Assessment of Hydrocarbon Inputs and Temporal Evaluation in Guanabara Bay, Brazil

M.F.G. Meniconi
PETROBRAS/CENPES, Research & Development Center

C.G. Massone
Gorceix Foundation

A.L. Scofield
PUC- Catholic University, Department of Chemistry
Rio de Janeiro - RJ – Brazil

Abstract
The 16 EPA priority polycyclic aromatic hydrocarbons (PAH) and their alkylated homologues (total of 38 compounds) have been quantified in 21 sediment samples from Guanabara Bay, Rio de Janeiro, Brazil, in two campaigns. The first campaign was carried out immediately after the oil spill accident in January/2000 and the second, three years later. It was observed a slight difference in total PAH level from one measurement to another, indicating a higher PAH concentration of the samples in 2000 as a result of both petrogenic and pyrolitic contribution to the sediments. The first field study presented a range of PAH concentration from 559 to 58,439 ng/g dry weight (median value of 4,877 ng/g) while the 2003 campaign showed PAH varying from 400 to 52,384 ng/g dry weight (median value of 3,603 ng/g). The hydrocarbon sources identification have been done by using PAH indexes of the samples studied and statistical analysis (PCA), indicating a mixed pattern of petrogenic and pyrolytic introduction in the Guanabara Bay sediments. Being the bay a complex urban area, the anthropogenic processes of introduction of PAH may be from the extensive industrial and domestic waste discharges, indirect atmospheric deposition of incomplete fuel oil combustion, accidental oil spills and direct runoff.

Keywords: Polycyclic Aromatic Hydrocarbons, Souce, Compositional Index, Principal Component Analysis

Introduction
Polycyclic aromatic hydrocarbons (PAHs), present worldwide in the environmental ecosystems, may be introduced by natural and anthropogenic processes from direct runoff and discharges and indirect atmospheric deposition (Yunker et al., 2000, Stout et al., 2001, Readman et al., 2002). Sources of naturally occurring PAHs include natural fires, natural oil seepage and recent biological or diagenetic processes - biogenic origin (Hites and Biemann, 1975, Youngblood and Blumer, 1975, Philp, 1985, Kennicutt II et al., 1994, Kennicutt II, 1995). Anthropogenic sources of PAHs are combustion or pyrolysis of organic matter (petroleum, coal, wood) and waste and releases/spills of petroleum and derivatives (river runoff, sewage outfalls, maritime transport, pipelines) (Lipatou and Albaigés, 1994, Budzinski et al., 1997, Elias et al., 2000). These compounds tend to interact with the different types of environmental compartments and are subject to many processes that lead to geochemical fates such as physical-chemical transformation, biodegradation and photo-oxidation. Numerous successful studies on sources of PAHs in environmental samples have relied on the increasingly rigorous and quantitative characterization of not only the 16 EPA priority pollutant PAHs but also on the PAH homologue distributions.

In this study, the sources of PAHs in the estuarine sediment of Guanabara Bay, Brazil are investigated in two campaigns: years 2000 and 2003. The objectives of the study were to identify the probable sources of hydrocarbons in the bay, considering the oil spill accident in January 2000. The bay is an urban ecosystem with a complex river drainage basin (about 50 rivers and channels), which is used to dispose of extensive municipal sewage, usually with minimal or no treatment, urban runoff and industrial waste of the second largest city in Brazil, with almost 10 million people. Figure 1 exhibits the points of municipal and industrial waste in Guanabara Bay (Feema, 2003).

Methods

Study Area and Sampling

The Guanabara Bay sampling strategy was based on visual and aerial observations of the ecosystem, reflecting areas potentially affected and unaffected by the spilled oil in January 2000 (Meniconi et al., 2002). The sediment samples were collected using cores and dredges from the intertidal and subtidal regions of the bay. A subsample of the top 3 cm of the sediment was transferred into wide-mouth glass jars with Teflon caps and then stored frozen prior to analysis. Figure 2 shows the geographical location of the sample stations in Guanabara Bay.

In the first campaign (year 2000) the samples were collected from 21 stations, just 10 days after the accident. In the second campaign (year 2003) the samples were collected from the same stations of 2000, which allowed a temporal investigation on the region.

Hydrocarbon Extraction and Determination

The analytical procedure for PAH for the sediment samples was based on standard methods as previously described (Meniconi et al., 2003). The samples were extracted following the methodology in EPA Method 3540. The sediment extracts were fractionated by adsorption chromatography, based on EPA Method 3630 and the gas chromatography-mass spectrometry (GC-MS) analysis for polycyclic aromatic hydrocarbons and their homologues (38 compounds in total) followed the EPA Method 8270-C, with modifications.

Results and Discussion

PAH Distributions – Parental and Alkylated composition

The concentration of individual PAH compounds and the sum of 16 EPA priority PAHs (Σ 16 PAHs) and the total 38 PAH (Σ PAH) in the sediments collected in Guanabara Bay in 2000 (just after the oil spill) and in 2003 are shown in Tables 1 and 2. For both campaigns total PAH varied significantly along the bay, ranging from 559 to 58,439 ng/g dry weight (median concentration: 4,877 ng/g) for the 2000 campaign and 400 to 52,384 ng/g dry weight (median concentration: 3,603 ng/g) for 2003 campaign. For the 2000 campaign the highest concentrations of total PAH were recorded for the sediments collected in the intertidal stations T22, T24 and T32, located in the vicinity of the accident, followed by stations T39 and D53, which are located in the subtidal area.

The PAH distribution for the samples collected in both campaigns is shown in Fig. 3. Samples T7, T9 and T22 showed a predominance of alkylated compounds for the after spill campaign compared to 2003 study while the samples D39 and D53 showed a predominace of non-alkylayted compounds. The other samples have not shown significant difference in the 38 compounds distribution and concentration. On the other hand, it was observed higher contribution of alkylated compounds in the 2003 campaign for the samples T31 and T32. Inspite of the slight difference in total PAH level from one measurement to the other, indicating a higher PAH concentration in 2000, it could be observed significant contributions of both petrogenic and pyrolitic inputs on the Guanabara Bay sediments in 2000 (Fig. 3 – sediments T7, T9, T22, D39 and 53).

Evaluating the Σ 16 PAH results of the samples studied, the range was 207 to 13,425 ng/g (median concentration: 1,264 ng/g) for the samples collected in 2000 and 184 to 3,653 ng/g (median concentration: 675 ng/g) for 2003 campaign. Figures 4 and 5 show a comparison of PAH distribution for the 16 EPA priority compounds and the total 38 compounds analysed for sediments from 2000 campaign. As expected, it can be observed the higher relative abundance of alkylated compounds for the samples near the accident of January 2000.

The comparison of this study data with data from other estuarine and coastal regions in the world reported in the literature is presented in Table 3. Despite the different numbers of PAH compounds analyzed in each study, the concentrations of PAHs in Guanabara Bay sediments by the time of the oil spill and 3 years after are not critical: they can be considered to be in the same range of various international estuarine sites. Comparing the data obtained in this study with the Rio de la Plata oil spill indicated lower PAH concentrations in Guanabara Bay (Colombo, 1989, 2000).

PAH Ratios – Sources Determinations

Some molecular ratios of PAHs have been developed in order to overcome the difficulty of identifying PAH sources in environmental samples (due to the complexity of the samples themselves and the weathering effects on the composition of the original source of the compounds) and help to investigate the source of these compounds, whether petrogenic, biogenic or pyrolytic (Gschwend and Hites, 1981, Sicre et al., 1987, Colombo et al., 1989, Budzinski et al., 1997, Baumard et al., 1998, Wang et al., 1999, Readman et al., 2002, Yunker et al., 2002).

The literature reports frequently the use of the double ratio plot of Phenantrene/Antracene versus Fluorantene/Pyrene for distinguishing a mixture of petrogenic and pyrolytic input for sediments (Baumard et al., 1998, Tam et el., 2001, Readman et al., 2002, Yunker et al., 2002, Ke et el., 2002). Figure 6 depicts this parental ratio diagram for Guanabara Bay samples collected in both campaigns, 2000 and 2003, plotted together with the spilled oil in January 2000 (MF 380 based on a Campos Basin crude oil), an Arabian oil (AR), frequently used in Brazilian refineries, and a Diesel oil (DM) produced in a refinery from the south of the country, based on another Brazilian basin oil. It can be seen that this ratio could not give a robust interpretation of PAH sources. Only some intertidal sediments (T1, T9, T15 and T18) showed clear pyrogenic characteristics. All other samples presented mixture features. This was expected since the PAH pair Phenantrene and Antracene has less difference in thermodynamic stability between isomers and the ratio are likely to be less effective to determine PAH sources (Yunker, 2000).

On the other hand, the Fluorantene/(Fluorantene+Pyrene) ratio (Yunker et al, 2000, Yunker et al, 2002) showed a high ability to distinguish combustion and petroleum inputs for Guanabara Bay samples. This can be seen in Fig. 7 and 8, in which the ratio was plotted against two other ratios (Indeno1,2,3-cdPyrene/Indeno1,2,3-cdPyrene+BenzoghiPerylene) and (Anthracene/Anthracene+Phenanthrenes), respectively), both with low efficiency to determine PAH sources. It must be observed that this double ratio was also plotted together with the MF 380, Arabian oil and Diesel oil.

In addition to the Fluorantene/(Fluorantene+Pyrene) ratio, it was observed that the Phenanthrene+Anthracene/(Phenanthrene+Anthracene+C1Phenanthrene) ratio (Yunker et al, 2000) has also exhibited high source discrimination capacity. This can be seen in Fig. 9, in which this ratio was plotted against to Anthracene/Anthracene+Phenanthrenes. So, based on these results it was plotted the double ratio Fluorantene/(Fluorantene+Pyrene) *versus* Phenanthrene+Anthracene/(Phenanthrene+Anthracene+C1Phenanthrene), that showed the highest ability to distinguish pyrogenic and petrogenic sources in this study (Fig 10). Samples with Fluorantene/(Fluorantene+Pyrene) less than 0.4 and Phenanthrene+Anthracene/(Phenanthrene+Anthracene+C1Phenanthrene) less than 0.5 suggests that petroleum is the dominant source. Those samples are T7, T22, T28, T31 and T32. It should be highlighted that the analysed oils (MF 380, Arabian Oil and Diesel Oil) were clearly allocated as petrogenic characteristics on the diagram.

The majority of other samples analysed showed pyrolytic characteristics, i.e., Phenanthrene+Anthracene/(Phenanthrene+Anthracene+C1Phenanthrene) higher than 0.5 and Fluorantene/(Fluorantene+Pyrene) higher than 0.4. The samples with characteristics of Fluorantene/(Fluorantene+Pyrene) higher than 0.4 and Phenanthrene+Anthracene/(Phenanthrene+Anthracene+C1Phenanthrene) less than 0.5 also suggested combustion inputs. The exception was for sediment from station T56 which PAH source could not be clearly identified, probably due a mixture of petrogenic and pyrolytic inputs.

Another compositional index used to differentiate the pyrogenic and petrogenic PAHs is the pyrogenic index reported by Wang *et al.* (1999), which is defined as the ratio of the other EPA priority 3-6-ring PAHs to the total of 5 target alkylated PAH homologues (Σ (other 3-6 ring PAHs)/Σ (5 alkylated PAH series)). Based on more than 60 oils and petroleum products analyzed by Wang and collaborators, values up to 0.05 for the pyrogenic index unambiguously indicated the contribution of oil and refined products in the samples while values greater than 0.5 (ratio tenfold increased) indicated combustion-derived sources for the samples. This ratio yield high acuracy and consistency once minimizes interferences from flutuation of concentration from one compound to another. For Guanabara Bay samples this ratio showed a good resolution, encompassing the majority of subtidal samples and T1 and T9 with pyrolytic characteristics and T22 and T32 clearly with petrogenic sources (Fig. 11). The ratio still showed a mixture feature for some samples, mainly for intertidal ones.

