Resources and Environment 2012, 2(4): 141-149
DOI: 10.5923/j.re.20120204.03

Persistent toxic substances in surface water of Todos Os Santos Bay, Brazil

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Abstract Persistent toxic substances (PTSs) such as polycyclic aromatic hydrocarbons (PAHs) are of great concern due to their persistence, bioaccumulation and toxic effects. In this work, 14 PAHs included in the US Environmental Protection Agency's (EPA) priority pollutant list were analysed using gas chromatography–mass spectrometry (GC–MS). Surface water sampling was undertaken in Todos os Santos Bay, northern Brazil. Total PAH concentrations varied from 0.0029 to 0.1079 ng/L in surface waters (main rivers, tributaries, etc.) with mean value of 0.0344 ng/L. Such concentrations can be taken as background values for the studied region and show that PAHs are within or lower than levels reported in certain other areas. The PAH profiles were dominated by high molecular weight PAHs (four- and five-ring components) in surface water samples. It indicated that PAHs in surface water have its origin from oil or sewage contamination (petrogenic input). The collected data, based on indices among phenanthrene versus anthracene, showed that petrogenic input was predominant at almost all the stations investigated. Principal component analysis (PCA), using a correlation matrix, revealed the latent relationships among all the surface water stations investigated and confirmed our analytical results.

Keywords Polycyclic Aromatic Hydrocarbons (PAHs), Surface Water, Estuary, Gas Chromatography–Mass Spectrometry (GC–MS), Principal Component Analysis (PCA)

1. Introduction

Water pollution by organic compounds, many of which are known to be toxic or carcinogenic, has caused considerable and worldwide concern. Persistent toxic substances (PTSs) are semi-volatile chemicals that can be bioaccumulated by living organisms, that are resistant to degradation and that possess toxic properties[1-2]. Among PTS chemicals, PAHs (Polycyclic Aromatic Hydrocarbons) are important classes of compounds that have caused serious environmental problems. Polycyclic aromatic hydrocarbons (PAHs), hydrocarbons containing two or more fused benzene rings, are a group of ubiquitous organic pollutants of great environmental concern because of the documented carcinogenicity in experimental animals and the widespread occurrence of several of its members[3]. Due to their ubiquitous occurrence, recalcitrance and suspected carcinogenicity and mutagenicity[4], PAHs are included in the U.S. Environmental Protection Agency (EPA) and in the European Union priority lists of pollutants.

The US EPA fixed 16 parent PAHs as priority pollutants, the latest being effective from 1997[5–9], some of which are considered to be possible or probable to human carcinogens, and the endocrine disrupting activities of PAHs have been recently reported[10,11]. Therefore, their distributions in the environment and potential human health risks have become the focus of much attention.

Most surveys of PAH contamination in water bodies have been in conducted in North America and Europe, such as in USA[12–14], Canada[15], Germany[16–19], England[20], France[21], Greece[3] and other countries[22]. Information concerning water pollution with PAHs in South America has been reported for Brazil[23-25] and Chile[26]. The majority of these surveys worldwide were mainly focused on seawater (coastal of offshore) and estuarine water. However, few data are available for PAH contamination of the inland waters of Todos os Santos Bay, Bahia, which usually act as receptors for sewage, industrial effluents and urban or rural run off[27-28].

PAHs are introduced into the environment mainly as a consequence of incomplete combustion originated from both, natural and anthropogenic processes. However, in many areas affected by human activities, natural sources are overwhelmed by anthropogenic sources except perylene. Anthropogenic sources include both high and low temperature combustion of fossil fuels and the direct release of oil and its products. For parent PAHs, combustion and/or an-

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thropogenic input is often inferred from an increase in the proportion of the less stable, "kinetic" PAH isomers relative to the more stable, "thermodynamic" isomers and the stability of the lighter PAH isomers has been calculated to support such interpretations[29].

The ratios of Ph/An within the two-ring PAH group and Fl/Py within four-ring PAH group were used to differentiate PAHs of distinct origins. Ph is more thermochemically stable than An, and therefore at low maturation temperatures much higher molar fraction of Ph is produced compared to An[30]. These molar ratios of Ph/An at petroleum maturation temperatures lead to higher values. It can be as high as 50 at 373 K. On the other hand, high temperature processes (800–1000 K), such as the incomplete combustion of organic materials (coal burning, wood burning, vehicular exhaust emission, waste crankcase oil and asphalt roofing material), are characterized by low Ph/An ratio value [6–12].

