vs BPE

as human activities decrease; thus, pointing to anthropogenic-related PAHs sources. Finally, the highly correlated PAHs concentrations can also suggest either that air/water/sediment transport mechanisms are spreading PAHs in similar ways, and/or PAH compounds might be undergoing similar environmental processes independent from the sampling sites. However, all these items need further assessment.

Perylene In this study, perylene was qualitatively evaluated to assess diagenetic PAH contribution. Perylene identification was done by literature time retention values and its contribution evaluated by percent area of total PAHs. It was found at low concentrations in all the sediments investigated (<2% of total PAHs). Typically, for pyrogenic PAHs, perylene represents about the 1–4% of the total PAHs concentration (Wakeham et al. 1980; Wang et al. 1999), and for diagenetic origin, concentrations higher than 10% of the total Penta aromatic isomers has been suggested (Readman et al. 2002). As in the case of diagenetic origin, only a few compounds are generated in comparison to the complex mixtures of PAHs generated by other sources (Yim et al. 2005), and measured perylene contributions were negligible, the potential diagenetic origin of detected PAHs at Bahia Blanca estuary sediments was discarded.

PAHs ratios PAHs ratios are traditionally used to determine PAHs sources, classify samples by location, and estimate the importance of combustion and petroleum derived PAHs (Lipiatou and Saliot 1991; Yunker et al. 1999, 2001; Budzinski et al. 1997).

The usual index of combustion and/or anthropogenic input is an increase in the proportion of the less stable and/or kinetically produced parent PAH isomers relative to the thermodynamically stable isomers; e.g., fluoranthene relative to pyrene, or to the molecular mass totals (Yunker et al. 2001). Index calculations are traditionally restricted to PAHs within a given molecular mass to minimize factors such as differences in volatility, water/carbon partition coefficients, adsorption (McVeety and Hites 1988) and, in most cases, appear to closely reflect the source characteristics of PAHs (Yunker et al. 2002). In this study, we have selected a limited set of five ratios to simultaneous consideration, in order to achieve the best potential for interpreting the PAH geochemistry of Bahia Blanca estuary.

Primarily, the proportions of fluoranthene to fluoranthene plus pyrene (Fl/202) and indeno-[1,2,3-*cd*]pyrene (IP) to IP plus benzo[*ghi*]perylene (IP/276) (Fig. 3) were used. Fl/202 ratios less than about 0.40 usually indicate petroleum (oil, diesel, coal) between 0.40 and 0.50 indicate liquid fossil fuel (vehicle and crude oil) combustion, while ratios over 0.50 are attributable to grass, wood, or coal combustion. Similarly, IP/276 ratios less than approximately 0.20 imply petroleum, between 0.20 and 0.50 liquid fossil fuel (vehicle and crude oil) combustion, while ratios over 0.50 are attributable to grass, wood, or coal combustion (Yunker et al. 2001). Further, these two parent PAHs ratios are supplemented by anthracene (An) to An plus phenanthrene (An/178) and benz[*a*]anthracene (BaA) to BaA plus chrysene [BaA/228] (Fig. 3). An/178 ratios <0.10 are usually taken as an indication of petroleum, while ratios >0.10 indicate combustion (Budzinski et al. 1997; Soclo et al. 2000; Yunker et al. 2001). Moreover, the low molecular weight PAH/high molecular weight PAH (LMW/HMW) ratio may also be used to determine the petrogenic and pyrogenic source: relative low values (<1) suggest pyrolytic PAHs input, whereas high value point to petrogenic sources (Yuam et al. 2001). These molecular ratio ranges are summarized in Table 4.

Thus, results show uniform PAHs ratios for the 24 samples analyzed, in particular, this uniformity

Table 4 Physicochemical parameters of sediments at sampling locations

	Pyrolytic origin	Petrogenic origin	This study	
			Range	Mean
FLU/202[a,b]	> 0.40	< 0.40	0.37–0.78	0.51
IP/276[b]	> 0.20	< 0.20	0.47–0.51	0.49
An/178[b]	> 0.10	< 0.10	0.02–0.66	0.30
BaA/228[b]	> 0.35	< 0.20	0.05–0.82	0.38
LMW/HMW[c]	< 1	> 1	0.52–2.08	0.88

[a] Budzinski et al. (1997)

[b] Yunker et al. (2002)

[c] Yuam et al. (2001), Tam et al. (2001)

extends to a group of 15 samples at S1, S2, S4, S5, and S6 sites sampled along the 2004–2005 period.