In addition to molecular PAH ratios as a tool for PAH sources, a PCA model was also used in this study (Statistica version 5.0). In order to prevent the influence of the wide range of sample concentrations, a normalisation to the total concentration of PAH was applied before PCA. Figures 12 and 13 depict the results for 2000 and 2003 campaigns, in which the majority of the samples were separated in groups. In the plot the distance and direction from the axis centre has the same meaning for both samples and PAH variables.

For both campaigns the first PC defines 2 variable groups by separating alkylated PAH form parent PAH: left and right sides, respectively. The second PC separates the PAH into 2 groups: predominantly projected by all alkyl Naphthalenes, alkyl Fluoranthenes and

C1Dibenzothiophenes on the upper side; and alkyl Dibenzothiophene and alkyl Phenanthrenes on the lower side.

The PCA model separated the sediment samples of Guanabara Bay and the oils analysed. For both campaigns, the oils projected on the upper left side of the y-axis with high contribution of low molecular weight compounds, which are presented in crudes but are usually weathered in the environment. Some samples (T7, T22, T24, T31, T32) projected on the lower left side of the y-axis, suggesting predominance of petrogenic input due to contribution of alkylated Phenanthrenes and Dibenzothiophenes. On the other hand, another samples projected on the right side of y-axis, encompassing a group of samples with pyrolitic characteristics showed by the dominance of high molecular weight compounds (T36, D43, T51, D53, T54, T55, T56, T57). So, upper left side of y-axis correlates to oils; lower left side correlates to samples with petrogenic source predominance; upper right side correlates to sample with pyrolitic source predominance.

From one campaign to another, it was verified that only two samples (T1, T28) presented different contributions, suggesting that the class of predominant source of the samples has not significantly changed.

Conclusions

Parent and alkyl PAH (total of 38 compounds) have been quantified in 21 sediment samples from Guanabara Bay, Rio de Janeiro, Brazil, in two campaigns, the first was carried out immediately after the oil spill accident in January/2000 and the second, three years later. It was observed a slight difference in total PAH level from one measurement to another, indicating a higher PAH concentration of the samples in 2000 as a result of both petrogenic and pyrolitic contribution to the sediments. However normalised data by organic carbon or grain size should be done in order to confirm these conclusions. The hydrocarbon source determinations have been done by using PAH ratios for the samples studied. Some diagnostic ratios exhibited high ability to distinguish combustion and petroleum inputs for Guanabara Bay sediments:
Σ (other 3-6 ring PAHs)/Σ (5 alkylated PAH series); Fluorantene/(Fluorantene+Pyrene); Phenanthrene+Anthracene/(Phenanthrene+Anthracene+C1Phenanthrene). Additionally, the PCA results also exhibited promissing capacity of separating the samples into groups. Summarizing, the Guanabara Bay sediments could be separated into groups:

- samples with clear pattern of petrogenic input – the majority localized near the vicinity of the accident on January/2000
- samples with combustion characteristics – those from the majority of subtidal stations
- samples without clear contribution of petrogenic or pyrolytic input

Still more investigation appears to be necessary since Guanabara Bay is a complex urban area with the anthropogenic processes of introduction of PAH being from the extensive industrial and domestic waste discharges, indirect atmospheric deposition of incomplete fuel oil combustion, accidental oil spills and direct runoff.

References

Anderson, J.W., F. C. Newton, J. Hardin, R.H. Tukey and K.E. Richter (1996) Chemistry and Toxicity of Sediments from San Diego Bay, including a Biomarker (P450 RGS) Response. In Environmental Toxicology and Risk Assessment: Biomarkers and Risk Assessment, eds D.A. Bengtson and D.S. Henshel, Vol. 5, pp. 53–78. American Society for Testing and Materials, Philadelphia, USA.

Baumard, P, H. Budzinski, Q. Mchin, P. Garrigues, T. Burgeot, and J. Bellocq. (1998) Origin and Bioavailability of PAH in Mediterranean Sea from Mussel and Sediment Records, Estuarine, Coastal and Shelf Science, Vol. 47, pp. 77-90.

Budzinki, H., I. Jones, J. Bellocq, C. Piérard, P. Garrigues. (1997) Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary, Marine Chemistry, Vol. 48, pp. 85-97.

Colombo, J.C. (2000), Biogeochemical Assessment of the 1999 Rio de la Plata Oil Spill. Proceedings VII Latin American Congress on Organic Geochemistry, Foz do Iguaçu, Brazil.

Colombo, J.C., E. Pelletier, C. Brochu and M. Khalil, (1989) Determination of Hydrocarbon Sources using n-alkane and Polyaromatic Hydrocarbon Indexes. Case Study: Rio de La Plata Estuary, Argentina, Environment Science Technology, Vol. 23, pp. 888-894.

Elias, V.O., B.R.T. Simoneit, J.N. Cardoso, (2000) "Levoglucosan, a Molecular Fossil as Indicator of Biomass Burning Contribution in Sediments of the Amazon Shelf", Proceedings of the Seventh Latin-American Congress on Organic Geochemistry, Foz do Iguaçu, Paraná, Brazil, pp 243-244.

Feema (2003). www.feema.rj.gov.br. Accessed on 08/01/2003.

Gschwend, P.M. and R.A. Hites. (1981) Fluxes of Polycyclic Aromatic Hydrocarbons to Marine and Lacustrine Sediments in the Northeastern United States, Geochimica et Cosmochimica Acta 45, 2359–2367.

Hites, R.A. and W.G. Biemann. (1975) Identification of Specific Organic Compounds in a Highly Anoxid Sediment by CG/MS and HRMS, Adv. Chem. Ser., Vol. 147, 188-201.

Kayal, S.I. and D.W. Connell. (1989) Occurrence and Distribution of Polycyclic Aromatic Hydrocarbons in Surface Sediments and Water from the Brisbane River Estuary, Australia, Estuarine Coastal and Shelf Science, Vol. 29, pp. 473-487.

Ke, L., T.W.Y. Wong, Y.S. Wong and N.F.Y. Tam. (2002) Fate of Polycyclic Aromatic Hydrocarbon (PAH) Contamination in a Mangrove Swamp in Hong Kong following an Oil Spill, Marine Pollution Bulletin, Vol. 45, pp. 339-347.

Kennicutt II, M.C., T.L. Wadw, B.J. Presley, A.G. Requejo, J.M. Brooks and G.J. Denoux. (1994) Sediment Contaminants in Casco Bay, Maine: Inventories, Source and Potential for Biological Impact, Environment Science Technology, Vol. 28, (1), pp. 1-15.

Kennicutt II, M.C. (editor) (1995) Gulf of Mexico Offshore Operations Monitoring Experiment, Final Report, U.S. Department of the Interior Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA, 700 p.

Khim, J.S., K. Kannan, D.L. Villeneuve, C.H. Koh and J.P. Giesy (1999) Characterization and Distribution of Trace Organic Contaminants in Sediment from Masan Bay, Korea. 1. Instrumental Analysis, Environmental Science and Technology, Vol. 33, pp. 4199–4205.

Lipatou, E. and J. Albaigés. (1994) Atmospheric Deposition of Hydrophobic Organic Chemicals in the Northwestern Mediterrean Sea: Comparison with the Rhone River Input, Marine Chemistry, Vol. 46, pp. 153-164.

Meniconi, M.F.G., I.T. Gabardo, M.E.R. Carneiro, S.M. Barbanti, G.C. Silva and C.G. Massone (2002), Brazilian Oil Spills Chemical Characterization – Case Studies, in Proceedings of the 25th Artic and Marine Oil Spill Program (AMOP), Calgary, Canada.

Meniconi, M.F.G, Scofield, A.L, Massone, C.G. (2003) Distribution and Sources of Polycyclic Aromatic Hydrocarbons in Sediments of Guanabara Bay, Brazil. in Proceedings of the 26th Artic and Marine Oil Spill Program (AMOP), Victoria, Canada.

Pereira, W.E., F.D. Hostettler and J.B. Rapp. (1996) Distributions and Fate of Chlorinated Pesticides, Biomarkers and Polycyclic Aromatic Hydrocarbons in Sediments along a Contamination Gradient from a Point-source in San Francisco Bay, California, Marine Environmental Research, Vol. 41, 299–314.

Readman, J.W., M.R. Preston and R.F.C. Mantoura. (1986) An Integrated Technique to Quantify Sewage, Oil and PAH Pollution in Estuarine and Coastal Environments, Marine Pollution Bulletin, Vol. 17, pp. 298-308.

Readman, J.W., G. Fillman, I. Tolosa, J. Bartocci, J.P. Villeneuve, C. Catinni and L.D. Mee. (2002) Petroleum and PAH Contamination of the Black Sea, Marine Pollution Bulletin, Vol. 44, pp. 48-62.

Sherblom, P.M., D. Kelly and R.H. Pierce (1995) Baseline Survey of Pesticide and PAH Concentrations from Sarasota Bay, Florida, USA, Marine Pollution Bulletin Vol. 30, pp. 568–673.

Sicre, M.A., J.C. Marty, A. Saliot, X. Aparicio, J. Grimalt and J. Albaige. (1987) Aliphatic and Aromatic Hydrocarbons in Different Sized Aerosols over the Mediterranean Sea: Occurrence and Origin, Atmosphere Environment, Vol. 21, pp. 2247–2259.

Stout, S.A., V.S. Mager, R.M. Uhler, J. Ickes, J. Abbott and R. Brenner.(2001) Characterization of Naturally-occurring and Anthropogenic PAHs in Urban Sediments – Wycoff/Eagle Harbour Superfund Site, Environmental Forensics, Vol. 2, pp. 287-300.

Tam, N.F.Y., L. Ke, X.H. Wang and Y.S. Wong. (2001) Contamination of Polycyclic Aromatic Hydrocarbons in Surface Sediments of Mangroves Swamps, Environmental Pollution, Vol. 114, pp. 255-2631.

Wang, Z., M. Fingas and D.S. Page. (1999) Oil Spill Identification, Journal of Chromatography A, Vol. 843, pp.369-411.

Youngblood, W.W. and M. Blumer (1975) Polycyclic Aromatic Hydrocarbons in Gulf of Maine Sediments and Nova Scotia Soils, Geochimica. et Cosmochimica. Acta., Vol. 38, pp. 303-1314.

Yunker, M.B., R.W. Macdonald, R. Brewer, S. Sylvestre, T. Tuominen, M. Sekela, R.H. Mitchell, D.W. Paton, B.R. Fowler, C. Gray, D. Goyette and D. Sullivan. (2000) Assessment of Natural and Anthropogenic Hydrocarbon Inputs using PAHs as Tracers. The Fraser River Basin and Strait of Georgia 1987-1997, Report DOE FRAP, Environment Canada and Fisheries and Oceans Canada, Vancouver, BC, 128 p.

Yunker, M.B., R.W. Macdonald, R. Brewer, R. Vingarzan, R.H. Mitchell, D. Goyette, S. Sylvestre. , (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry, Vol. 33, pp 489-515.

Zhou, J.L. and K. Maskaoui (2003) Distribution of polycyclic aromatic hydrocarbons in water and surface sediments from Daya Bay, China. Environmental Pollution, Vol. 121, pp. 269-281.