In the northeastern area of Todos os Santos Bay (TSB), Bahia, Brazil, the extraction, transport and refinement of petroleum is the most conspicuous industrial activity[31-32].

The region is bordered by extensive mangrove communities[33], whose characteristics and necessary preservation make it imperative to prevent and/or to determine the extension of any impact[34].

In Brazil, very limited study for the monitoring of PAHs on surface water is performed[35–39]. In order to evaluate the contamination status of PAHs in surface water from estuarine region and Todos os Santos Bay, northern Brazil, an investigation has been performed with a quantitative GC–MS method.

2. Materials and Methods

2.1. Area Description and Sampling

Todos os Santos Bay is situated on the northern of Brazil. With a population of almost 2,1 million and the surface area of the bay about 1,052 km^2, it is a huge commercial and industrial center.

Todos os Santos Bay has a hot and wet climate with distinct four seasons, sufficient sunshine and moderate rainfall. The annual mean temperature is 24℃ and the annual average rainfall is 2100 mm. The Todos os Santos Bay urban/ industrial complex is highly polluted with the development of industry and rapid urbanization. Industry and automobiles are two major sources of pollution.

Rivers in the Todos os Santos Bay are severely polluted with high loads of persistent inorganic/organic pollutants. According to the Reports of Todos os Santos Bay Environmental Quality in 2004[39], the sewage discharge was 297 million tonnes including 120 million tonnes of industrial effluents and 177 million tonnes of domestic wastewater. Industrial effluent was treated completely by sewage treatment plants (STP); the total treatment ratio of sewage was up to 50%. There are mainly nine rivers in Todos os Santos Bay: Paraguaçu River, Subaé River, Caipe River, Suape River, Jaguaripe River, Açu River, Traripe River, Dona River and Cachoeirinha River. The surface water samples were collected (0–10 cm) by using cylinder samplers aboard a chartered vessel during axial surveys on february and july, 2007, and the nineteen locations of sampling sites of surface water are shown in Fig. 1. The data for the master parameters are shown in Table 1.

2.2. Chemicals

Standard PAHs (16 compounds specified on EPA Method 610, each at 100, 200, 1000 or 2000μg/mL) in a mixture were obtained from Supelco (Bellefonte, PA, USA). These compounds are as follows: naphthalene (Np), metil-naphthalene (mNp), dimetil-naphthalene (dNp), acenaphthylene (Acy), acenaphthene(Ace), fluorine(F), phenanthrene (Ph), anthracene (An), fluoranthene (Fl), pyrene (Py), chrysene (Chry), benzo[a]anthracene (BaAn), benzo[b]fluoranthene (BbFl), benzo[k]fluoranthene (BkFl), benzo[a]pyrene (BaPy), benzo [g,h,i]perylene (B[ghi] Pe) and dibenzo[a,h] anthracene (dB[ah]An). Deuterated internal standards (naphthalene-d8, acenaphthene-d10, phenanthrened10 and chrysene-d12) were obtained from Sigma–Aldrich.

Working standards of PAHs were prepared by combining the standard mixture with the corresponding IS stock solution, respectively. These solutions were further diluted with dichloromethane to prepare calibration solutions in the range 0.01–10 ng/μL. All solvents used for sample processing and analyses (dichloromethane, ethyl acetate, acetone, hexane and methanol) were analytical grade and further distilled twice to remove impurities.

2.3. Sample Treatment and Sample Extraction

After returning to the laboratory, aliquots of the sample (1.0 L) were filtered through 0.45 μm microporous filter membrane under vacuum in order to remove algae, zooplankton and suspended particles and a measured aliquot of an internal standard mixture containing naphthalene-d8, acenaphthene-d10, phenanthrene-d10 and chrysene-d12 was added to each sample. The cartridges were first conditioned with 2×5mL of methanol followed by 2×5mL of deionized water. Water samples were passed through the cartridges at a flow rate of 6 mL/min under vacuum.