Sediment samples of the Bahía Blanca inner estuary (S1–S6) presented a mean Fl/202 ratio of 0.51 ± 0.09 ($n = 22$) and an IP/276 mean ratio of 0.49 ± 0.01 ($n = 10$). These values imply different combustion processes as the main input for the majority of samples. Consistent results were obtained for mean An/178 and BaA/228 ratios: 0.30 ± 0.21 ($n = 24$) and 0.38 ± 0.23 ($n = 22$), respectively. As Fig. 3 shows, these ratios ± (SD) are settled in the combustion PAHs origin area.

Individual sediment samples with elevated petroleum input ratios were found mainly at harbors and navigation channel stations (S1, S2, S4, S5, S6). For these cases, the GC-chromatograms showed the characteristic unresolved complex mixture "hump" signature confirming a petrogenic source contribution. This group of samples are responsible of the "spreading" at the An/178 and BaA/228 ratio values.

Finally, the abundance ratio of two- and three-ring hydrocarbons (LMW) to four- to six-ring hydrocarbon (HMW) PAHs is another commonly used ratio to help in distinguishing the petrogenic and pyrolytic sources (Robertson 1998). Values below 1 are considered as combustion sources and values above 1 are considered for petrogenic contributions (Yuam et al. 2001). The mean LMW/HMW ratio was 0.88 ± 0.37 ($n = 24$), indicating a slight overimposition of pyrolytic inputs along the estuary. The spread SD value is reflecting individual sediment samples with elevated petroleum input ratios.

The general predominance of fluoranthene over pyrene consistent with elevated IP/276 and BaA/228 ratios (Fig. 3) implicate both liquid fossil fuel combustion and biomass (coal, grass, wood) as the major PAHs sources. Biomass combustion can have both local and long range atmospheric transport sources, as the estuary is surrounded by agriculture lands, in which controlled and uncontrolled fires frequently occur. Liquid fuel fossil combustion source is probably a quite local source due to the high level of anthropogenic activities at the south area of the estuary (S1, S2, and S3), as described in the "PAHs concentrations".

Besides, petrogenic inputs indicators were found mainly at stations located over the navigation channel (S1, S2, S4, and S5). LMW PAHs predominance, alkylated naphthalene, and UCMs signatures have been observed for these set of stations. Only quite recent external sources are likely to be responsibly for these inputs. Intensive

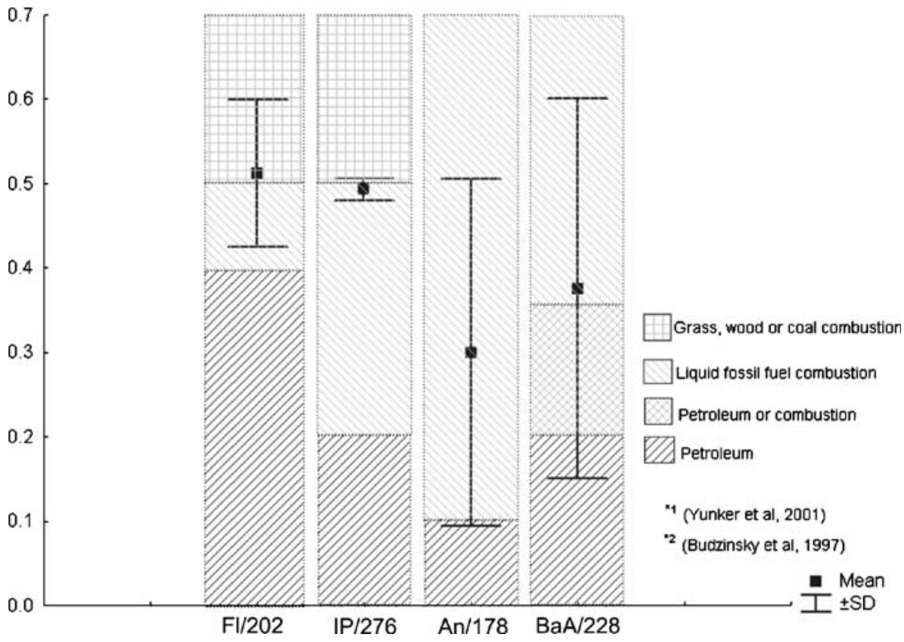

Fig. 3 Comparison of selected PAHs ratios (mean ± 1 SD) for 24 sediment samples along the inner Bahía Blanca estuary. Abbreviations refer to the ratios of fluoranthene plus pyrene (Fl/202), indeno-[1,2,3-*cd*]pyrene (IP) to IP plus benzo[*ghi*] perylene (IP/276), anthracene (An) to An plus phenanthrene (An/178) and benz[*a*]anthracene (BaA) to BaA plus chrysene [BaA/228]

boating activities appear to be the most likely petrogenic PAHs contributor.