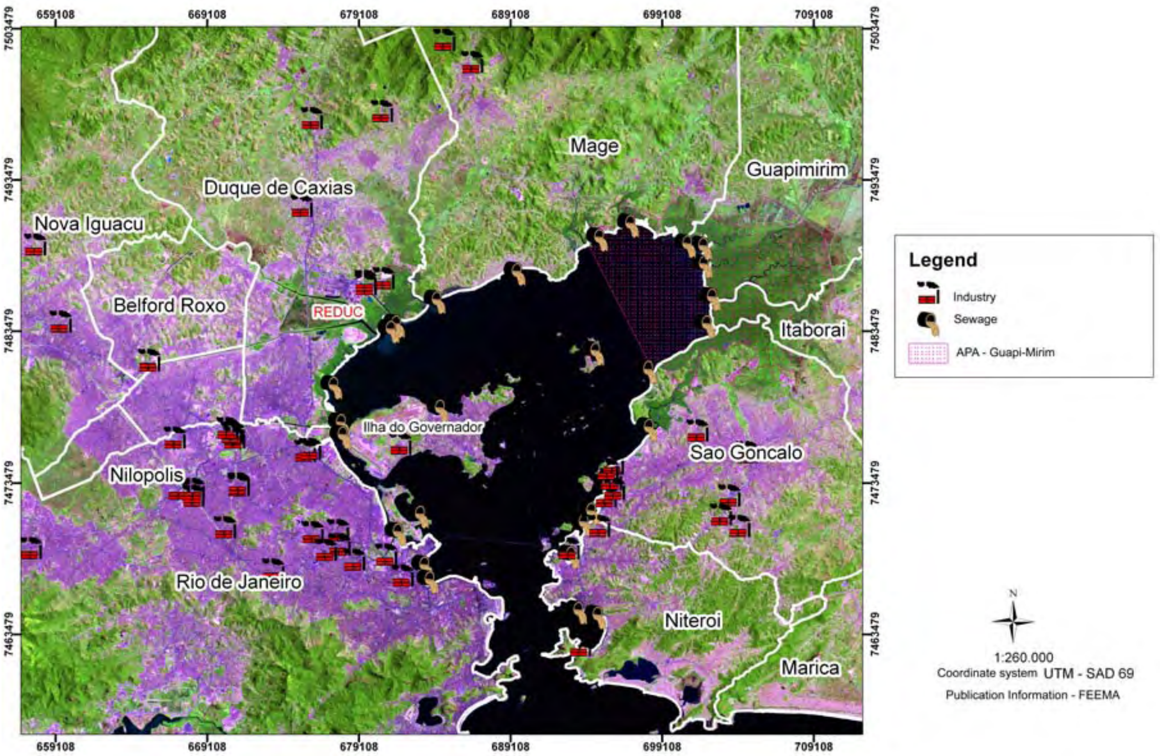

Figure 1. Points of municipal and industrial waste in Guanabara Bay

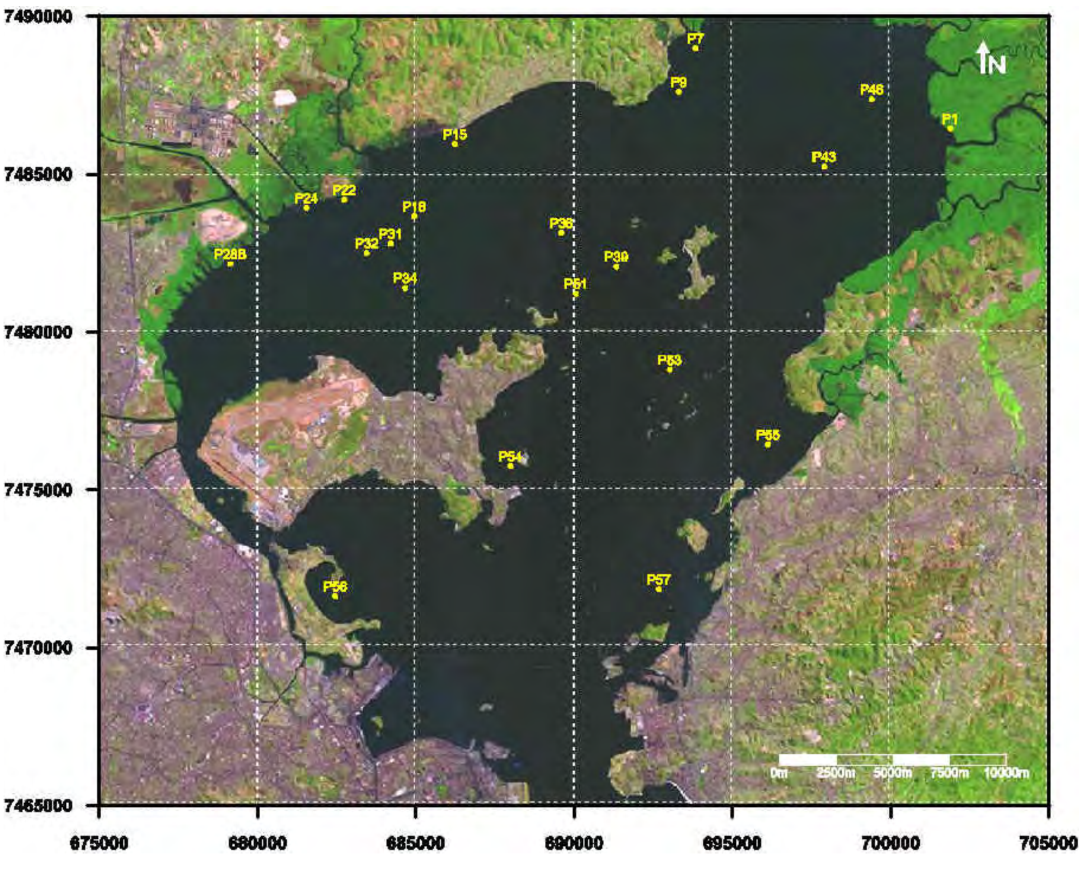

Figure 2. Geographic localization of the sediment sampling stations in Guanabara Bay

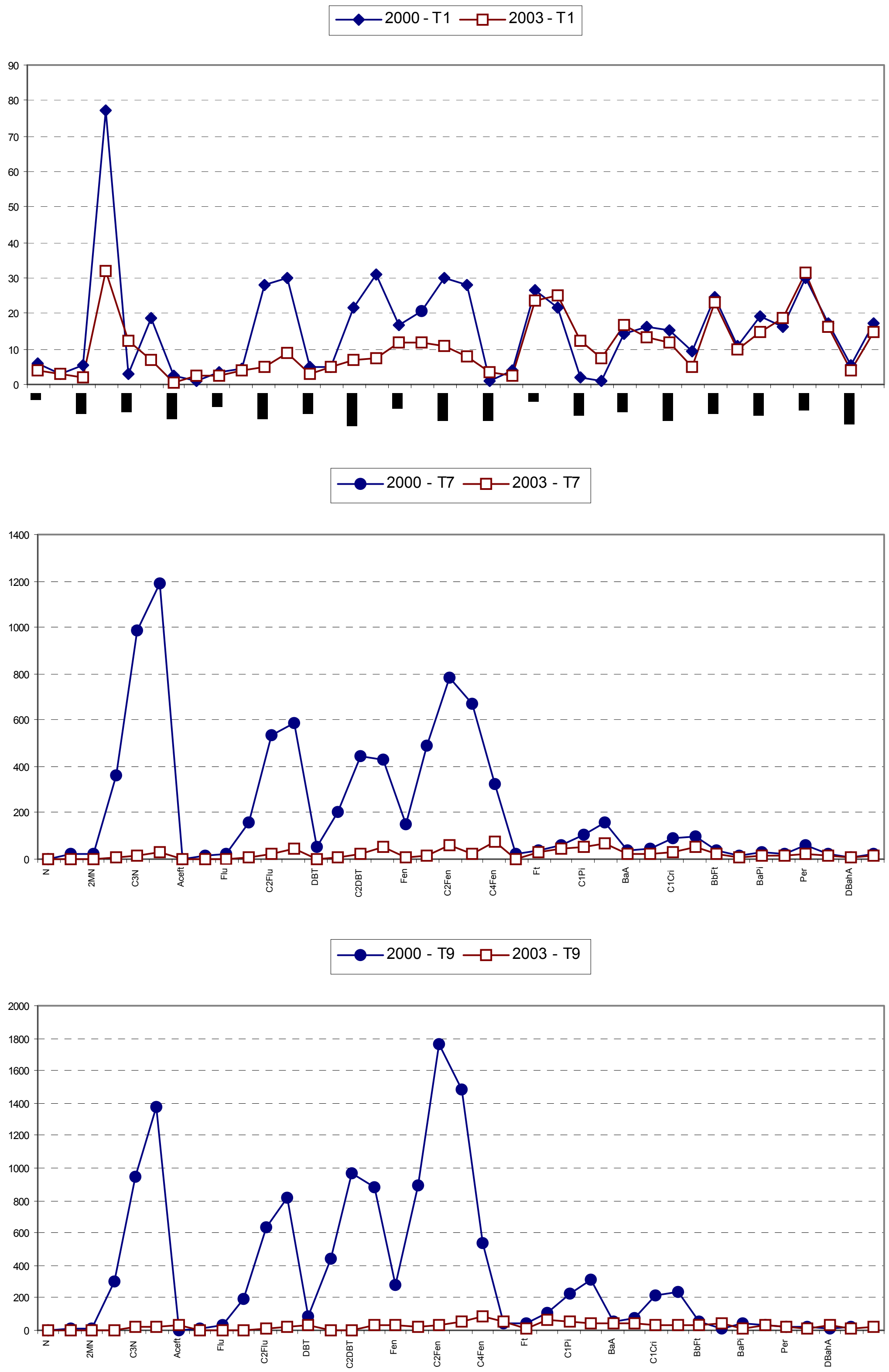

Figure 3. HPA Distribution in sediment samples from Guanabara Bay, campaigns 2000 and 2003

See Table 1 for the PAH analyte list, abbreviation and units.