Following extraction, the cartridges were eluted with 6mL of ethyl acetate, which was combined with an ethyl acetate rinse (5 mL) from the extraction glassware. After water was removed from the extracts by ashed Na_2SO_4, the volume of the extracts was reduced by N_2 blow-down in a water bath (35 ℃) to a final volume of 1 mL.

2.4. Sample Analyses

The analysis was performed on a 50 m fused-silica column (0.32 mm i.d.) coated with CPSil5-CB (0.25 μm thickness). Helium was used as the carrier gas at a flow rate of 1.5 mL min^{-1} (pressure 0.8 kPa). The following temperature program was employed: 70℃ to 280℃ with ramping at 4℃ min^{-1}. Injector and detector temperature were held at 320℃. Detection was monitored by flame ionisation detector (FID). The structure of PAHs was confirmed by gas chromatogra-

phy coupled to mass spectrometry (trace 2000 GC–MS, Thermo Finnigan, USA). A fused-silica DB-5MS capillary column (30m×0.32mmi.d., 0.25μm film thickness) was used. Helium with a purity of 99.999% was used as the carrier gas at a constant flow of 1.0 mL/min. A 2μL volume was injected by applying a hot splitless injection technique. The temperature program of the oven was started at 70 ℃ (for 1 min) and increased at a rate 10 ℃/min to 300℃ and was held for 10 min. The mass spectrometer was operated in the electronic impact (EI) mode with an ion source at 200 ℃ and the electron impact energy was set at 70 eV. Identification of the PAH compounds was performed by comparing GC retention time with those of authentic standards. Quantification of individual compounds was based on comparison of peak areas with those of the recovery standards.

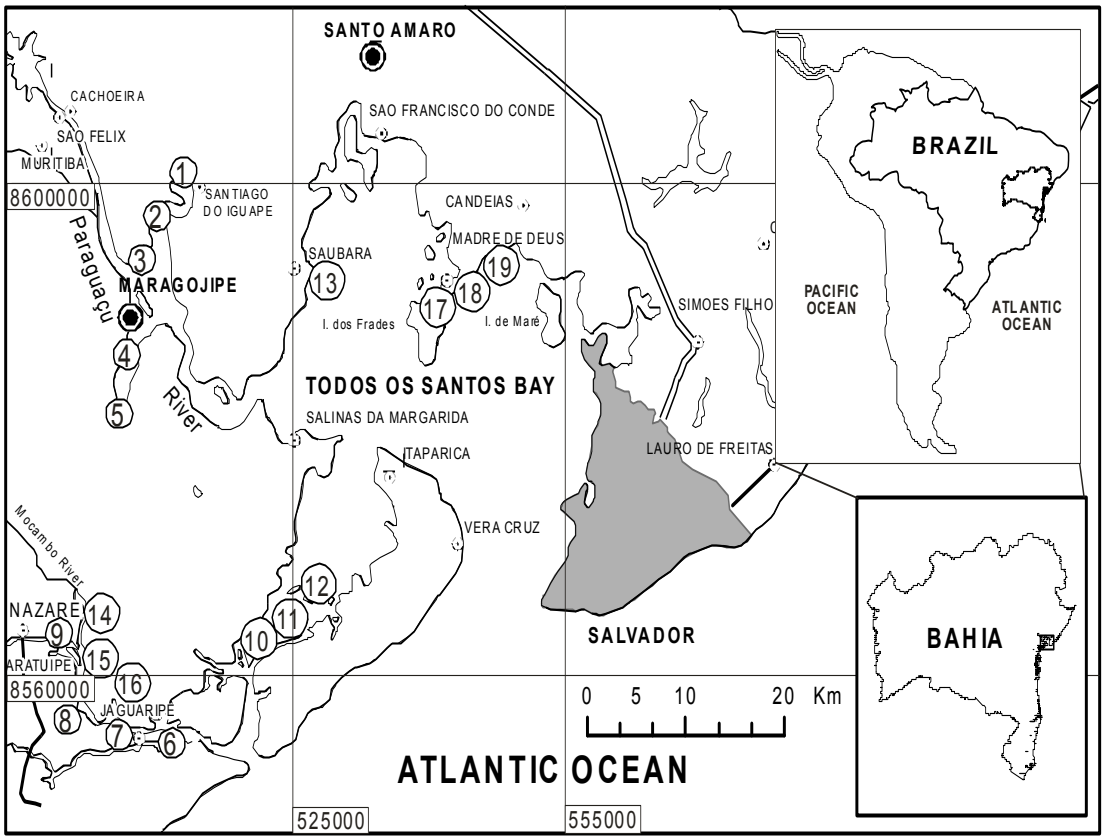

Figure 1. Map of Todos os Santos Bay, Bahia, Brazil, indicate sampling sites of surface water

