



Polycyclic aromatic hydrocarbons (PAHs) in plastic pellets: Variability in the concentration and composition at different sediment depths in a sandy beach

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ABSTRACT

Plastic pellets have the ability to adsorb organic pollutants such as PAHs. This study analyzed the variability in the concentration and composition of PAHs on plastic pellets sampled up to 1 m deep in the sediment of a sandy beach. The toxic potential of PAHs was analyzed, and the possible sources of contamination are discussed. The total PAHs varied, with the highest concentrations in the surface layer; the priority PAHs showed a different pattern. PAHs at greater depths did not reach toxicity levels above the PEL. The composition of PAHs differed between pellets from the shallower and from deeper sediment layers, and was suggested a mixture of sources. These results provided the first information on the depth distribution of PAHs in sandy beaches, associated with plastic pellets; and evidenced the potential environmental risk. Similarly to the abundance of pellets, the toxic potential is underestimated in surface samples.

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1. Introduction

Plastics are one of the most used and indispensable materials in modern life, due to factors such as their low cost of production, versatility and durability (Gregory, 1999; Barnes, 2005; Hammer et al., 2012). Their persistence is increasingly evident in the marine environment, and their occurrence is not limited to the seas and coastal areas close to industries (Barnes, 2005). These contaminants can reach high levels, particularly the small and usually imperceptible fraction, the plastic pellets, as demonstrated by their widespread occurrence throughout the world since the 1970s (e.g., Carpenter et al., 1972; McDermid and McMullen, 2004; Karapanagioti and Klontza, 2007; Frias et al., 2010; Claessens et al., 2011; Van et al., 2012). Because of several characteristics including the composition, shape, and buoyancy, as determined by the different densities of the polymers (Browne et al., 2010; Cole et al., 2011), and also their small size, the pellets can be easily dispersed (Morét-Ferguson et al., 2010). In the marine environment they can also act as a transportation vehicle for many hydrophobic pollutants, such as polycyclic aromatic hydrocarbons (PAHs) (Mato et al., 2001; Frias et al., 2010).

PAHs are one of the most significant classes of organic contaminants. Owing to their potential toxicity, wide distribution, and per-

sistence in the environment they have been of great interest to environmental chemists, toxicologists and regulatory agencies for almost three decades (Guzzella and De Paolis, 1994; Mai et al., 2001; Boonyatumanond et al., 2006). Because of their importance, especially related to their carcinogenic and mutagenic potential, 16 PAHs were listed by the US EPA (US Environmental Protection Agency) and considered as a priority for environmental monitoring (ATSDR, 2007). These compounds are: naphthalene, acenaphthylene, acenaphthene, phenanthrene, anthracene, fluorene, fluoranthene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[ah]anthracene and benzo[ghi]perylene.

PAHs are mainly present in locations such as harbor areas, estuaries and other coastal areas exposed to anthropogenic inputs (Perra et al., 2009), i.e., industrialized and urbanized areas. PAHs derive from two main sources in these areas: pyrolytic, which includes the compounds formed by fossil fuel combustion, waste incineration, and asphalt production; and petrogenic, composed by PAHs associated with spills of crude and refined oil (Law and Biscaya, 1994; McCready et al., 2000; Bertolotto et al., 2003).

Several studies have demonstrated that plastic pellets are ingested by a range of seabirds and fishes (e.g., Azzarello and VanVleet, 1987; Robards et al., 1995; Colabuono et al., 2009). Additives (emollients, coloring agents, and antioxidants) used in the production of pellets may have severe effects when ingested by these organisms (e.g., Ryan et al., 1988; Ananthaswamy, 2001). Plastic polymers act as carriers for some toxic compounds such as hydro-

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phobic DDT (dichlorodiphenyltrichloroethane), PCBs (polychlorinated biphenyls), phenols, and PAHs (polycyclic aromatic hydrocarbons) (e.g., Carpenter et al., 1972; Mato et al., 2001; Endo et al., 2005; Rios et al., 2007; Frias et al., 2010), which may also affect organisms after ingestion (e.g., Barnes 2002; Ogata et al. 2009). Pellets may affect organisms even when the pellets are buried in the sediment. Mascarenhas et al. (2008) suggested that plastic fragments found in turtle nest chambers can alter the exchange of gases, changing the incubation temperature and thus affect the natural sex determination of the embryos, and even obstruct the opening of the egg chamber and/or prevent the hatchlings from exiting the nest. A recent study by Carson et al. (2011) showed that the addition of small plastic fragments significantly increased the permeability of the sediment and that sediment containing plastic warmed more slowly. These changes may have a variety of effects on beach organisms, such as on their composition and abundance.