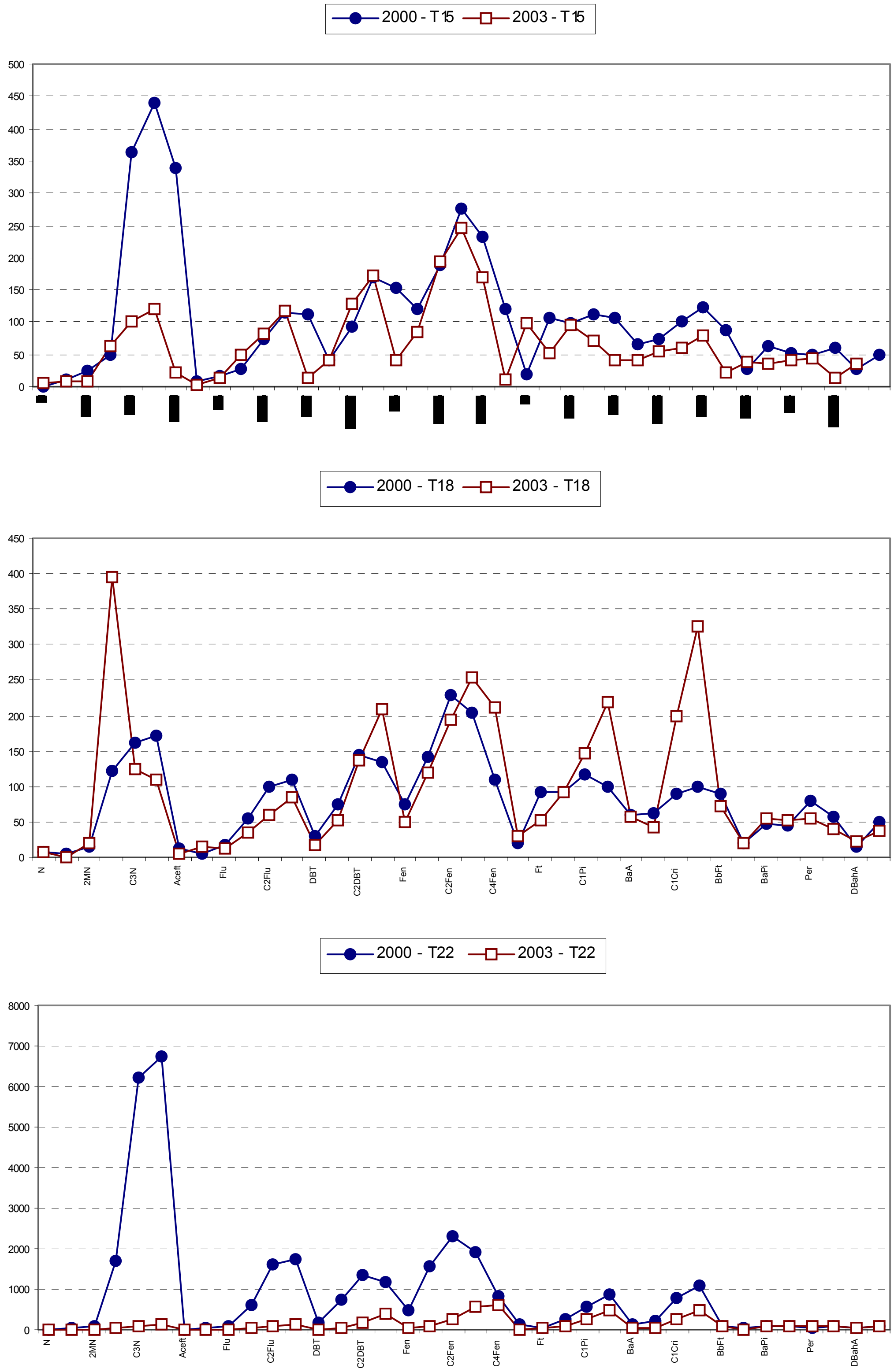

Figure 3. HPA Distribution in sediment samples from Guanabara Bay, campaigns 2000 and 2003 (cont.)

See Table 1 for the PAH analyte list, abbreviation and units.

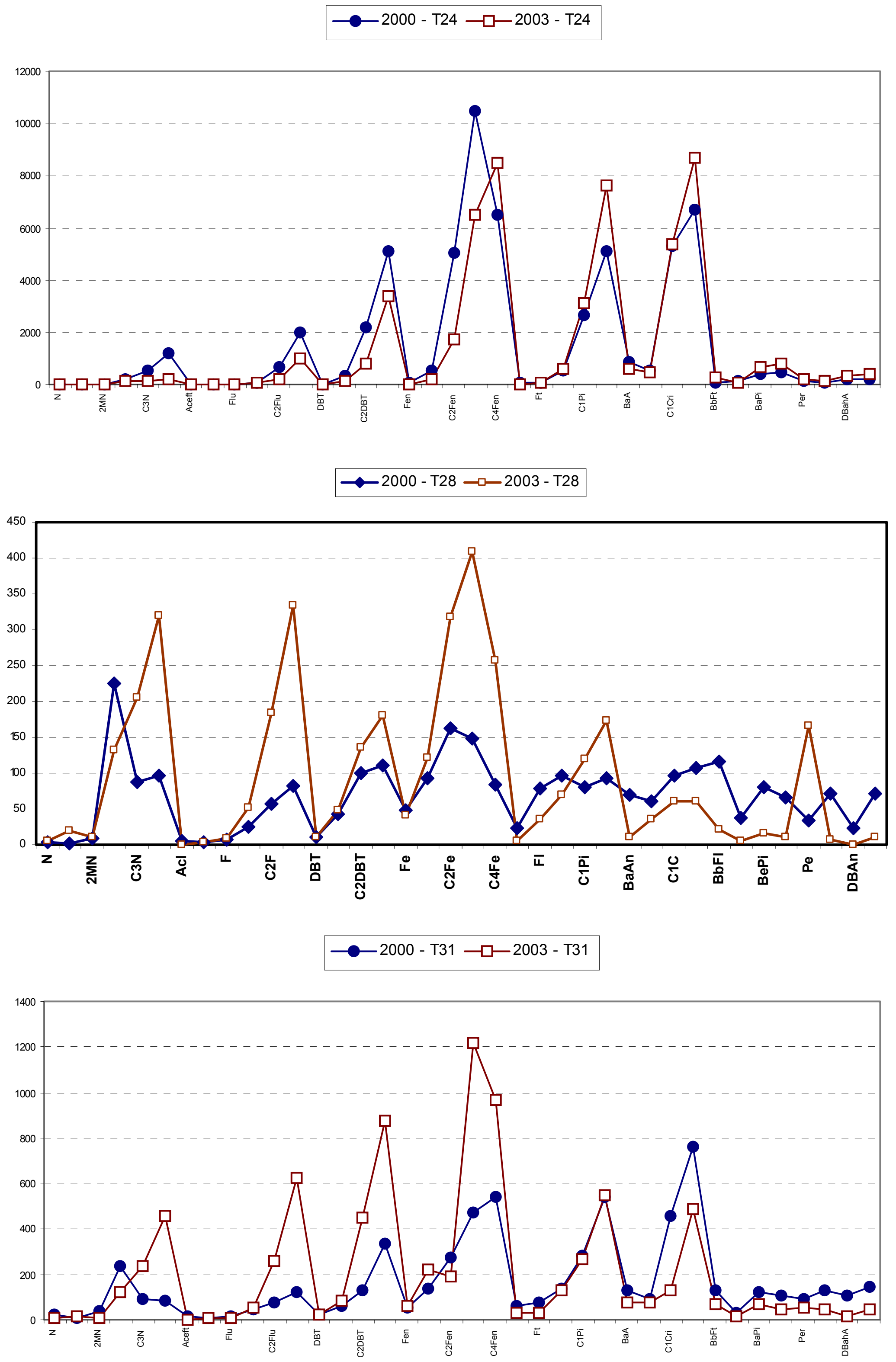

Figure 3. HPA Distribution in sediment samples from Guanabara Bay, campaigns 2000 and 2003 (cont.)

See Table 1 for the PAH analyte list, abbreviation and units.

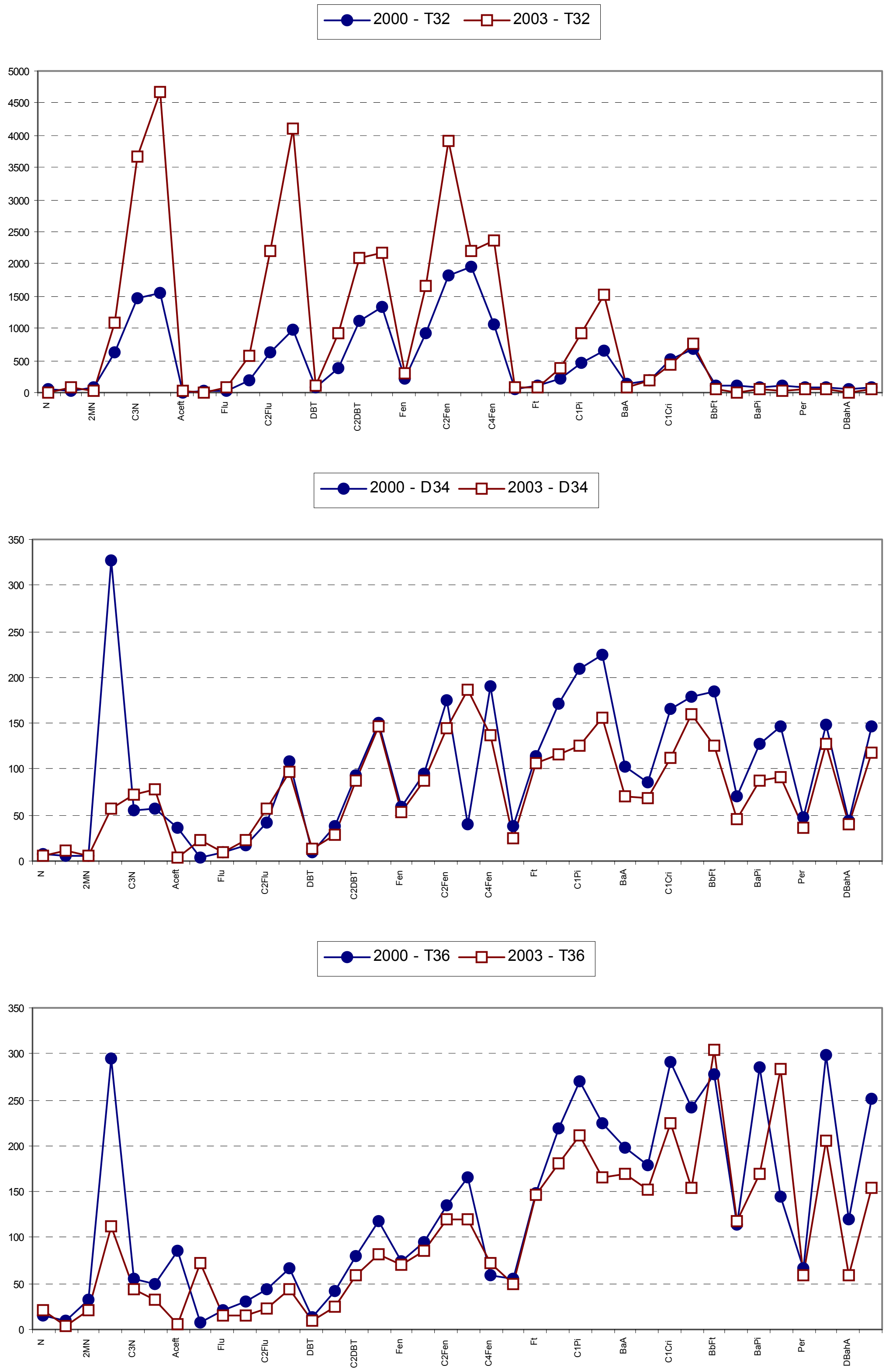

Figure 3. HPA Distribution in sediment samples from Guanabara Bay, campaigns 2000 and 2003 (cont.)

See Table 1 for the PAH analyte list, abbreviation and units.

