

Investigation of main source and composition of polycyclic aromatic hydrocarbons in sediments from a very contaminated estuary in Brazil

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ABSTRACT

A study on the concentrations and inputs of PAHs to marine sediments of Santos and São Vicente Estuary System, located in southeastern São Paulo State, Brazil, is presented here. Sediment samples, collected at 16 sites in the estuary and surrounding channels, were extracted and analyzed by gas chromatography coupled to a mass spectrometer detector. Total concentrations varied from 0.226 to 41758 ng.g⁻¹(dw) for PAH. Isomers pair ratios were used as a tool for identify the main sources of PAHs to SES. Anthropogenic contributions were apparent, indicating the influences of the Cubatão industrial complex originating from combustion of coal in metallurgical processes, crude oil and diesel fuel from refineries, shipping and road haulage, storage facilities for petroleum and derivatives, based on the isomers ratio of PAHs concentrations in sediments.

Keywords – Contaminants; Anthropogenic inputs; PAHs isomers ratios

INTRODUCTION

The Santos Estuary System (SES), located on the southeastern Brazilian coast lies in one of the most economically important areas of Brazil. The city of Santos has the largest commercial harbor in South America as well as one of the most important petrochemical and metallurgical industrial center in Brazil, the Cubatão industrial complex, which has some 1100 industries. It is composed of 23 large factories including a steel mill, an oil refinery, fertilizer, cement and chemical/petrochemical plants that sum up to 260 pollutant emission sources (LAMPARELLI *et al.*, 2001).

SES has been characterized by increasingly intensive anthropogenic activity over the last 100 years, where the combustion of fossil-fuels in industrial and human activities contribute to the input of a large amount of particulate material rich in pollutants such as polycyclic aromatic hydrocarbons (PAHs). The increase in the intensity of urbanization and industrialization on the banks of the estuary, mainly over the last 50 years, has been responsible for the degradation of the mangrove vegetation, the emission of industrial effluents and the discharge of domestic sewage and solid residues. In addition, port activities involve oil, sand, other transportation and fishing activities.

The tourism is the second economic activity and population increases three times over the local population and most of people have a primary contact with water for recreation, swimming, paddle, commercial and sportive fishing activities (i.e. crabs, mussels and fishes), among others. Apart from outstanding economic importance, SES has also considerable environmental relevance since the estuary is surrounded by mangrove swamps, which account for 43% of the total mangrove area of the state of São Paulo (LAMPARELLI *et al.*, 2001). As a consequence of the low hydrodynamic, high percentage of fines and the intense industrial activities, PAHs are present in the sediments of SES.

This research presents the use of isomers pair ratios of PAHs in the sediments as a tool of investigation and the identification of main PAHs sources for SES.

MATERIALS AND METHODS

Sixteen surface sediment samples were collected in winter/2010 in the SES (fig 1).

The samples were placed in pre-cleaned aluminum boxes, and then stored in a freezer until laboratory analysis.

The sediment samples were lyophilized for 72 hours and an amount of 20 g was Soxhlet-extracted with a 50% mixture of residue grade n-hexane and dichloromethane for 8h in accordance

with UNEP (1992). Before extraction, d_8 -naphthalene, d_{10} -acenaphthene, d_{10} -phenanthrene, d_{12} -chrysene and d_{12} -perylene were added to all samples, blanks and reference material (NIST – SRM 1944) as surrogates. The PAHs extracts were cleaned up by silica gel–alumina chromatography column. PAHs were quantitatively analysed by an Agilent 6890 gas chromatograph coupled to a 5973N mass spectrometer (GC-MS) in the selected ion monitoring (SIM) mode. A 25x0.25 mm i.d.x0.25 μ m HP 5MS film capillary column from Agilent was temperature programmed from 40°C to 60°C at 20°C min⁻¹, 60°C to 300°C at 4°C min⁻¹ and held at 300°C for 10 min GC–MS. All compounds were identified and quantified based on analytical curve built with by injection of certified standards at five different concentrations. PAH identification was based on GC retention times of certified standards, individual mass spectra and comparison with literature and library data. The detection limit (LD) of the method was 1.00-3.70ng.g⁻¹ for PAHs.



FIG 1: The map of Brazil showing the localization of the Santos – São Vicente Estuary System.

RESULTS AND DISCUSSION

Individual and total concentrations of PAHs for this study are given in Table 1. The Σ PAH concentrations varied from <LDM to 15617.42 ng.g⁻¹(dw). Low concentrations (<500 ng.g⁻¹) occurred in sites 1, 2, 8 and 16 which were collected far from major industrial and urban centers. High concentrations (>500 ng.g⁻¹) occurred at sites 3, 4, 5, 6, 7, 9, 10, 11, 12, 13 and 14 which were collected near of the anthropogenic sources. The station 15 presented values of recuperation under the limit accept for the method (60-120%), therefore the station 15 won't be use for discussed the polycyclic aromatic hydrocarbons results.

There are two mainly sources of the PAHs in coastal marine sediments: pyrogenic and petrogenic. The major sources to be expected for pyrogenic PAHs are power plants, exhaust fumes from diesel engines and used crankcase oil. The petrogenic PAHs may come from oil spill directly into the seawater as well as domestic and industrial effluents runoff. Some of the ratios between individual compounds are use to identification of PAHs origin. These ratios are based on the formation temperature of the compounds. Some isomer pairs are also used to distinguish PAHs of various origins (YUNKER *et al.*, 2002). It is generally to be expected that a methylphenanthrenes/phenanthrene (Σ C1P/P) ratio with values between 0.5 and 1.0 should be typical of combustion processes and for petrogenic sources these ratios are >2. None of sites presented ratio >2, thus the combustion origin of PAHs is predominant and more probable in all studies sites.