Therefore, because of the ecological risk that these plastic pellets represent to the environment, there has been growing interest in using pellets as passive samplers for monitoring pollution around the world (Ogata et al., 2009; Karapanagioti et al., 2010; Hirai et al., 2011; Heskett et al., 2012). Studies using these pellets as a matrix for the analysis of organic contaminants have considered, however, only those found in the surface layers of sandy beaches (Rios et al., 2007; Frias et al., 2010; Karapanagioti et al., 2011; Van et al., 2012). Nevertheless, plastic pellets are known to occur up to 2 m deep in beach sediment (Manzano, 2009), and as PAHs are adsorbed by these particles, it is possible that the concentration of these pollutants in the pellets varies from the surface to greater depths in the sediment.

The aim of this study was, therefore, to analyze the variability in the concentration and composition of PAHs in plastic pellets, sampled to a 1 m depth in sandy-beach sediments. Additionally, the toxic potential to marine organisms of PAHs adsorbed on the pellets is discussed, and the possible sources of PAH contamination in the study area are suggested.

2. Methods

2.1. Sampling design

Sampling of plastic pellets was conducted in May 2010 at Ponta da Praia (23°97'94"S and 46°31'46"W), located in Santos Bay on the southeastern coast of São Paulo state, Brazil (Fig. 1). This is a region of great importance, as it is the site of Santos Harbor, the largest port in Latin America, and one of the most important industrial complexes in the country (Cubatão industrial complex). A large quantity of plastic pellets was reported at this location by Manzano (2009).

One sample was collected from each 10 cm depth (0–1 m deep) in an area of 1 m² in the upper portion of the backshore. The sediment was removed by means of a metal shovel, to avoid contaminating the sample. The color of the plastic pellets varied from transparent or white to darker, and all the pellets were collected in order to reflect what is found in the environment. Samples were taken to a depth of 1 m because most of the pellets are concentrated at this depth (Manzano, 2009). The granules were separated by flotation, for each 10 cm of the sediment, with the aid of a fine-mesh metal sieve. The pellets were placed in foil envelopes and identified with parchment-paper labels.

2.2. Analytical methods

The composition and concentration of PAHs in the plastic pellets were analyzed using approximately 1 g of randomly selected pellets, following the method described by UNEP (1992), with a

few modifications. Each sample, as well as the blanks and reference material (sediment from NIST – SRM 1491b), was Soxhlet-extracted for 8 h. The organic extracts were concentrated, and were then cleaned into two fractions, F1 (aliphatic hydrocarbons; data not presented here) and F2 (PAHs) in a chromatographic column using silica and alumina, both 5% deactivated with pre-extracted water. PAHs were identified and quantified by a gas chromatograph with mass spectrometer (GC/MS) in a selected ion mode (SIM).

The PAHs analyzed included the 16 priority pollutants designated by the US EPA (ATSDR, 2007), their alkyl-substituted PAHs, and biphenyl, retene, benzo[c]phenanthrene, benzo[j]fluoranthene, benzo[e]pyrene, perylene and benzo[b]chrysene. Rather than analyzing only the 16 priority PAHs, the alkylated and other compounds were also analyzed in order to show the contamination in the study area in more detail.

2.3. Data analysis

The concentration of PAHs in plastic pellets was obtained by the sum of the concentrations of the analyzed compounds (Σ -total PAHs) and by the sum of the concentrations of the priority compounds (Σ -priority PAHs), and then compared among the different depth layers of the sediment.

The analysis of the potential toxicity caused by contamination of PAHs to organisms was based on reference values for TEL (Threshold Effect Level) and PEL (Probable Effect Level), available for marine sediment (Buchman, 1999). There are no specific reference values for plastic pellets as the matrix analyzed.

The differences in composition of PAHs among depths were analyzed by multivariate techniques including principal components analysis (PCA) and hierarchical clustering (using the mean of groups). The analysis was based on the similarity of the relative abundances of each compound in the different layers. For this purpose the data were standardized, and the plot of the ordination analysis used PCA axes 1 and 2. We considered eigenvectors $>|0.2|$ as the most important contribution. The hierarchical clustering was obtained using a similarity matrix based on the Euclidean distance.

The possible sources of contamination (pyrolytic and petrogenic) were identified for the different sediment depths by calculating the ratio of compounds of the same molecular weight. This identification was made according to the ratios that are commonly used in studies related to sediment analyzes, such as: (1) anthracene/anthracene + phenanthrene ($Ant/(Ant + Phe)$), where values <0.10 suggest the predominance of petrogenic sources, and >0.10 the dominance of pyrolytic sources; (2) fluoranthene/fluoranthene + pyrene ($Fluo/(Fluo + Py)$), where values <0.40 indicate the dominance of petrogenic, and >0.50 the dominance of pyrolytic input; (3) benz[a]anthracene/benzo[a]anthracene + chrysene ($BaA/(BaA + Ch)$), where values <0.20 indicate the dominance of petrogenic inputs, 0.20–0.35 a mixture of sources, and >0.35 the dominance of pyrolytic inputs; and (4) indeno[1,2,3-cd]pyrene/indeno[1,2,3-cd]pyrene + benzo[g,h,i]perylene ($IP/(IP + Bghi)$), where values <0.20 indicate the dominance of petrogenic sources, 0.20–0.50 a mixture of sources, and >0.50 the dominance of pyrolytic sources (Yunker et al., 2002; Yunker and Macdonald, 2003).