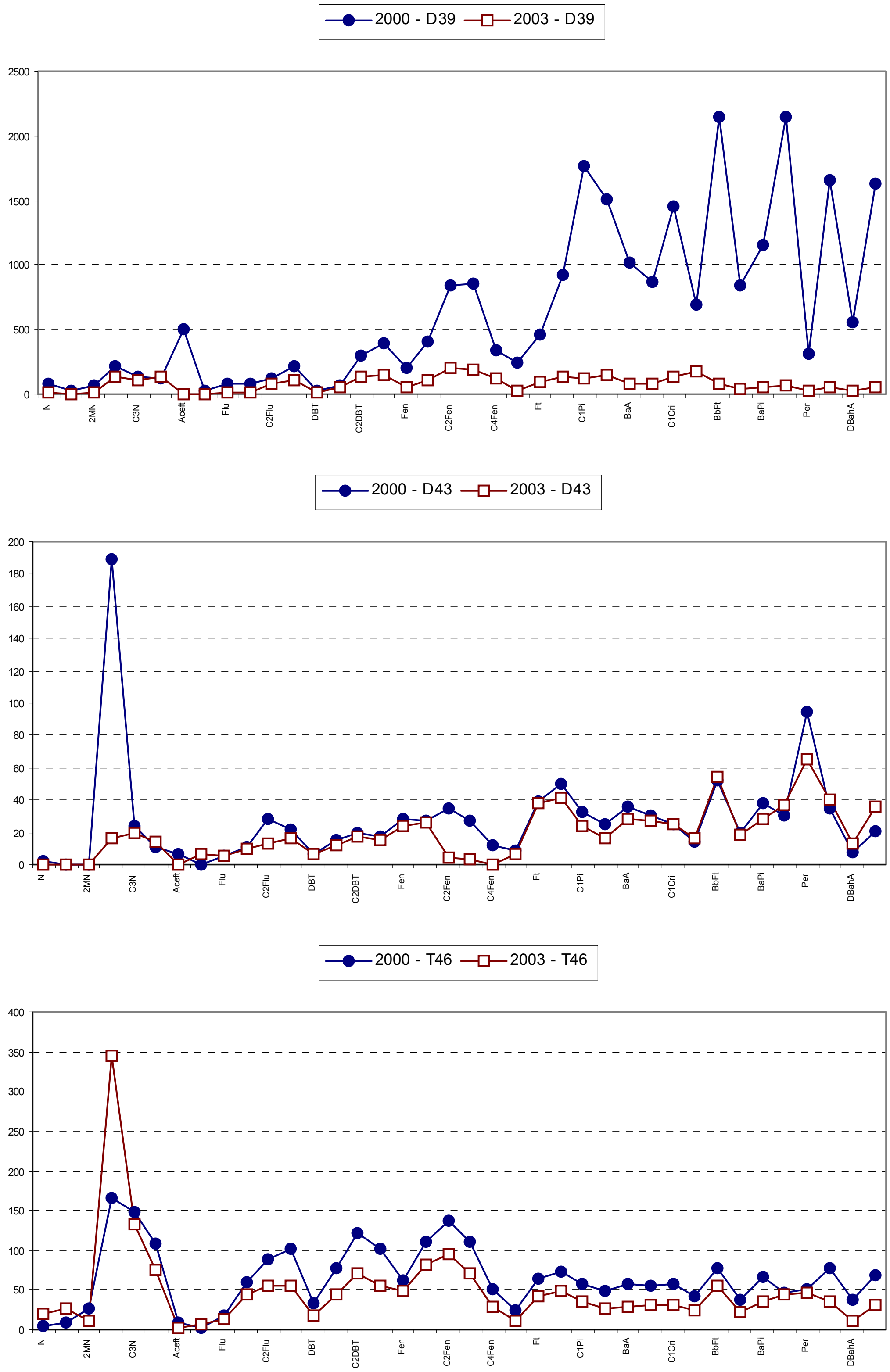

Figure 3. HPA Distribution in sediment samples from Guanabara Bay, campaigns 2000 and 2003 (cont.)

See Table 1 for the PAH analyte list, abbreviation and units.

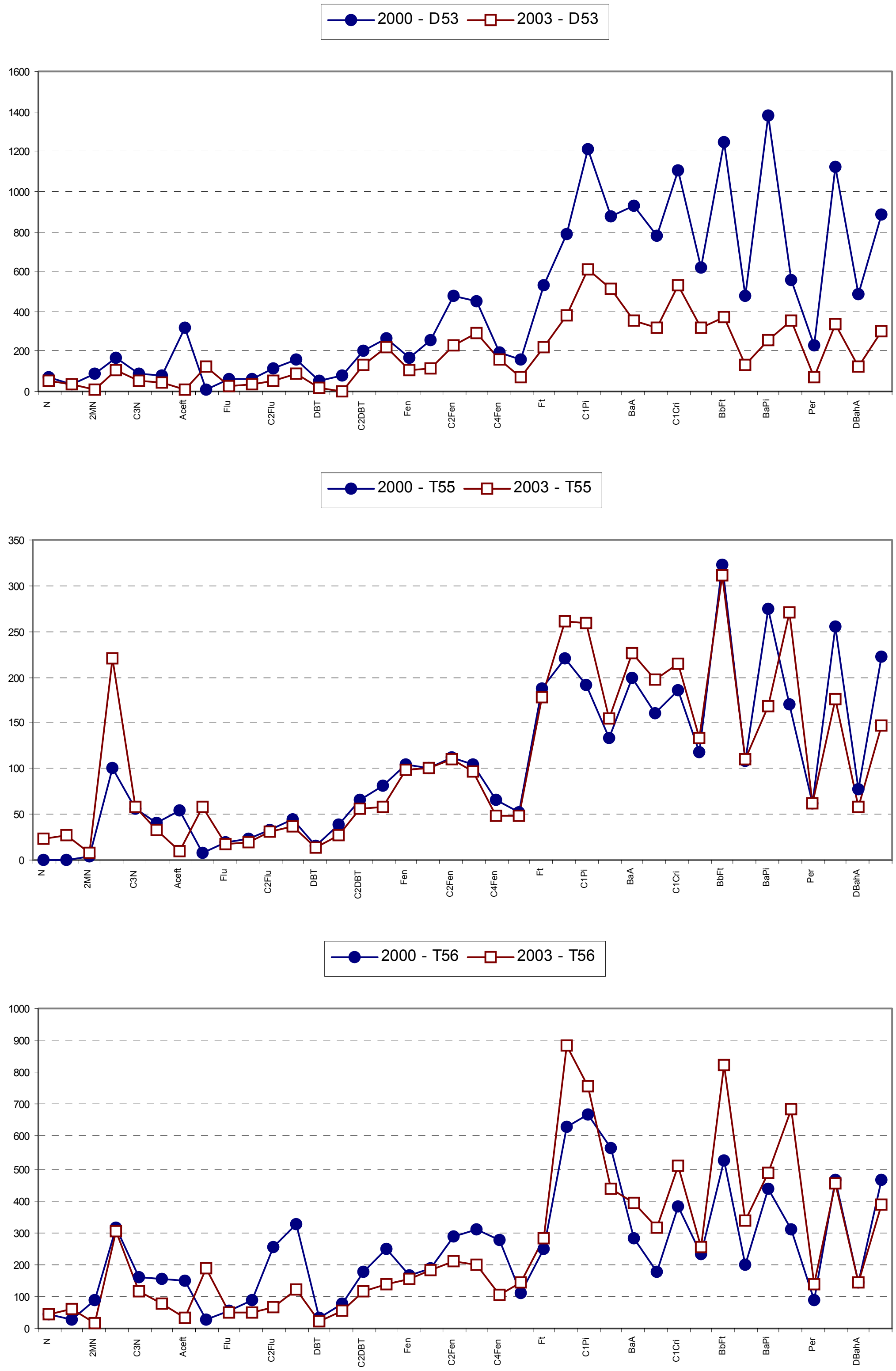

Figure 3. HPA Distribution in sediment samples from Guanabara Bay, campaigns 2000 and 2003 (cont.)

See Table 1 for the PAH analyte list, abbreviation and units.