Principal components analysis

Principal components analysis (PCA) is a multivariate analytical tool used to reduce the number of variables, e.g., measured PAHs content in bottom sediment samples and to extract underlying common factors (principal components, PCs) for analyzing relationships among the observed variables. As a result of an effective extraction process, PC1 accounts for the major proportion of the total data variance, while the second and following PCs progressively explain smaller amounts of data variation. PCA has been applied to analyze PAHs levels variance in some study (Freeman and Catteli 1990; Doong and Lin 2004; Zhang et al. 2004; Fang et al. 2006; Golobocanin et al. 2004; Yim et al. 2005; Xu et al. 2007). Prior to analysis, values under the limit of detection (LOD) in the data set were replaced with random values under the LOD value.

Concentrations of 17 PAHs as active variables and 24 samples as cases were used. The number of factors extracted from the variables was determined according to Kaiser's rule, which retains only factors with eigenvalues that exceed one. As performed in other studies, e.g., Golobocanin et al. (2004), a way of factor rotation to get as many positive loadings as possible to achieve a more meaningful and interpretable solution was preferred.

The majority of the variance (87.08%) was explained by two principal components vectors. PC1 explained 80.46% of the total variance and PC2 accounted for 7.03%. Figure 4 shows the loadings for the individual PAHs at the principal components plot. Along the PC1 axis, all the compounds were found to positive coordinate. PC1 had strong correlations (>0.7) with acenaphthylene, anthracene, chrysene, fluorene, fluoranthene, naphthalene, acenaphthylene, pyrene, 2-methyl-naphthalene. All these compounds gave strong correlation with the total PAHs concentration ($r > 0.90$; mean $r^2 = 0.91$). These facts indicate PC1 as a quantitative correlation component and correspond to the total PAHs concentration. PC2 presented significant positive loadings for a (3 + 4) ring PAH mixed group (>0.5) and, in particular, for a (5 + 6) ring PAH group (>0.70). As seen before, such PAHs are the result of combustion/pyrolitic processes and are absent in crude oil or refined products. Consequently, PC2 is defined as a pyrogenic component.

An overview of the principal components plot (Fig. 4a) shows different PAH clustering according to the number of aromatic rings in their structure. PAHs in the three main clusters may be originated from different origin source (s). As previously stated, PAHs at (5 + 6) ring cluster are identified as anthropogenic pyrolitic/combustion origin, also the (3 + 4) ring PAHs cluster could be named in the same way. The (2 + 3 + 4) ring cluster, with low loadings on PC2, is primarily a petrogenic cluster; however, it could either be named "mixed." Following these approaches, a portion of the total variance of PAHs concentrations is explained by source contribution, resulting in the pyrolitic origin the prevalent contribution over the sampled area. These results are consistent with our previous molecular ratios findings.

Contrarily, phenanthrene and dibenz-*ah*-anthracene presented low PC1 loadings. Dibenzo-*ah*-anthracene was not detected at the majority of samples; this lead to the poor correlation recorded with the total PAHs correlation axis (PC1). On the other hand, phenanthrene concentrations were found to be distributed with a different pattern from the main PAHs group. As Phe/An ratios were <10 for all samples, a petrogenic origin was discarded. Although a rationale cannot be given at the moment, possible explanations might be either different weathering kinetics from other PAHs and/or punctual phenantrene inputs. In fact, further research on these topics is being done.

Figure 4b shows the score plot of the first two components. This allows for the characterization of the sampling stations according to the first and the second component. The plot reveals how the samples are related to each other given the measurements that have been made. In this context, we identified three major groups of samples distributed along the pyrogenic component (PC2) axis. Samples named S3 are well differentiated by the higher scores on the second component. These samples are located in a petro-chemical industrial