3. Results

The presence of PAHs was recorded in all samples of plastic pellets collected at different depths of the sediment, except Σ -methylfluoranthenes, which showed values below the detection limit at all depths. The Σ -total PAHs ranged from 386 to 1996 ng g⁻¹ (Table 1). The highest concentration was observed in pellets col-

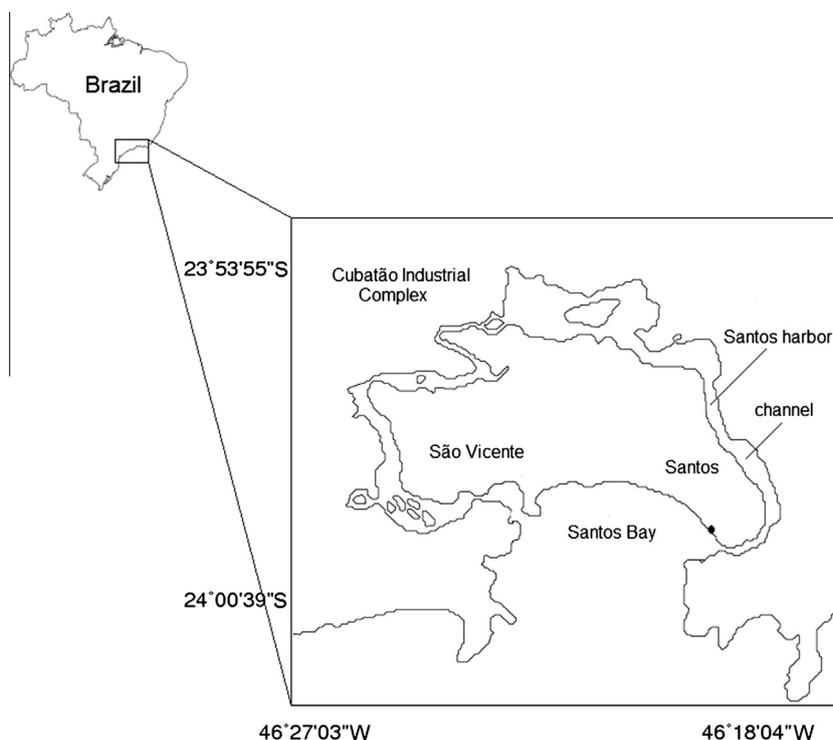


Fig. 1. Study area: (A) Brazil with the location of São Paulo State, and its coastal zone showing Santos Bay, and (B) Ponta da Praia (sampling point) in Santos Bay in detail.

lected in the surface layer of the sediment (0–10 cm with 1996 ng g^{-1}), with smaller peaks recorded at 60–70 cm and 30–40 cm (1336 ng g^{-1} and 1004 ng g^{-1} , respectively). A slight increase in concentration was recorded in the 90–100 cm layer. The lowest concentrations were recorded at the 10–20 cm depth (386 ng g^{-1}). Some variability in the concentration of PAHs was observed across the different depths. The variation was, however, relatively small at depths of 20–30 cm to 50–60, and 70–80 to 90–100 cm ($802\text{--}1004 \text{ ng g}^{-1}$ and $768\text{--}996 \text{ ng g}^{-1}$, respectively) (Fig. 2).

The values of Σ -priority PAHs ranged between 198 and 1042 ng g^{-1} (Table 1). Differently from Σ -total PAHs, the highest concentrations were observed in pellets sampled at 60–70 cm in the sediment ($1,042 \text{ ng g}^{-1}$), followed by the surface layer (0–10 cm) and the 70–80 cm depth (746 and 735 ng g^{-1} , respectively). The lowest concentration (198 ng g^{-1}) was observed at the 10–20 cm depth. Similarly to the distribution pattern observed for the Σ -total PAHs, the variability in the concentration of PAHs within the ranges of 20–30 to 50–60 cm and 70–80 to 90–100 cm depth was relatively small ($417\text{--}571 \text{ ng g}^{-1}$ and $603\text{--}735 \text{ ng g}^{-1}$, respectively), but with a slight increase in concentration in the 90–100 cm layer (Fig. 2 and Table 1).