Table 1. Summary of conditions when water samples were taken from Todos os Santos Bay, Brazil

Station	pH	Eh	T(℃)	Salinity	D.O.(mg/l)
1	6,23	56	35	30	5,4
2	6,86	15	35	29	7,3
3	6,94	17	34	30	6,3
4	6,72	35	33	34	4,8
5	6,49	35	36	31	3,5
6	7,05	19	29	35	5,8
7	7,02	17	30	30	4,9
8	6,59	30	30	24	6,1
9	7,06	25	29	20	3,4
10	6,71	41	25	31	5,9
11	6,58	46	25	32	5,9
12	6,82	36	25	32	5,8
13	7,81	-12	28	29	7,5
14	6,22	68	26	20	2,6
15	6,23	67	26	20	1,3
16	6,16	71	28	20	5,3
17	8,21	-35	29	31	7,5
18	8,27	-38	29	31	7,5
19	8,30	-39	30	32	7,5

Before sample analysis, relevant standards were analyzed to check column performance, peak height and resolution, and the limits of detection (LOD). With each set of samples to be analyzed, a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, peak identification and quantification. Compounds were identified mainly by their retention times.

2.5. Analytical Quality Controls

All data were subject to strict quality control procedures. For PAHs, deuterated IS were used to compensate for losses involved in the sample extraction and work-up. The four IS in water were determined with good precision, and their recoveries ranged from 70±5 to 93±10% for water samples. Detection limits derived from replicate procedural blanks were aproximately 1 ng/L. GC/MS data were acquired and processed by using Xcalibur software.

2.6. Statistical Treatment

In order to explore more latent relationships among all the stations investigated, the principal component analysis (PCA) was applied to the obtained results.

PCA reduces the number of variables in the original data set into fewer factors (or principal components) without significant loss in the total variance of the data. The loading that each variable in the original data contributes to the principal components enables grouping of data with similar behaviors[40].

3. Results and Discussion

3.1. PAH Concentrations and Compositional Patterns

This report presents results from analyses of parent PAHs in Todos os Santos Bay, Brazil. The concentration ranges of individual and total PAHs in surface water are shown in Table 2.

The total PAH concentrations ranged from 0,0029 to 0,1079 ng/L in surface waters (main rivers, tributaries, etc.) with mean value of 0,0344 ng/L (Tab. 2). The highest concentration of surface water was observed at station S3, which is situated in the mouth where Iguape River merges into the main river—Paraguaçu River (Fig. 2). With increasingly intense urban and industrial development in Maragojipe, the amount of PAHs detected there is obviously related to urban runoffs, sewage discharges, vehicular exhaust emission and intense shipping activities that were observed during the sampling. Similarly, high concentration (>0.08 ng/L) was also found at station S5. In addition, there were a lot of industries (e.g. chemical, power) around the study area, many of which were discharging waste effluents; hence, there were many non-point sources in the area, contributing to the very high concentrations of PAHs detected.

Table 2. Range of concentrations (ng/L) of parent PAHs in surface water from Todos os Santos Bay, Brazil. See text for more information