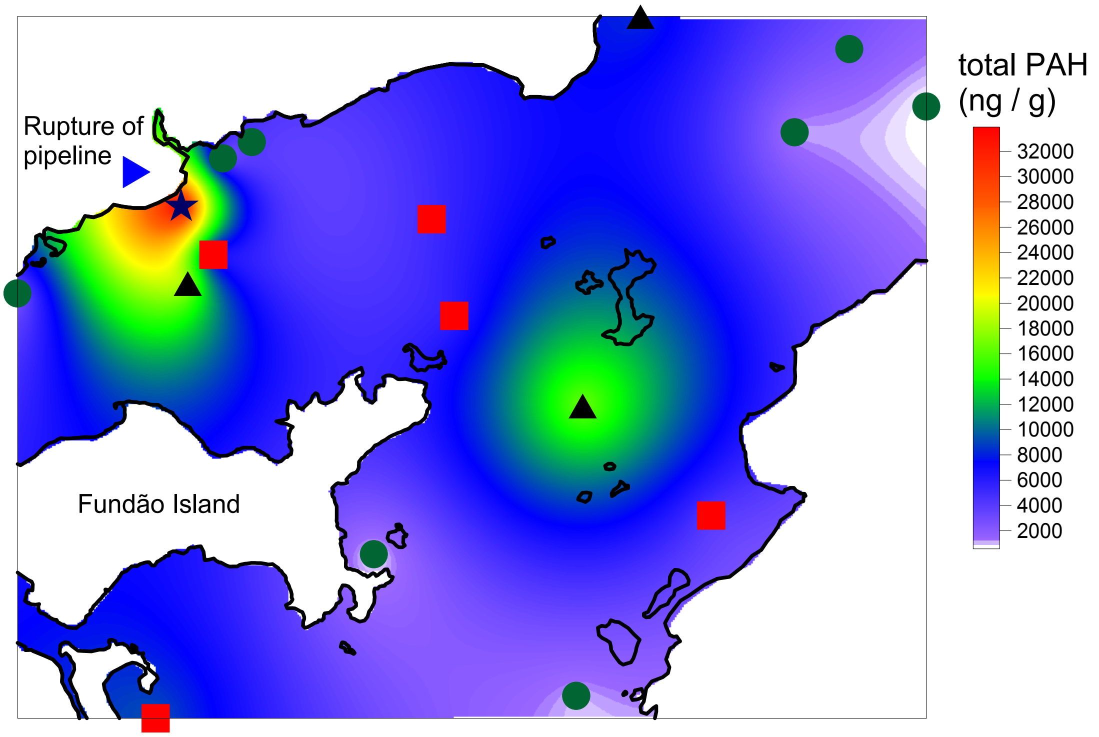

Figure 4. Total PAH Distribution in Guanabara Bay, campaign 2000

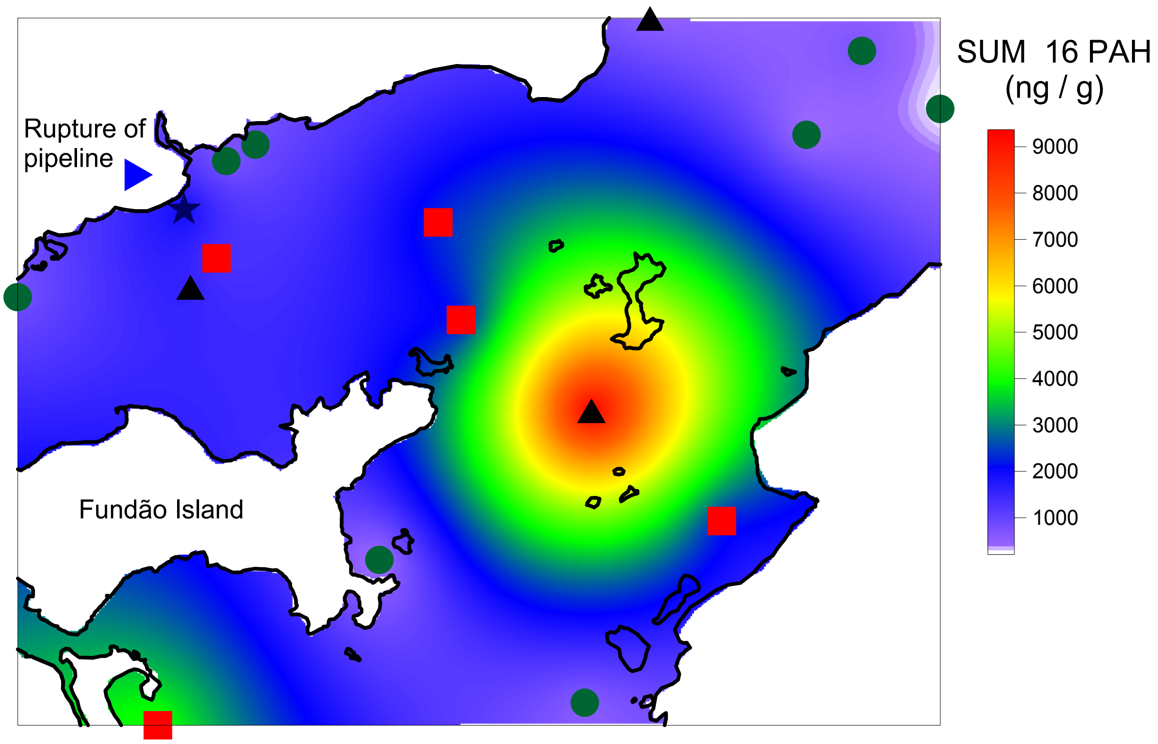

Figure 5. Σ 16 PAH Distribution in Guanabara Bay, campaign 2000

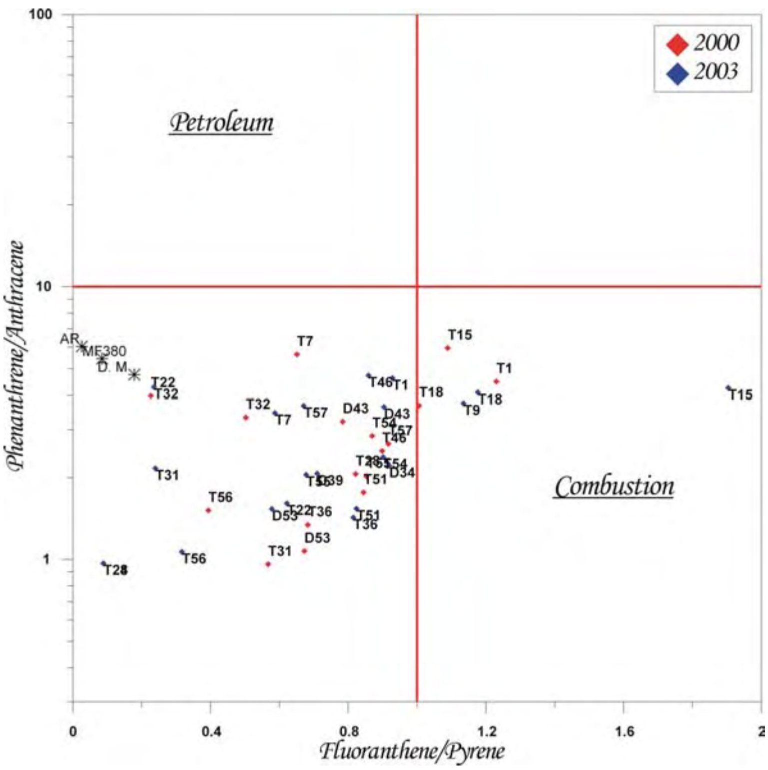

Figure 6. Plot of Phenantrene/Antracene *versus* Fluorantene/Pyrene

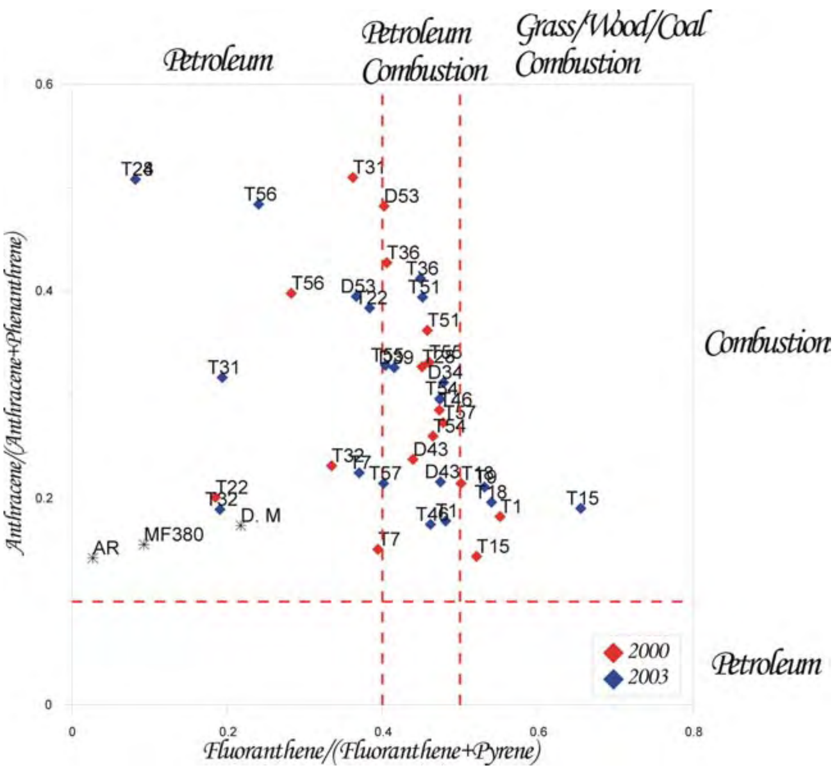

Figure 7. PAH cross plot of Anthracene/Anthracene+Phenanthrenes *versus* Fluorantene/(Fluorantene+Pyrene)

Figure 8. PAH cross plot of Indeno1,2,3-cdPyrene/Indeno1,2,3-cdPyrene+BenzoghiPerylene *versus* Fluorantene/(Fluorantene+Pyrene)

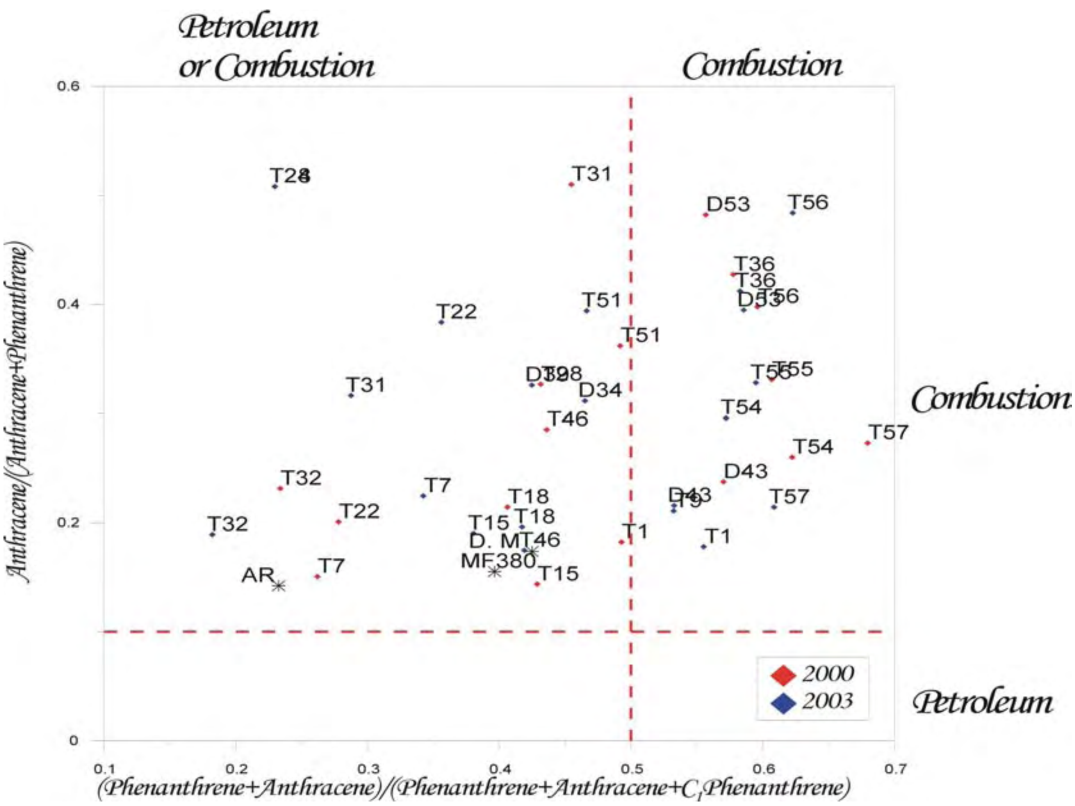

Figure 9. PAH cross plot for Anthracene/Anthracene+Phenanthrenes *versus* Phenanthrene+Anthracene/(Phenanthrene+Anthracene+C1Phenanthrene)

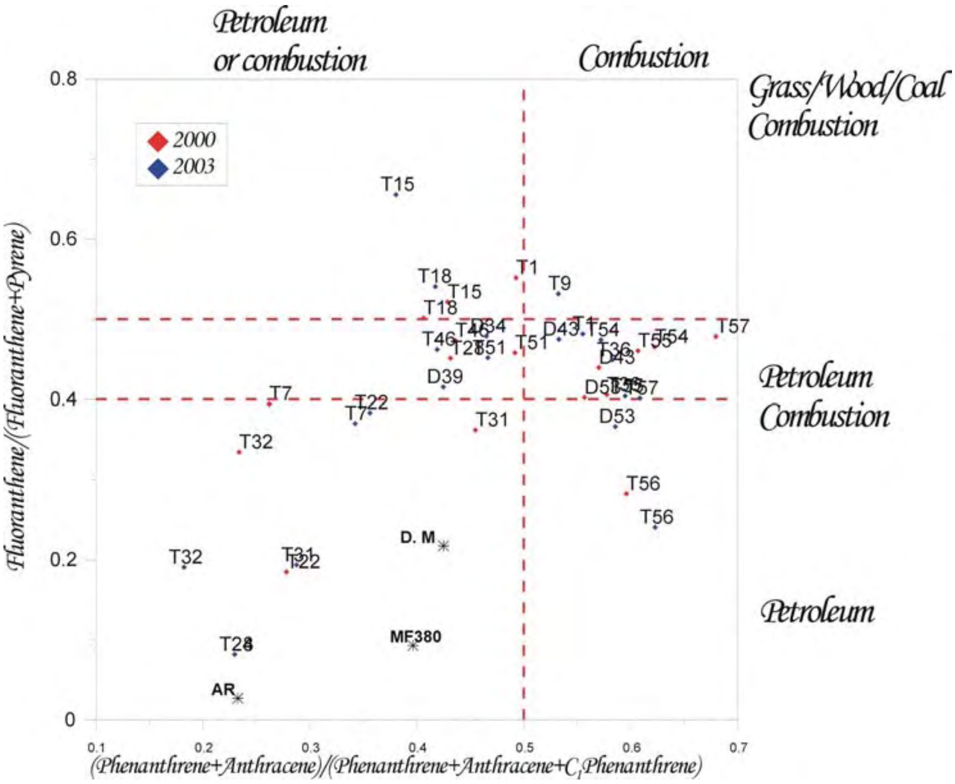

Figure 10. PAH cross plot for Fluorantene/(Fluorantene+Pyrene) *versus* Phenanthrene+Anthracene/(Phenanthrene+Anthracene+C1Phenanthrene)