The concentrations of the compounds considered for the analysis of toxicity (TEL and PEL) ranged from 79.33 to 302 ng g^{-1} . The reference values for the toxic potential of PAHs are 1684 and $16,770 \text{ ng g}^{-1}$ for TEL and PEL respectively (Buchman, 1999). Therefore, the Σ -PAHs showed, in the different depth layers, concentrations below the level of the potential toxicity to the biota (TEL). Concentrations above the reference values for PEL were not recorded, after the individual compounds were analyzed and compared to the concentrations obtained at the values proposed by NOAA (Buchman, 1999). Concentrations in the range between TEL and PEL were, however, observed for dibenz[ah]anthracene in most layers (0–10 cm and between 20–30 and 60–70 cm); followed by Σ -methylnaphthalenes (40–50 cm and 80–90 cm), acenaphthylene (20–30 cm) and chrysene (0–10 cm). The compound that showed toxic potential (interval between TEL and PEL) at most

depths sampled was dibenz[ah]anthracene. However, chrysene, rather than dibenz[ah]anthracene, was present in the highest concentration (Table 1).

The principal components analysis (PCA) for the comparison of the relative abundance (standardized data) of PAHs among different depths showed that the first principal component (PC1) accounted for 78.5% of the variation of the data, while the second main component (PC2) corresponded to 16.7%. Together, these two components were responsible for almost all the variability (95.2%).

The different depth layers formed two major groups and one smaller group, divided as: Group I – including the upper layers of the sediment (10–20 cm, 20–30 cm, 30–40 cm, 40–50 cm and 50–60 cm). These depths were grouped together due to the highest relative abundance of the Σ -dimethylnaphthalenes and Σ -dimethylchrysenes. The depth of 10–20 cm showed a weaker bond with this group, due to the relatively smaller concentrations, mainly related to benzo[e]pyrene and benzo[ghi]perylene. The 30–40 cm depth had relatively smaller concentrations of Σ -dimethylchrysenes compared to the other compounds. Group II, formed by the deeper layers (60–70 cm, 70–80 cm, 80–90 cm and 90–100 cm), had the highest relative proportions of the compounds indeno[1,2,3-cd]pyrene and benzo[ghi]perylene, and smaller proportions of Σ -dimethylnaphthalenes and Σ -dimethylchrysenes. The 80–90 cm depth was separated due to the smaller relative proportion of benzo[ghi]perylene, compared to other depths of this group. Group III was formed only by the surface layer (0–10 cm), which was not linked to any of the other groups because of the higher relative abundance of benzo[e]pyrene and Σ -dimethylchrysenes. In general, the predominance of alkylated compounds such as Σ -dimethylchrysenes was observed in the upper layers (0–10 to 50–60 cm); while high-molecular-weight compounds, especially benzo[ghi]perylene and indeno[1,2,3-cd]pyrene, were more concentrated close to the base of the profile (60–70 cm and 90–100 cm) (Fig. 3A and B).

The identification of the sources of contamination in the area, using the ratio of Ant/(Ant + Phe), showed values between 0.30

Table 1
Individual, Σ -total PAHs and Σ -priority PAHs concentrations (ng g^{-1}), and graphical representations of the distribution of individual compounds on plastic pellets, sampled every 10 cm to a depth of 1 m in sandy-beach sediment. The “<” symbol indicates PAH concentration below the detection limit, which is different for each PAH compound. Compounds in bold represent those used by NOAA (Buchman, 1999) for TEL and PEL analyzes. Reference values for TEL and PEL respectively are: naphthalene: 34.57 and 390.64; acenaphthylene: 5.87 and 127.87; acenaphthene: 6.71 and 88.9; fluorene: 21.17 and 144.35; phenanthrene: 86.68 and 543.53; anthracene: 46.85 and 245; fluoranthene: 112.82 and 1493.54; pyrene: 152.66 and 1397.6; benzo[a]anthracene: 74.83 and 692.53; chrysene: 107.77 and 845.98; benzo[a]pyrene: 88.81 and 763.22; dibenz[ah]anthracene: 6.22 and 134.61.