	Valid N	Mean	Median	Minimum	Maximum	Variance	Std.Dev.
Np	19	0,0010	0,0009	0,0001	0,0055	0,0000	0,0013
mNp	18	0,0005	0,0003	0,0000	0,0020	0,0000	0,0005
dNp	15	0,0007	0,0002	0,0000	0,0037	0,0000	0,0012
Acy	19	0,0017	0,0002	0,0000	0,0087	0,0000	0,0027
Ace	19	0,0004	0,0003	0,0000	0,0015	0,0000	0,0004
F	19	0,0026	0,0012	0,0001	0,0271	0,0000	0,0060
Ph	19	0,0011	0,0010	0,0000	0,0027	0,0000	0,0008
An	16	0,0011	0,0011	0,0001	0,0031	0,0000	0,0009
Fl	9	0,0124	0,0034	0,0010	0,0570	0,0000	0,0186
Py	19	0,0045	0,0015	0,0001	0,0266	0,0000	0,0070
BaAn	12	0,0030	0,0013	0,0001	0,0159	0,0000	0,0046
Chry	13	0,0029	0,0008	0,0001	0,0145	0,0000	0,0049
BbFl	10	0,0004	0,0005	0,0000	0,0011	0,0000	0,0003
BkFl	8	0,0027	0,0014	0,0007	0,0104	0,0000	0,0033
BaPy	13	0,0146	0,0047	0,0011	0,0592	0,0000	0,0180
Total PAHs	19	0,0344	0,0213	0,0029	0,1079	0,0010	0,0314
LMM PAHs	19	0,0088	0,0078	0,0017	0,0280	0,0000	0,0055
HMM PAHs	19	0,0256	0,0119	0,0003	0,0986	0,0010	0,0310
Ph/An	16	1,0270	0,7950	0,3812	3,0487	0,4570	0,6763
BaAn/(BaAn+Chry)	13	8,2544	0,5240	0,1942	101,0000	776,5900	27,8674
Fl/(Fl+Py)	9	0,5477	0,5040	0,2841	0,9378	0,0590	0,2436
An/(An+Ph)	16	0,5297	0,5571	0,2470	0,7240	0,0150	0,1223

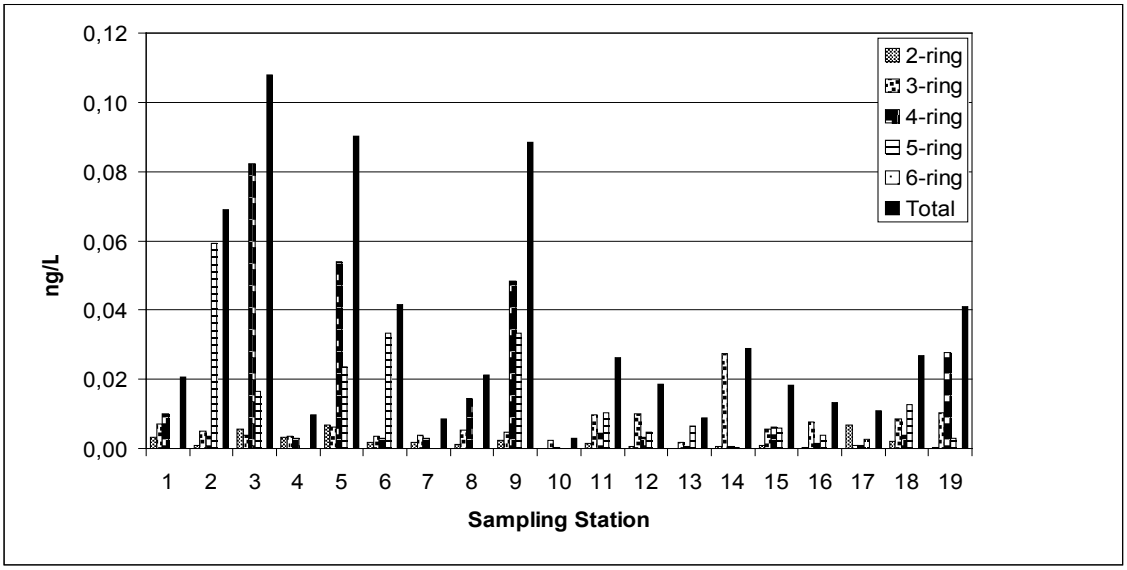

Figure 2. Concentrations (ng/L) of two-, three-, four-, five-, six-ring and total PAHs in the surface water column of Todos os Santos Bay. Two-ring PAHs include naphthalene; three-ring PAHs include acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene; four-ring PAHs include fluoranthene, pyrene, benzo[a]anthracene and chrysene; five-ring PAHs include benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and dibenzo[a,h]anthracene; six-ring PAHs include indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene