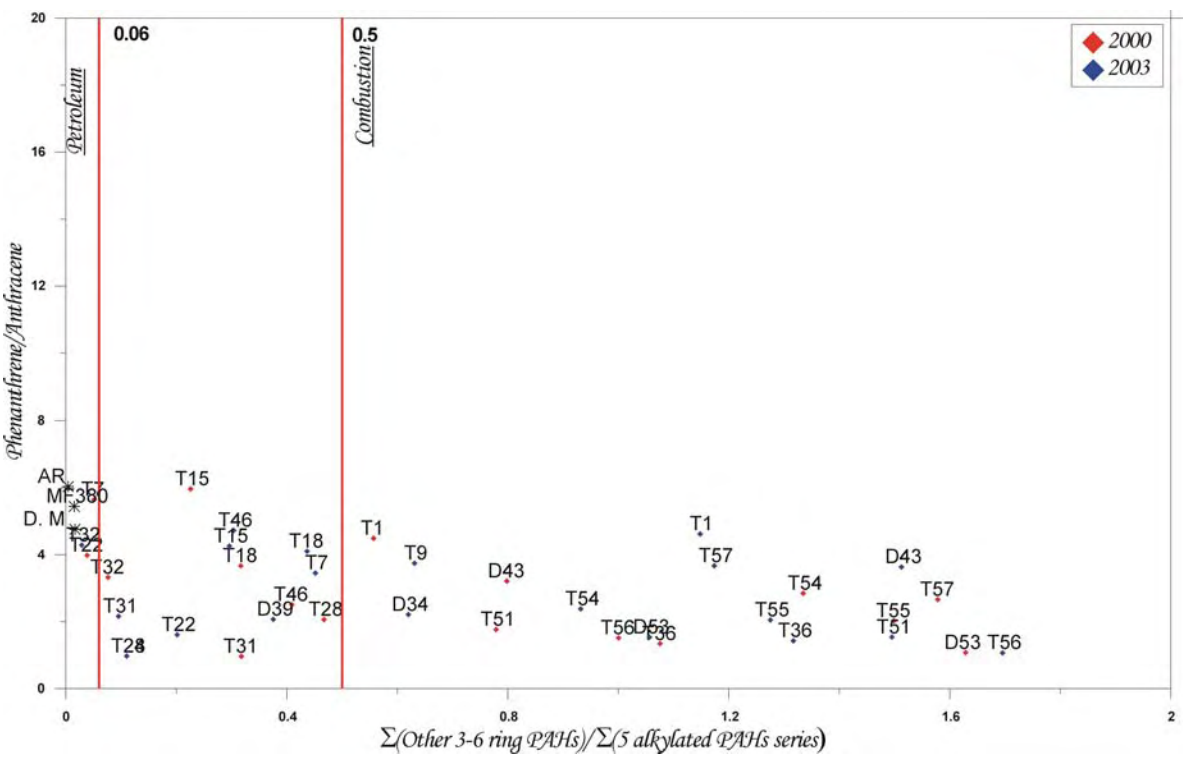

Figure 11.Plot of the relative ratios Σ (other 3-6 ring PAHs)/Σ (5 alkylated PAH series) over Phenanthrene/Anthracene for the sediment samples of Guanabara Bay and oils MF380, Arabian and Diesel

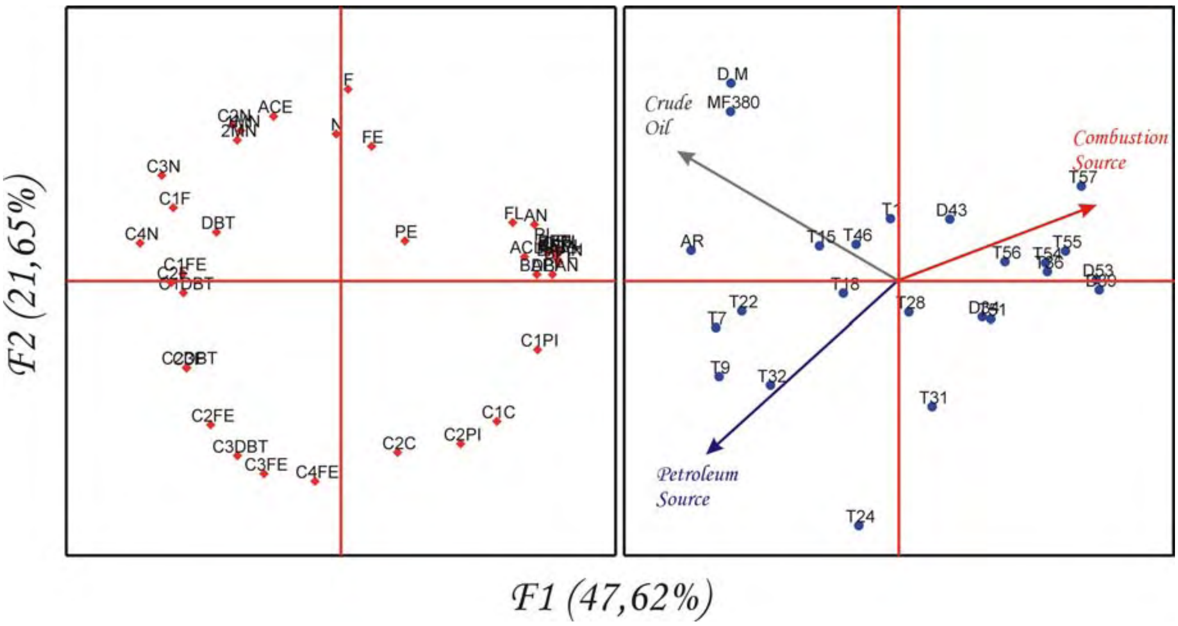

Figure 12. PCA projections of PAH variables and sediment samples from campaign 2000

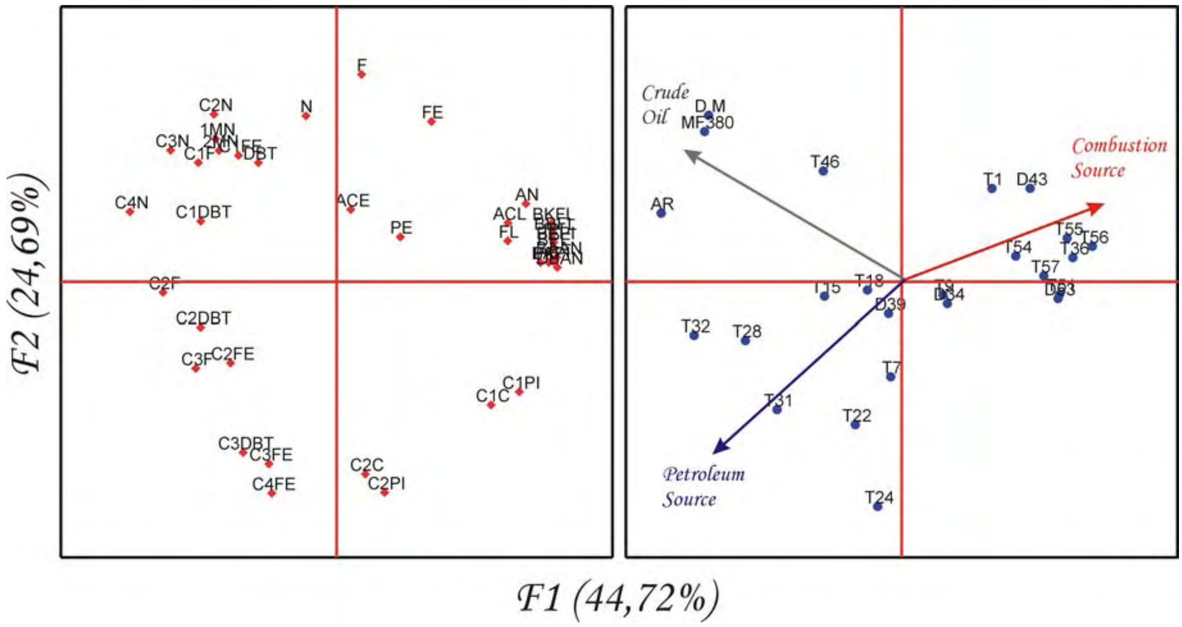

Figure 13. PCA Projections of PAH variables and sediment samples from campaign 2003

Table 1. Results for the Individual PAH (ng/g dry weight)* of Sediment Samples from Guanabara Bay – Campaign 2000