Compounds (ng g^{-1})	Depths (cm)										Graphic (0–100 cm)
	0–10	10–20	20–30	30–40	40–50	50–60	60–70	70–80	80–90	90–100	
Naphthalene	18.4	23.0	16.3	24.9	15.9	12.8	10.8	17.8	30.8	14.8	
Σ -Methylnaphthalenes	17.3	19.8	13.4	10.0	20.7	8.69	10.3	15.0	26.9	10.3	
Biphenyl	2.76	1.85	2.29	1.66	1.87	<1.30	<1.30	1.66	2.97	<1.30	
Σ -Ethylnaphthalenes	4.72	3.00	4.39	<2.60	3.95	<2.60	<2.60	2.68	4.91	<2.60	
Σ -Dimethylnaphthalenes	39.4	35.2	41.6	14.1	39.6	12.0	14.1	26.7	40.8	13.1	
Acenaphthylene	4.70	4.67	6.00	5.46	3.99	5.15	5.31	4.14	4.68	3.58	
Acenaphthene	1.44	<1.30	1.36	<1.30	3.51	<1.30	<1.30	2.06	<1.30	<1.30	
Σ -Trimethylnaphthalenes	41.2	21.9	44.5	11.3	42.5	16.1	6.41	34.3	13.1	9.66	
Fluorene	3.98	<1.30	1.49	<1.30	2.01	<1.30	<1.30	1.50	<1.30	<1.30	
Σ -Methylfluorenes	3.87	<1.30	11.8	7.88	8.87	10.6	7.66	14.4	14.7	10.3	
Phenanthrene	10.6	4.30	6.56	7.40	8.17	3.86	3.56	13.0	4.82	2.67	
Anthracene	12.7	2.29	4.84	13.4	3.50	6.51	10.4	23.1	34.2	17.7	
Σ -Dimethylfluorenes	8.84	<1.30	15.0	13.3	7.18	12.2	9.48	13.5	8.04	19.6	
Σ -Methylphenanthrenes	69.8	14.1	27.5	44.3	30.8	23.8	18.7	30.5	25.8	26.4	
Σ -Dimethylphenanthrenes	72.1	23.2	29.8	36.3	43.2	30.9	15.1	33.7	<2.20	20.5	
Fluoranthene	11.2	3.10	4.68	9.49	3.99	7.70	5.79	8.60	3.05	2.82	
Pyrene	30.0	2.34	7.88	10.73	3.72	6.26	5.13	6.99	3.14	2.15	
Σ -Methylfluoranthenes	<1.30	<1.30	<1.30	<1.30	<1.30	<1.30	<1.30	<1.30	<1.30	<1.30	
Retene	16.8	<1.30	6.34	<1.30	4.45	<1.30	<1.30	<1.30	<1.30	<1.30	
Σ -Methylpyrenes	164	14.2	15.7	8.58	20.3	<1.30	4.02	<1.30	1.99	<1.30	
Benzo[c]phenanthrene	5.51	<1.20	<1.20	<1.20	<1.20	<1.20	<1.20	<1.20	<1.20	<1.20	
Benzo[a]anthracene	3.43	1.28	1.71	6.55	1.44	3.98	5.83	7.31	8.28	4.27	
Chrysene	153	16.7	16.2	15.5	33.7	11.3	6.78	18.1	4.37	5.04	
Σ -Methylchrysenes	169	20.1	24.2	41.6	23.2	5.29	9.18	8.85	<1.20	<1.20	
Σ -Dimethylchrysenes	414	33.9	65.4	115	54.1	38.1	35.7	36.0	<1.20	<1.20	
Benzo[b]fluoranthene	54.6	<1.30	<1.30	<1.30	7.38	<1.30	<1.30	<1.30	<1.30	<1.30	
Benzo[j]fluoranthene	38.3	<1.30	<1.30	<1.30	10.4	<1.30	<1.30	<1.30	<1.30	<1.30	
Benzo[k]fluoranthene	36.1	<1.30	<1.30	<1.30	5.82	<1.30	<1.30	<1.30	<1.30	<1.30	
Benzo[e]pyrene	181	<1.30	60.9	99.0	55.1	59.6	35.7	31.6	18.3	18.1	
Benzo[a]pyrene	19.8	<1.10	7.09	29.3	4.45	7.76	6.66	5.82	2.94	11.0	
Perylene	0.00	<1.20	<1.20	23.8	<1.20	9.25	105	7.86	3.75	7.37	
Indeno[1,2,3cd]pyrene	234	84.7	157	143	147	173	335	196	220	174	
Dibenzo[ah]anthracene	15.1	2.72	9.14	22.3	6.59	7.10	18.7	5.71	4.20	3.09	
Benzo[b]chrysene	2.09	<1.10	1.88	5.58	<1.10	2.69	21.9	3.13	3.45	3.52	
Benzo[ghi]perylene	136	52.2	196	282	166	161	627	426	282	453	
Σ -Total PAHs	1996	386	802	1004	783	637	1336	996	768	834	
Σ -Priority PAHs	746	198	437	571	417	407	1042	735	603	695	

and 0.88, which was indicative of the predominance of pyrolytic contamination sources at all depth layers of the sediment (Fig. 4A). The ratio of Fluo/(Fluo + Py) showed values between 0.27 and 0.57, suggesting that pyrolytic sources of contamination predominated, except in the surface layer (0–10 cm) and the 20–30 cm depth, where there was an indication of petrogenic sources (Fig. 4B). The ratio BaA/(BaA + Ch) showed values between 0.02 and 0.65, which indicated contamination predominantly by petrogenic sources between the surface and the 30 cm depth layers. Below this depth, the prevalence of contamination sources were reversed, down to the last depth layers sampled (Fig. 4C). Finally, the ratio IP/(IP + Bghi) resulted in values between 0.28 and 0.63, suggesting that compounds from pyrolytic sources predominated in all layers of the sediment (Fig. 4D).