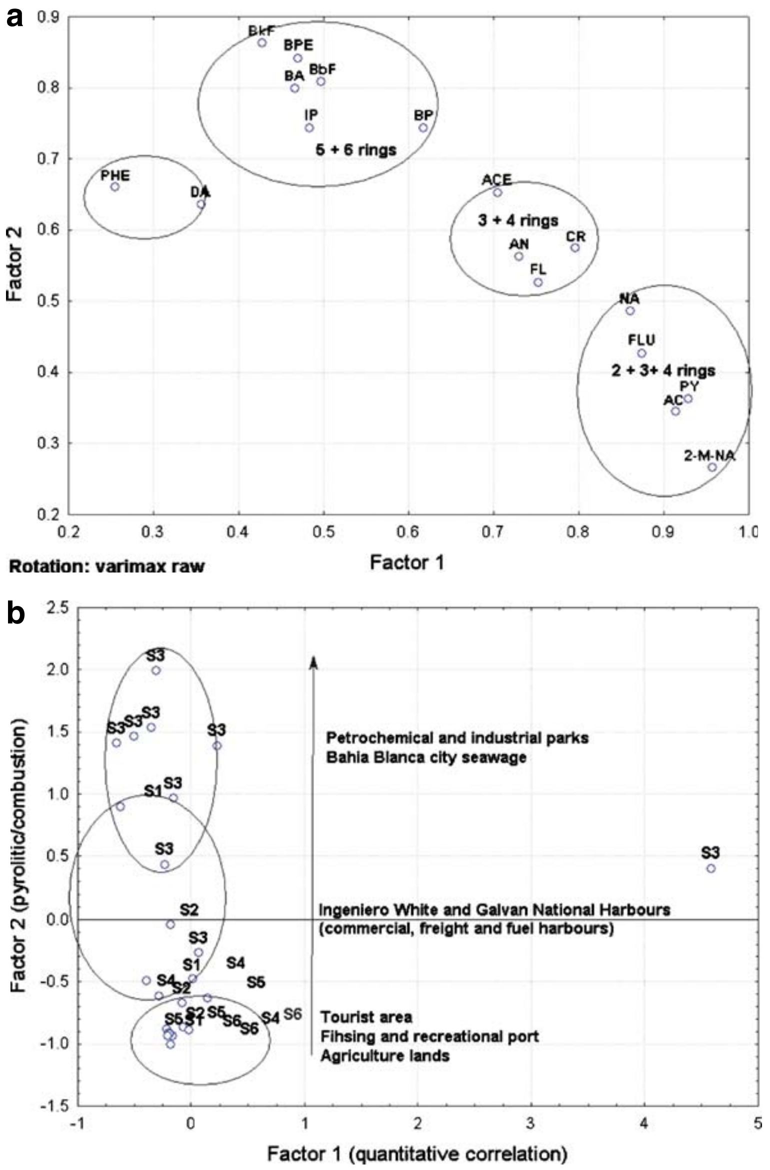

Fig. 4 **a** The PCA loading plot of sedimentary PAHs; **b** Score plot illustrating the distribution of PAHs compounds in the sampled areas along PC1 and PC2 axis. A general geographical reference of the stations is attached

park wastewater discharge zone, an area defined above as a hotspot because of its total PAHs levels. The remaining samples can be divided into different PC2 contributions, namely, commercial port areas (S1 and S2) achieving higher pyrolitic/combustion (PC2) scores than fishing, recreational, and agriculture areas (S4, S5 and S6), presenting a minor anthropogenic activity level.

In brief, PCA allowed us to separate ring group compounds clearly just as Golobocanin et al. did (2004), thus, enabling the determination of pyrolitic/combustion PAHs dominancy. Accordingly, it also allowed the classification of sampling sites over the estuary. These facts are in excellent agreement with molecular ratios analysis seen on section “ratios”. To conclude, similar literature results are found for other industrialized coastal environments, strongly suggesting that pyrogenic PAHs are a dominant signature in urban aquatic environments (Budzinski et al. 1997; Zeng et al. 1997; Pereira et al. 1999; Notar et al. 2001; Stout et al. 2004).

Conclusions

This paper presents the first comprehensive survey of PAHs in sediments, and provides very useful information on PAHs concentrations, composition and sources in Bahia Blanca Estuary, home to the fifth city of Argentina, two commercial harbors, and a heavy industrial area.

All sediment samples contained detectable amount of PAHs; the levels were low to moderate in comparison to other coastal estuaries, bays, and sea, and some suspected carcinogenic 5-ring PAHs were detected at almost all sites.

The spatial distribution of PAHs showed that the proximity to sources was the most important determining factor for the distribution of these contaminants. PAHs concentrations were greater in those samples collected near industrial areas than those from nonindustrial locations.

Ring-PAH distribution showed a "mixed" contamination pattern. In addition, the calculation of molecular indices such as Fl/202, IP/276, An/178, BaA/228, LMW/HMW determined an overimposition of pyrolitic PAHs over the petrogenic input. The diagenetic PAH contribution was found negligible at all sampled locations.

Ratio findings determined that the pyrolitic PAHs input may be attributed to a liquid fuel fossil combustion source, related to the high level of anthropogenic activities in the south area of the estuary, and to biomass combustion due to agriculture and long-range atmospheric transport sources. In the other hand, intensive harbor and recreational boating activities appear to be the most likely petrogenic PAHs contributors.

The use of PCA clearly separated ring group compounds and enabled the determination of pyrolitic/combustion PAHs dominancy, also allowing the classification of sampling sites over the estuary; in particular, S3 sampling station was determined as a pyrolitic/combustion PAHs "hot spot."

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