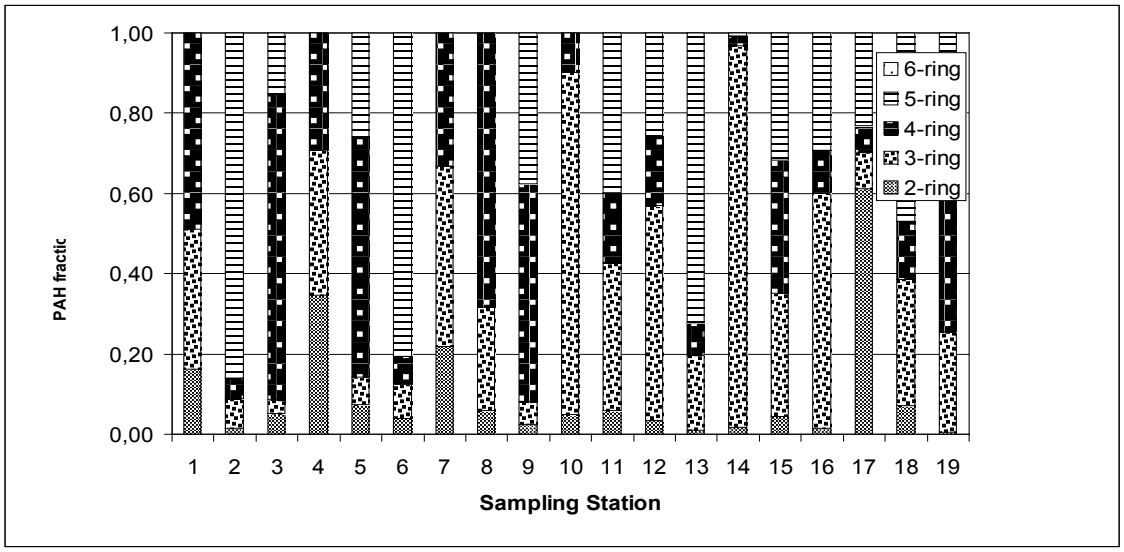

Figure 3. Composition pattern of parent PAHs in surface water of Todos os Santos Bay. Two-ring PAHs include naphthalene; three-ring PAHs include acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene; four-ring PAHs include fluoranthene, pyrene, benzo[a]anthracene and chrysene; five-ring PAHs include benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and dibenzo[a,h]anthracene; six-ring PAHs include indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene

Table 3. Summary of total parent PAH concentration (ng/L) in surface water from various sites in the world

Location	Date of sampling	N[a]	n[b]	Range(ng/L)	Reference
Todos os Santos Bay (Brazil)	February-July 2007	19	14	0.002-0.108	This work
Northern Greece	July–August 1996	8	16	184–856	[1]
Aegean Sea (eastern mediterranean)			14	0.113–0.489	[14]
Baltic Sea	August 1995		14	0.300–0.594	[14]
Danube Estuary	August 1995	2	14	0.183–0.214	[14]
Seawater around England and Wales	June 1993–July 1995	63	15	<1–24821	[17]

[a] N, number of samples analysed.
[b] n, number of compounds analyzed.

The compositional pattern of PAH by ring size along the contamination gradient is shown in Fig. 3. It is clear that two- and three-ring PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene) are the most abundant PAHs, which on average occupied 96 and 10% of total PAHs in surface water. In addition, four and five-ring

PAHs on average occupied 90 and 4% of total PAHs in surface water. Benzo[a]pyrene is one of the most frequently detected compounds in almost all surface water samples (except S1, S4, S7, S8, S10 and S14). Higher proportions (about 90% of benzo[a]pyrene) were observed at stations S2, S6 and S13.

The total PAH concentrations in water found in the study area are four to five orders of magnitude lower than those found in waters in Danube Estuary[14], Aegean[14] and Baltic Sea[14] (Table 3). Concentrations were also lower than total PAH levels detected in northern Greece [1] and Seawater around England and Wales[17].