Given the calculated ratios and analysing the different depth layers, the input of compounds from pyrolytic sources was pre-

dominant in the 60–70 and 80–100 cm depths. In general, the PAH contamination of plastic pellets in the different depth layers of the sandy-beach sediment from Ponta da Praia provided to be a mixture of contamination from pyrolytic and petrogenic sources.

4. Discussion

This study revealed wide variability of PAHs in the different depths of the sediment. This variability is due to the inherent characteristics of the matrix, plastic pellets, such as their persistence, exposure time in the marine environment, and also their buoyancy (Barnes, 2005; Morét-Ferguson et al., 2010).

In the region of Santos Bay, contamination by PAHs has been analyzed in the sediment of the estuary (Nishigima et al., 2001; Medeiros and Bicego, 2004; Bicego et al., 2006; Martins et al.,

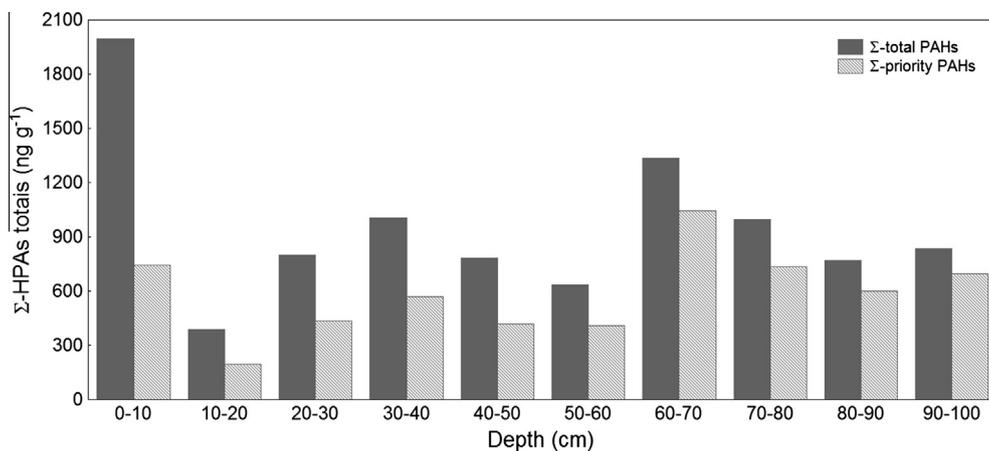


Fig. 2. Distribution of (A) Σ -total PAHs and (B) Σ -priority PAHs (ng g^{-1}) on plastic pellets collected in 10 cm layers to a depth of 1 m in a sandy beach. Dark-grey bars indicate Σ -PAHs, and light-grey bars indicate Σ -priority PAHs.