According to Yunker *et al.* (2002), it is possible to use the following four PAH isomer pair ratios to identify possible sources in sediments: anthracene/anthracene + phenanthrene (Ant/178) ratio < 0.10 indicates the dominance of petroleum and >0.10 indicates the dominance of combustion; benzo[a]anthracene/benzo[a]anthracene + chrysene (BaA/228) ratio < 0.20 petroleum, 0.20–0.35 petroleum and combustion (mixed sources), and >0.35 combustion; fluoranthene/fluoranthene + pyrene (Fl/Fl + Py) ratio <0.40 petroleum, 0.40–0.50 petroleum combustion, and >0.50 combustion of coal, grasses and wood; Indeno[1,2,3-c,d]pyrene/indeno[1,2,3-c,d]pyrene + benzo[g,h,i]perylene (IP/IP + BghiP) < 0.20 petroleum, 0.20–0.50 petroleum combustion, and >0.50 combustion of coal, grasses and wood. These PAH isomer pair ratios determined for sediment samples in this study are given in Table 1. The Ant/178 isomer pair ratios show that PAHs are derived primarily from combustion (Ant/178 > 0.10 in all sites) with no occurrence of PAHs originating from petroleum. The combustion of crude oil is possibly the major source of PAHs in sediments because the SES is situated in an area of refineries, oil terminals and intense shipping traffic.

Table 1 Polycyclic aromatic hydrocarbons (PAHs) concentrations in sediment samples from the Santos Estuary System (ng g⁻¹ dw)

Site N ^o /Compounds	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P16
Phenanthrene	4.52	11.77	29.49	232.11	217.37	53.2	31.64	13.06	38.27	76.06	200.88	1746.51	203.18	968.37	<LDM
Σ-Methyl-phenanthrenes	4.75	10.53	32.47	188.49	171.65	48.89	44.09	14.76	37.78	119.56	190.21	887.27	109.44	483.35	<LDM
Anthracene	1.47	3.11	11.15	151.81	119.44	14.35	10.94	4.3	17.34	23.8	46.63	562.4	89.84	288.05	<LDM
Fluoranthene	12.29	30.2	89.83	683.78	915.6	221.46	136.98	28.26	85.81	251.06	273.17	2051.39	379.8	1883.82	<LDM
Pyrene	12.58	29.94	88.48	687.57	949.53	224.02	137.89	28.42	87.01	257.55	279.2	2154.63	397.93	1873.6	<LDM
Benzo(a)anthracene	5.4	13.58	48.3	445.61	461.77	151.37	71.38	18.23	50.26	89.7	138.68	1016.81	233.66	537.17	<LDM
Chrysene	6.99	17.94	65.26	586.04	536.41	170.51	85.44	21.08	92.37	200.49	235.41	1728.96	319.27	1181.08	<LDM
Indeno[123-cd]pyrene	13.54	32.87	148	959.75	831.38	290.9	234.59	122.45	77.72	151.03	219.45	2784.42	507.61	1249.74	<LDM
Benzo(ghi)perylene	14.14	32.6	131.65	935.46	701.24	233.59	194.34	105.28	116.7	231.92	319.79	2685.03	431.45	1311.75	<LDM
ΣPAHs	75.68	215.41	644.63	4870.62	4904.39	1408.29	947.29	355.82	602.86	1401.17	1903.42	15617.42	2672.18	9776.93	n.c
ΣC ₁ P/P	0.39	0.42	0.37	0.47	0.5	0.45	0.35	0.36	0.38	0.24	0.39	0.6	0.59	0.6	n.c
Ant/178	0.25	0.21	0.27	0.4	0.35	0.21	0.26	0.25	0.31	0.24	0.19	0.24	0.31	0.23	n.c
BaA/228	0.44	0.43	0.43	0.43	0.46	0.47	0.46	0.46	0.35	0.31	0.37	0.37	0.42	0.31	n.c
Fl/Fl+Py	0.49	0.5	0.5	0.5	0.49	0.5	0.5	0.5	0.5	0.49	0.49	0.49	0.49	0.5	n.c
IP/IP+BghiP	0.49	0.5	0.53	0.51	0.54	0.55	0.55	0.54	0.4	0.39	0.41	0.51	0.54	0.49	n.c

The Fl/Fl + Py isomer pair ratios showed that no PAHs were introduced directly from petroleum combustion from the oil refinery and ships in all sites. The BaA/228 isomer pair ratios showed that PAHs are derived from the combustion of coal and biomass for all sites, except sites 10 e 14 that showed sources of petroleum and combustion (mixed sources). The IP/IP + BghiP isomer pair ratios showed that PAHs are derived from petroleum combustion at sites 1, 2, 9, 10, 11 and 14. Sites 3, 4, 5, 6, 7, 8, 12 and 13 the ratios showed sources of biomass and coal combustion. The industrial complex, which uses large quantities of coal in its activities and the presence of refineries, is the source of petroleum and combustion derived PAHs. The burning of biomass occurs along the shores of the estuary where the population is concentrated.

CONCLUSION

The sediments of the SES showed a large predominance of PAHs originating from combustion of coal in metallurgical processes in industrial process, crude oil and diesel fuel from refineries, shipping in port activities and road haulage and biomass burning resulting from the settlement of the population in the vicinities of the estuary as view in the isomers par ratios. The studies sites near the industrial complex, inner portions of estuary, presented highest levels of PAHs in sediments. Contamination is mainly associated Cubatão industrial complex or the oil refinery, which revealed higher levels than other sampling sites.. Thus it is suggested that further investigations be accomplished in the most contaminated areas of the SES to support policy makers towards adequate mitigation initiatives.

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