3.2. Sources of PAHs

3.2.1. Ratio Analysis

The ratios of Ph/An within the two-ring PAH group and Fl/Py within four-ring PAH group were used to differentiate PAHs of distinct origins. Therefore, Ph/An > 15 for petrogenic sources and Ph/An < 10 for pyrolytic sources. Due to the wide range of values for this index found in literature, values between 10 and 15 are considered indefinite relating to the source [29,43].

Likewise, discrimination also occurs in the fluoranthene/pyrene (Fl/Py) ratio. In petroleum-derived PAHs, pyrene is more abundant than fluoranthene. At higher combustion temperatures a predominance of fluoranthene over pyrene is characteristic. As such, a value greater than 1 is classically related to pyrogenic sources[44]. Hence, in combination, a Ph/An ratio value <10 and Fl/Py ratio >1 indicates that PAHs originate from pyrogenic sources[29]. The ratios of Ph/An, Fl/Py in surface water were calculated and are listed in Table 4. As shown in Table 3, almost all the ratios of Ph/An < 15 and Fl/Py < 1 tended to indicate that PAHs were coming from petrogenic sources.

Table 4. Ratios of phenanthrene/anthracene (Ph/An), fluoranthene/pyrene (Fl/Py) in surface water samples from Todos os Santos Bay, Brazil

Station	Ph/An	Fl/Py
1	0,89	0,52
2	0,93	0,40
3	0,77	8,81
4	1,17	2,03
5	0,64	15,07
6	0,54	0,96
7	0,81	1,06
8	0,72	0,41
9	0,78	1,02
10	3,05	-
11	-	-
12	-	-
13	0,68	-
14	0,38	-
15	0,96	-
16	1,50	-
17	0,56	-
18	-	-
19	2,06	-

3.2.2. Principal Component Analysis

Distribution of the normalized PAHs data of surface water to factor coordinates of the variables is shown in Fig. 4. The two principal components selected are able to account for 46.69% of total variance of the original data. The first and second PCs in surface water represented 30.01 and 16.68% of the variability, respectively (Fig.5).

	Factor 1	Factor 2	Factor 3	Factor 4
Np	0,521255	0,033444	0,115881	0,408983
mNp	-0,172326	0,454353	0,252124	-0,618207
dNp	0,127942	0,657307	0,289376	-0,324506
Acy	-0,639772	-0,092470	-0,614900	0,012819
Ace	-0,889856	-0,223834	0,236250	-0,108880
F	-0,050950	0,167310	0,008049	0,103348
Ph	-0,037388	-0,716425	0,390563	0,274196
An	-0,687124	-0,426308	0,345865	0,134649
Fl	-0,826262	0,292146	-0,092348	-0,087523
Py	0,005066	-0,286053	-0,760834	0,016950
BaAn	0,414708	-0,607498	-0,104373	-0,549912
Chry	0,376707	-0,593719	0,017962	-0,556311
BbFl	-0,866578	-0,078270	-0,318990	-0,177448
BkFl	-0,727831	-0,289672	0,455519	-0,018638
BaPy	0,479085	-0,319336	0,072423	-0,127263