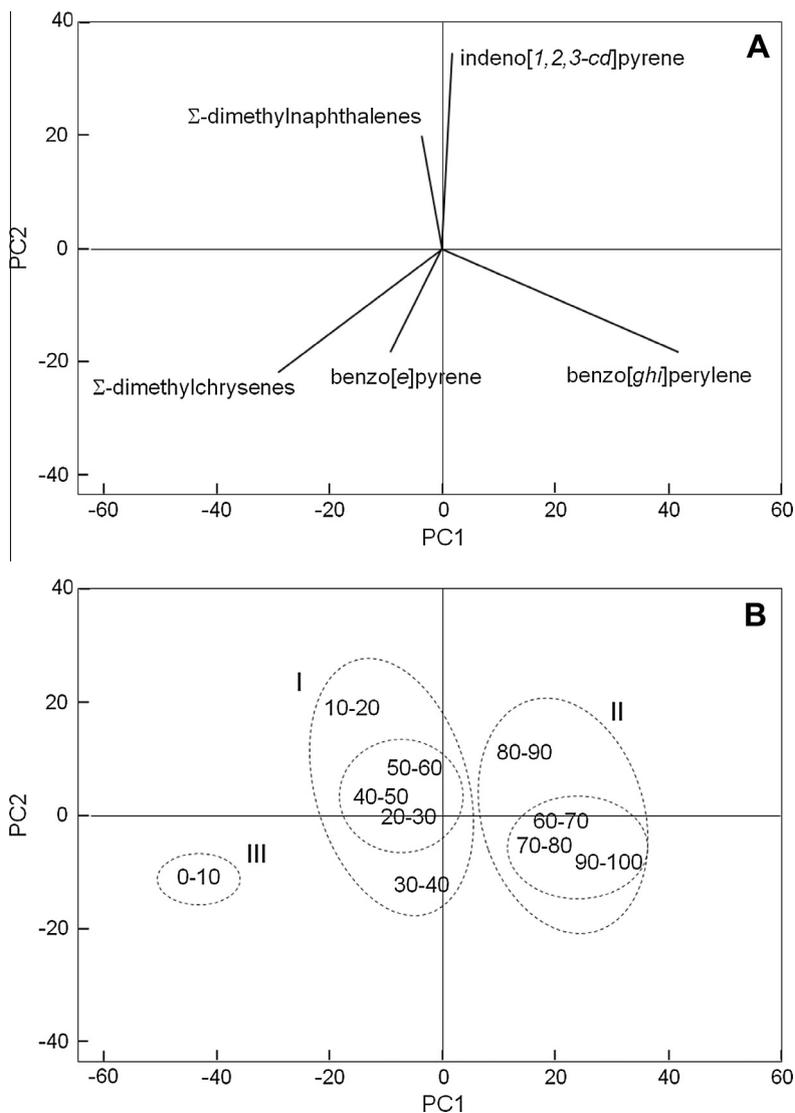


Fig. 3. Principal components analysis, considering (A) relative abundance of the compounds present in the highest proportions, (B) sampling layers, in each 10 cm layer to a depth of 1 m, grouped according to their similarity (cluster) in PAH composition on plastic pellets collected in Santos Bay. Dashed lines indicate strong links in these compositions.

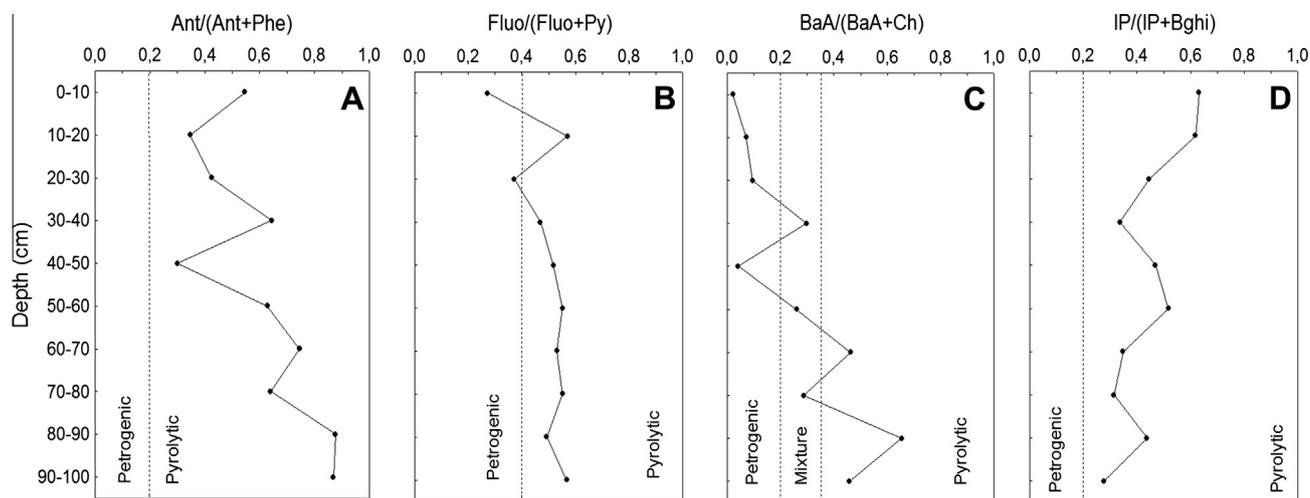


Fig. 4. Calculated ratios for the identification of sources of PAH contamination in plastic pellets sampled to 1 m depth in a sandy beach. (A) Ant/(Ant + Phe), (B) Fluo/(Fluo + Py), (C) BaA/(BaA + Ch), (D) IP/(IP + Bghi). Ant = anthracene; Phe = phenanthrene; Fluo = fluoranthene; Py = pyrene; BaA = benzo[a]anthracene; Ch = chrysene; IP = indeno[1,2,3-cd]pyrene; Bghi = benzo[ghi]perylene.

2007). Only the study by Martins et al. (2007) considered sediment cores, and the remaining studies used only the surface sediment. Therefore, our comparisons of PAH contamination used the available bibliography, which included a different matrix (sediment instead of pellets), and for that reason may not have shown a similar behavior. The distribution pattern of PAHs in the sediment samples can, however, provide important information about the location where the pellets were collected, and can help in the interpretation of the results presented here.