Compound	Rings	Code	T1	T7	T9	T15	T18	T22	T24	T28	T31	T32	T36	T46	T51	T54	T55	T56	T57	D34	D39	D43	D53
Naphthalene	**2**	**N**	6	2	2	12	7	5	12	4	20	55	16	5	16	3	<1	45	8	8	83	3	71
1-methylnaphthalene	**2**	**1MN**	3	19	6	24	6	45	6	2	10	39	9	8	10	<1	<1	28	2	6	21	<1	37
2-methylnaphthalene	**2**	**2MN**	6	26	7	48	15	67	21	9	35	84	33	27	25	4	5	89	8	6	67	<1	93
C_2Naphthalenes	**2**	**C_2N**	77	363	303	364	122	1695	211	226	234	629	294	166	294	9	100	315	16	328	218	189	166
C_3Naphthalenes	**2**	**C_3N**	3	983	944	440	163	6236	524	88	92	1458	55	148	56	7	56	163	10	55	132	24	91
C_4Naphthalenes	**2**	**C_4N**	19	1189	1377	338	172	6738	1214	97	84	1536	50	109	59	9	41	156	<1	56	120	11	76
Acenaphthylene	**3**	**Acl**	2	2	2	9	12	12	7	6	13	7	86	10	77	3	55	147	4	35	507	6	315
Acenaphtene	**3**	**Ace**	1	18	13	17	6	60	9	3	4	15	7	3	8	<1	7	28	3	5	29	<1	10
Fluorene	**3**	**F**	4	26	30	28	17	93	10	8	13	38	21	18	18	2	18	55	5	10	82	6	59
C_1Fluorenes	**3**	**C_1F**	5	160	199	74	55	601	80	24	47	192	31	60	10	2	23	87	6	17	88	11	66
C_2Fluorenes	**3**	**C_2F**	28	536	636	115	101	1602	682	57	73	618	43	90	114	4	33	255	8	41	128	28	118
C_3Fluorenes	**3**	**C_3F**	30	585	815	111	109	1748	1987	83	122	971	67	103	211	10	45	326	9	108	217	22	163
Dibenzothiophene	**3**	**DBT**	5	52	89	42	30	162	31	11	25	85	13	34	13	<1	16	31	3	10	24	6	53
C_1Dibenzothiophenes	**3**	**C_1DBT**	5	206	438	94	75	757	301	42	58	392	43	77	47	4	40	76	7	37	73	15	84
C_2Dibenzothiophenes	**3**	**C_2DBT**	22	441	963	170	145	1352	2160	100	127	1126	80	123	138	9	66	179	10	93	297	19	202
C_3Dibenzothiophenes	**3**	**C_3DBT**	31	425	884	152	135	1157	5109	111	334	1343	118	101	230	17	82	248	11	151	398	18	263
Phenanthrene	**3**	**Fe**	17	148	277	120	76	486	54	47	57	217	75	62	68	15	104	168	40	59	204	28	168
C_1Phenanthrenes	**3**	**C_1Fe**	21	490	888	187	141	1579	549	93	139	923	95	112	111	12	101	189	26	95	411	28	259
C_2Phenanthrenes	**3**	**C_2Fe**	30	781	1759	277	230	2294	5033	163	272	1815	134	136	248	15	112	286	23	175	846	35	480
C_3Phenanthrenes	**3**	**C_3Fe**	28	666	1479	231	204	1900	10485	148	474	1948	165	110	268	22	105	312	18	40	855	27	448
C_4Phenanthrenes	**3**	**C_4Fe**	1	321	538	120	110	839	6494	85	537	1068	60	50	192	18	65	276	11	191	341	12	196
Anthracene	**3**	**An**	4	26	46	20	21	122	38	23	59	65	56	25	39	5	51	111	15	38	251	9	157
Fluoranthene	**4**	**Fl**	27	37	45	108	91	56	72	79	78	113	149	65	192	29	188	248	77	115	468	40	532
Pyrene	**4**	**Pi**	22	57	110	99	91	247	499	96	138	225	218	72	227	34	221	629	84	171	921	51	791
C_1Pyrenes	**4**	**C_1Pi**	2	106	222	112	118	547	2679	81	280	453	270	57	337	21	192	667	53	210	1772	33	1209
C_2Pyrenes	**4**	**C_2Pi**	1	161	311	108	99	868	5114	93	544	661	224	48	306	20	133	561	29	225	1505	25	879
Benz (a) anthracene	**4**	**BaAn**	14	35	55	65	59	151	854	69	126	126	198	57	170	23	199	281	65	102	1025	36	927
Chrysene	**4**	**C**	16	46	78	74	61	226	543	61	89	183	179	56	175	21	161	176	57	85	875	30	776
C_1Chrysenes	**4**	**C_1C**	15.1	94	215	101	90	777	5298	96	457	517	291	57	264	21	187	383	40	165	1452	25	1105
C_2Chrysenes	**4**	**C_2C**	9	95	234	124	99	1070	6695	107	764	673	241	42	191	18	119	231	21	179	690	14	620
Benz (b) fluoranthene	**5**	**BbFl**	25	37	52	88	89	88	76	117	133	107	278	76	286	44	323	528	55	184	2153	53	1246
Benz (k) fluoranthene	**5**	**BkFl**	11	13	14	28	20	23	157	37	33	101	114	38	129	17	109	198	23	70	838	20	478
Benz (a) pyrene	**5**	**BePi**	19	29	48	62	47	87	370	81	122	88	286	66	272	34	274	434	51	128	1161	38	1382
Benz (e) pyrene	**5**	**BaPi**	16	25	33	52	45	89	451	66	110	96	144	47	167	25	170	309	29	147	2151	31	561
Perylene	**5**	**Pe**	30	62	18	50	79	62	159	33	94	89	67	50	68	9	63	91	14	47	315	95	227
Indeno (1,2,3-cd)pyrene	**6**	**IPi**	17	22	27	60	58	72	79	71	127	73	298	77	228	36	256	464	51	148	1660	35	1120
Dibenz(a,h)anthracene	**5**	**DBAn**	6	8	12	26	16	57	188	23	110	43	119	38	70	10	77	144	21	43	551	8	485
Benzo(ghi)perylene	**6**	**BPe**	17	21	23	50	49	82	186	72	143	68	252	68	215	27	223	464	41	146	1628	21	883
Σ 16HPA			207	526	819	866	719	1866	3235	797	1264	1524	2352	735	2189	303	2267	4119	600	1366	13425	381	9399
Σ Total HPA			691	8259	13191	4198	3058	34048	58439	2614	6174	18240	4877	2487	5398	559	4019	9816	952	3730	24555	1048	16793

* Surrogate recuperation: 68 – 117 % (average = 98%)

Table 2. Results for the Individual PAH (ng/g dry weight)* of Sediment Samples from Guanabara Bay – Campaign 2003

Compound	Rings	Code	T1	T7	T9	T15	T18	T22	T24	T28	T31	T32	T36	T46	T51	T54	T55	T56	T57	D34	D39	D43	D53
Naphthalene	**2**	**N**	4	1	3	5	6	6	13	6	7	13	20	19	7	20	24	45	< 1	6	10	< 1	49
1-methylnaphthalene	**2**	**1MN**	2	< 1	2	8	3	4	5	20	6	40	22	10	11	11	8	17	1	5	13	nd	13
2-methylnaphthalene	**2**	**2MN**	3	1	4	7	5	11	16	10	18	70	3	28	7	22	27	60	2	12	< 1	nd	39
C_2Naphthalenes	**2**	**C_2N**	32	5	18	64	35	55	100	133	121	1091	112	346	73	212	221	307	21	57	139	16	110
C_3Naphthalenes	**2**	**C_3N**	12	12	20	102	42	91	113	206	236	3657	44	133	34	56	59	118	9	71	104	20	53
C_4Naphthalenes	**2**	**C_4N**	7	32	33	120	60	143	219	319	453	4685	33	76	29	54	34	78	10	78	142	14	41
Acenaphthylene	**3**	**Acl**	2	2	3	4	5	7	7	< 2,5	5	2	73	6	5	36	57	186	9	23	6	6	120
Acenaphtene	**3**	**Ace**	<1	< 1	2	21	2	2	3	3	3	16	6	2	80	9	10	32	2	4	3	< 1	12
Fluorene	**3**	**F**	2	1	4	13	6	8	8	9	10	70	15	14	13	18	18	47	5	10	8	5	29
C_1Fluorenes	**3**	**C_1F**	4	4	8	50	22	28	35	52	54	560	15	45	19	23	19	51	6	23	12	10	33
C_2Fluorenes	**3**	**C_2F**	5	23	20	81	46	75	212	184	256	2204	23	55	36	35	30	66	18	57	77	13	52
C_3Fluorenes	**3**	**C_3F**	9	48	29	118	59	136	1003	334	620	4116	44	54	62	77	36	120	25	98	113	16	87
Dibenzothiophene	**3**	**DBT**	3	2	4	13	6	10	13	11	23	100	10	18	8	15	14	25	3	13	12	7	16
C_1Dibenzothiophenes	**3**	**C_1DBT**	5	7	5	41	18	44	117	47	87	921	25	44	21	38	28	58	7	28	53	12	< 1
C_2Dibenzothiophenes	**3**	**C_2DBT**	7	26	29	128	50	163	801	136	447	2087	59	71	84	94	56	116	24	88	140	18	131
C_3Dibenzothiophenes	**3**	**C_3DBT**	7	56	37	173	75	403	3350	180	872	2170	82	55	165	155	59	140	49	147	154	15	224
Phenanthrene	**3**	**Fe**	12	7	25	42	21	27	30	40	62	300	70	49	51	103	99	154	39	53	52	24	102
C_1Phenanthrenes	**3**	**C_1Fe**	12	17	28	84	36	79	205	121	223	1657	85	83	97	109	100	181	32	88	104	26	119
C_2Phenanthrenes	**3**	**C_2Fe**	11	60	58	194	75	249	1723	318	189	3905	119	96	60	129	111	209	51	146	199	4	233
C_3Phenanthrenes	**3**	**C_3Fe**	8	20	84	245	88	569	6493	408	1216	2191	120	71	270	168	96	197	35	187	185	3	295
C_4Phenanthrenes	**3**	**C_4Fe**	3	72	56	169	63	588	8491	257	964	2376	73	29	138	90	48	106	27	138	121	< 1	155
Anthracene	**3**	**An**	3	2	7	10	5	17	31	6	29	70	49	10	33	43	48	145	11	24	25	7	66
Fluoranthene	**4**	**Fl**	23	28	65	99	58	52	56	35	30	93	147	42	185	224	178	280	57	107	93	38	222
Pyrene	**4**	**Pi**	25	48	57	52	49	84	625	69	126	393	181	49	224	248	262	885	85	117	131	42	383
C_1Pyrenes	**4**	**C_1Pi**	12	56	47	97	63	244	3146	119	268	921	211	35	329	217	259	755	80	125	118	24	609
C_2Pyrenes	**4**	**C_2Pi**	7	71	43	72	49	496	7638	173	547	1529	165	26	298	168	155	435	62	157	149	16	516
Benz (a) anthracene	**4**	**BaAn**	17	20	38	41	24	48	622	10	75	94	170	29	219	155	227	392	62	71	86	28	351
Chrysene	**4**	**C**	13	19	32	42	30	55	467	35	73	190	151	31	199	150	198	315	60	69	82	28	316
C_1Chrysenes	**4**	**C_1C**	12	28	30	54	39	258	5349	61	130	435	225	31	246	175	216	506	53	112	138	25	533
C_2Chrysenes	**4**	**C_2C**	5	51	34	60	43	488	8711	61	486	757	153	25	159	132	134	256	29	159	175	17	316
Benz (b) fluoranthene	**5**	**BbFl**	23	22	46	78	48	82	279	21	69	46	305	55	411	200	311	825	84	126	86	55	373
Benz (k) fluoranthene	**5**	**BkFl**	10	8	15	21	13	20	41	5	15	9	118	23	144	81	110	335	29	46	36	19	136
Benz (a) pyrene	**5**	**BePi**	19	14	17	37	24	81	777	17	49	36	284	44	267	178	270	686	69	91	73	38	355
Benz (e) pyrene	**5**	**BaPi**	15	18	33	38	18	65	684	10	66	47	169	36	374	135	168	484	52	88	59	29	257
Perylene	**5**	**Pe**	32	24	13	41	51	72	215	167	53	58	60	46	66	41	61	139	16	37	25	65	75
Indeno (1,2,3-cd)pyrene	**6**	**IPi**	16	16	27	45	30	68	116	8	43	48	205	34	310	184	177	455	55	128	60	40	334
Dibenz(a,h)anthracene	**5**	**DBAn**	4	5	8	14	8	35	301	< 2,5	19	nd	60	11	76	56	58	144	16	39	24	13	127
Benzo(ghi)perylene	**6**	**BPe**	15	15	26	37	26	71	372	11	44	58	153	32	281	169	147	386	48	117	57	36	301
Σ 16HPA			184	212	388	560	349	647	3653	269	675	1448	1891	443	2611	1829	2090	5110	614	1028	818	368	3177
Σ Total HPA			400	838	1004	2516	1303	4931	52384	3603	7993	37014	3856	1861	5090	4028	4130	9734	1242	2944	3063	726	7182

* Surrogate recuperation: 61 – 119 % (average = 101%)

Table 3. Summary of PAH Concentration (ng/g dry weight) in Sediments from Various Coastal Sites in the World

Location	Number of PAH analyzed	Concentration Range (ng/g)	References
Casco Bay, USA	23	16-20,748	Kennicutt et al., 1994
San Diego, USA	36	80-20,000	Anderson et al., 1996
San Francisco Bay, USA	17	2,653-27,680	Pereira et al, 1996
Masan Bay, Korea	16	41-1,100	Khim et al., 1999
Gironde & Arcachon Bay, France	14	3.5-853	Sicre et al., 1987
Sarasota Bay, USA	11	17-26,771	Sherblom et al., 1995
Brisbane River Estuary, Australia	17	2,840-13,470	Kayal & Connell, 1989
Mersey Estuary, UK	13	5,310	Readman et al., 1986
Tamar Estuary, UK	13	8,630	Readman et al., 1986
Rio de La Plata Estuary, Argentina	18	50-555,000	Colombo et al., 1989
Daya Bay, Hong Kong, China	16	115-1,134	Zhou & Maskaoui, 2003
Channel of Rio de La Plata (after oil spill), Argentina	16	10 – 70,000	Colombo, 2000
Guanabara Bay (campaign 2000)	16 38	207-13,425 559-58,439	This study
Guanabara Bay (campaign 2003) Brazil	16 38	184-3,653 400-52,384	