Figure 4. Factor coordinates of the variables, based on correlations

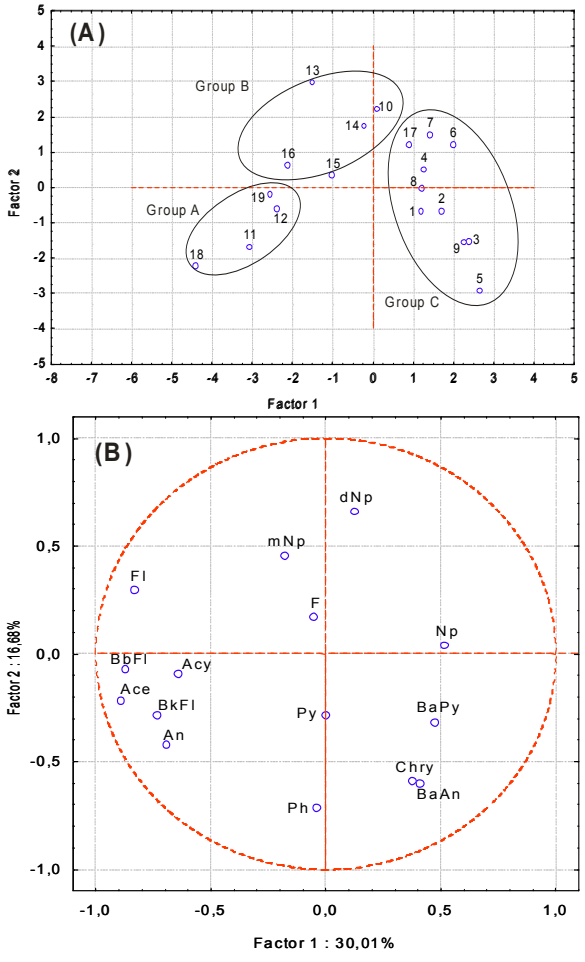

Figure 5. PCA showing the pattern of PAHs in the surface water: (A) factor loading plot and B) factor score plot—(Np) naphthalene, (Acy) acenaphthylene, (Ace) acenaphthene, (F) fluorene, (Ph) phenanthrene, (An) anthracene, (Fl) fluoranthene, (Py) pyrene, (Ba) benzo[a]anthracene, (Chy) chrysene, (BbFl) benzo[b]fluoranthene, (BkFl) benzo[k]fluoranthene, (BaP) benzo[a]pyrene and (dAn) dibenzo[a,h]anthracene

There are three groups discriminated on the factor loading plot (Fig. 5a). Group A clusters samples of stations 11, 12 and 18; group B contains samples collected from stations 10, 13 to 17 and 19; group C, samples collected from stations 1 to 9.

From Fig. 2, we can see both the samples of stations 11, 12 and 18 collected from the Jaguaripe River and Madre de Deus, probably containing similar contaminants, constituting the group A. As shown in Fig. 5a, group A is characterized by the negative axes of both principal components; on the other hand, from Fig. 5b, this quadrant is dominated by acenaphthylene. It indicated that acenaphthylene contributed significantly to the samples at group A, and the notable contribution of acenaphthylene over the contribution of the other PAHs notability.

The samples of stations 11, 12 and 18 were collected from the places nearby different interchanges, so they cluster together. However, the characteristic of the sample from station 19, is similar to those of samples in group B. The similarity may be caused by their complicated origins of contamination. Nevertheless, the sample of station 17 has some different characteristics from those of the other samples in group B. Contrary to the other samples in group B, the sample of station 17 is characterized by positive loading in the second principal component, so it got more contribution from the naphthalene than the other samples.

The samples for group B got the contribution from fluoranthene mostly among all the PAHs. However, compared with group C, the samples for group B gave a relatively low contribution to factor 2, so they got less contribution from naphthalene than group C. This conclusion can be confirmed by fig. 4.

The sample of station 13 was collected in Saubara, so the characteristic of this sample may be different from the others. As shown in Fig. 5a, the station 13 has a high value of factor 2 and it can be assumed that it is able to get the contribution from something with a high score value of factor 2, which seems to be the metilnaphthalene, giving the mostly contribution among these PAHs.

4. Conclusions

The PAH profiles of water samples revealed that the dominant PAHs were high molecular weight (four- and five ring) PAHs in surface water of Todos os Santos Bay, Brazil including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene.

The PAHs in surface water samples originated mainly from petrogenic inputs based on the high proportion of two-ring (naphthalene) and three ring PAHs. Although the calculated ratios of Ph/An, Fl/Py and principal component analysis are usually performed to analyze the origin of PAHs in sediments, we attempted to apply the ratios and PCA to the surface water in this study. The analysis results showed that the ratios and PCA could be applied to the surface water investigation to some extent.

Oil spill and leakage from boats and ships, vehicular exhaust emission, discharge from municipal and industrial wastewater and runoff might be important sources. It indicates that surface water received anthropogenic PAHs from different sources and although specific sources are known to be responsible for the presence of PAHs in surface waters, their occurrence cannot always be related to a particular source in Todos os Santos Bay, Brazil.

ACKNOWLEDGEMENTS

The authors are grateful to FINEP – CTPETRO no. 640002700 and JJCelino wishes to thank the Research Foundation of the State of Bahia - FAPESB - for granting him a research scholarship no. 297/2007.

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