The concentration of Σ -total PAHs in the plastic pellets varied throughout the different sediment depths. The layers with higher concentrations of these pollutants were the surface, 30–40 cm and 60–70 cm layers. This could be due to the proximity of the sampling points to the Cubatão industrial complex in the upper estuary. The abundance of pellets at the same location was previously found to be greater at similar depths (up to 30 cm and 50–60 cm) (Manzano, 2009). Similarly, the deposits of heavy minerals in the sediment column showed an increase in the mineral concentrations close to depths of 20, 30 and 50 cm (Dias and Mahiques, unpublished data). This suggests that, possibly, pellets that remained longer in the environment experienced several extreme events, which contributed to bury them, and accounts for why they can be found at greater depths. Furthermore, pellets that remain in the environment for longer periods undergo weathering and, consequently develop surface cracks, increasing their capacity to adsorb pollutants (Endo et al., 2005). This was demonstrated by the increased concentration of PAHs in pellets sampled deeper in the sediment column during the present study.

In the coastal sediment of the Gulf of Trieste, which is a harbor area with intense industrial activity similar to the study area, a variation similar to the present study was observed, with the highest concentration of PAHs in the portion closest to the surface (682, 29 ng g⁻¹), followed by a decrease in deeper layers (Notar et al., 2001). Comparing the depth layers that showed the highest PAH concentrations in plastic pellets in the present study, revealed a difference between the concentration of total and priority Σ -PAHs. This difference probably resulted from the high concentration of the alkylated compounds found in the surface layer (0–10 cm), which are not listed among the priority compounds. This depth layer contained the highest concentration of the Σ -total PAHs, while the highest concentrations of Σ -16 priority PAHs occurred at about 60–70 cm depth. The variability in the PAH composition is probably due to the different adsorption characteristics of organ-

ic pollutants by plastic resin pellets (Karapanagioti et al., 2010; Fries and Zarfl, 2012), and also the exposure time of the pellets in the environment, as well as the sources of contamination (compounds available) in the region where the pellets remained until they arrived on the beach.

Santos Bay has undergone an intensive increase in urbanization and industrialization, especially in the last 50 years (Martins et al., 2007). These activities, along with port activities, contribute to high levels of PAHs in a region (Pietzsch et al., 2010). The above factors explain not only the contamination of the region recorded in sediments of the Estuary of Santos and São Vicente (Nishigima et al., 2001; Bicego et al., 2006), but also help to understand the high concentrations observed in the plastic pellets during this study.

The toxic potential of PAHs adsorbed onto the pellets collected in the different layers of sediment, does not indicate at possibility of harmful effects to biota. Nevertheless, it is important to note that the reference values used here have been proposed for marine sediments. Because the PAHs have higher affinity to the plastic pellets than to the sediment (Teuten et al., 2007), the toxic potential associated with the pellets may be different than those estimate during this study.

The composition of individual PAH compounds varied through all the layers, but a pattern of concentration of at higher proportion of alkylated compounds in the upper layers and of higher-molecular-weight compounds in the deeper layers was apparent. The compounds with higher concentrations of PAHs, in plastic pellets from different depths in sandy sediments, are heavy compounds (4–6 rings), which are also indicative of pyrolytic sources, because the major contributions of these PAHs in the environment occur through combustion processes (Laflamme and Hites 1978; Yunker et al., 2002; Martins et al., 2007). Besides this class of compounds, there is also the contribution of alkylated compounds, which are commonly associated with input of wastewater containing oil and grease, as well as spills from ship traffic in the vicinity of marinas and port regions (Pietzsch et al., 2010). These main classes of compounds were also observed in samples from surface sediments in the same area (Fisner et al., unpublished data).

In general, the contamination suggested by the ratios obtained here is a mixture of compounds from petrogenic and pyrolytic sources, with a predominance of pyrolytic sources, in plastic pellets collected in deeper sediment at Ponta da Praia. This result agrees with the profiles found in analyzes of sediments from the

Estuary of Santos and São Vicente (Nishigima et al., 2001; Medeiros and Bicego, 2004).

In contrast to the analysis of sediment, where it is possible to trace the history of the contribution of hydrocarbons over the years and associate this with past events (Yunker and Macdonald, 2003), no published data are available for plastic pellets, which makes an association difficult. It may be possible to correlate historical events, such as an increase in the emission of certain compounds or accidents including oil spills, which contribute to the contamination of pellets, and to find a recent contribution from these occurrences. This might provide a better foundation for attempts to minimize such environmental effects.

The information presented in this study provides the first insights into contamination by PAHs in plastic pellets in deeper layers of sandy-beach sediment. Further studies are needed to verify if the observed pattern of distribution of these pollutants in pellets is consistent with other impacted areas and also to evaluate differences in the concentration and composition of PAHs among sandy beaches located near to or more distant from urbanized centers and port areas. Consideration should be also given to the potential environmental risk presented by the composition and concentration of PAHs adsorbed onto plastic pellets deposited in coastal environments, including the underestimated vertical distribution.

Importantly, the plastic pellets seemed to be a good tool to help to identify possible sources of hydrocarbon contamination, but should be used with caution (Saha et al., 2009; Pietzsch et al., 2010). This caution is necessary especially when the substance in question is plastic, because the ratios have been proposed based on another matrix, the sediments.

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