

## Distribution and Sources of Polycyclic Aromatic Hydrocarbons in Surface Sediments from Two Brazilian Estuarine Systems

Otávio L. G. Maioli,<sup>a</sup> Kamila C. Rodrigues,<sup>a</sup> Bastiaan A. Knoppers<sup>b</sup> and Débora A. Azevedo<sup>\*,a</sup>

<sup>a</sup>Instituto de Química, Universidade Federal do Rio de Janeiro, 21941-909 Rio de Janeiro-RJ, Brazil

<sup>b</sup>Departamento de Geoquímica, Universidade Federal Fluminense, 24020-150 Niterói-RJ, Brazil

Este estudo concentra-se nos sistemas estuarinos tropicais de Mundaú-Manguaba (MMELS) e do Rio Paraíba do Sul (PSR), ambos no Brasil e afetados por práticas da monocultura da cana-de-açúcar e por urbanização. Os níveis de 17 hidrocarbonetos policíclicos aromáticos (HPAs), 16 dos quais são classificados como poluentes prioritários para estudos ambientais pela US-EPA e o perileno (HPA biogênico) foram avaliados nos sedimentos superficiais para identificar fontes da poluição e determinar níveis base como estratégias para gerenciamentos futuros. O  $\Sigma 16\text{HPAs}$  variou de 2,90 a 231,30  $\mu\text{g kg}^{-1}$  em MMELS e de 87,10 a 9344,29  $\mu\text{g kg}^{-1}$  no PSR. As relações entre HPAs isômeros sugeriram principalmente fontes de origem pirogênica.

This study focuses on the tropical estuarine systems of Mundaú-Manguaba (MMELS) and Paraíba do Sul River (PSR), Brazil, affected by sugarcane monoculture practices and also urbanization. The levels of 17 polycyclic aromatic hydrocarbons (PAHs), 16 of which are classified as priority pollutants by the US-EPA and perylene (a biogenic PAH) were measured in surface sediments to identify pollution sources and determine baseline data looking for future management strategies. The  $\Sigma 16\text{PAH}$  ranged from 2.90 to 231.30  $\mu\text{g kg}^{-1}$  in MMELS and from 87.10 to 9344.29  $\mu\text{g kg}^{-1}$  in the PSR. PAH isomeric ratios suggested mainly pyrogenic input.

**Keywords:** PAH, sediments, pollution sources, Brazilian estuary, sugarcane burning

### Introduction

Marine coastal areas play an important role in the global carbon cycle, either as sources of organic matter to the open ocean or as carbon sinks in the form of accumulation in sediments.<sup>1</sup> Marine sediments serve as an ultimate reservoir for natural and anthropogenic organic matter generated by organisms living in the sediment and the overlying water column and supplied by river discharge and atmospheric transport.<sup>2</sup>

Hydrocarbons are abundant components of organic material in coastal zones, and one of the major classes of organic compounds.<sup>1</sup> Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental contaminants and are known for their carcinogenic and mutagenic effects. They are generally more resistant to biodegradation than many saturated biomarkers and tend to persist in contaminated sediments, water, soil, atmospheric particulate matter and

some organisms like mussels.<sup>3-8</sup> The PAH sources are mainly anthropogenic and originate from several sources: (i) petroleum inputs; (ii) hydrocarbons released as the result of incomplete combustions of fuels; (iii) PAHs originating from forest, sugarcane and grass fires (transported to the marine environment *via* eolian (atmospheric) and fluvial (riverine) processes); (iv) biosynthesis of hydrocarbons by marine or terrigenous organisms; (v) early diagenetic transformation from natural products and hydrocarbons; and (vi) hydrocarbons diffusing from the mantle, petroleum source rocks or reservoirs.<sup>9-11</sup> Atmospheric particulate matter emitted by sugarcane burning contains considerable concentrations of PAHs and can be accumulated in sediments.<sup>12</sup> Despite their low aqueous solubility and hydrophobic nature, PAHs tend to associate with particulate material, which will finally be deposited in soil and in the underlying sediments of lacustrine, estuarine and marine environments.<sup>13</sup> Because of these characteristics, many environmental studies use PAH concentrations from sediments to distinguish between sources of contaminants

\*e-mail: debora@iq.ufrj.br

and evaluate the degree of ecological impact. Generally, the anthropogenic sources of PAHs may be classified as pyrogenic or petrogenic by individual PAH ratios, based on peculiarities in PAH composition and distribution as a function of the emission source.<sup>14,15</sup> Many ratios between PAHs in sediments are diffused to identification source emissions as Ant/(Ant+Phen), BaA/(BaA+Chry), Flt/(Flt+Py) and InP/(InP+BghiP).

The sample areas in this work represent reference sites for studies on the transport pathways and transformations of effluents and pollutants in sediments, and for the reconstruction of the sugarcane impacts since the beginning of the practice in the 17th century. Sugarcane monoculture and industry are important pollutant sources for water, air and soils in northeastern and eastern Brazilian agriculture. In Brazil, after the 1970s, sugarcane production expanded greatly, mainly due to PROÁLCOOL, the program developed by Brazilian government for the production of ethanol used as automotive fuel. In 2004, Brazil has responded for approximately 27% of sugarcane plantation worldwide and has been the major sugarcane producer. To facilitate manual reaping and to increase production, the sugarcane crops are always burned before being harvested, emitting contaminants to its surroundings.

In this regard, this study addresses the sedimentary concentrations of PAHs in the tropical estuarine systems of Mundaú-Manguaba, in Northeastern Brazil, and of the Paraíba do Sul River, Southeastern Brazil, affected by sugarcane monoculture practices and also urbanization. A total of 17 PAHs, including 16 identified by the U. S. Environmental Protection Agency (USEPA) as priority pollutants and perylene, known to be of biogenic origin were analyzed. Source identification was evaluated by PAH isomeric ratios.

## Materials and Methods

### Study areas

The study areas correspond to the Mundaú-Manguaba estuarine-lagoon system (MMELS), located in the state of Alagoas, NE-Brazil (Lat. 9° 35' and 9° 46' S, Long. 35° 44' and 35° 58' W), and the Paraíba do Sul River estuary (PSR), state of Rio de Janeiro, SE-Brazil (Lat. 21° 48' S, Long. 41° 02' W) (Figure 1). MMELS falls into the category of a choked estuarine-lagoon system, with long residence times of water, a large potential for material recycling and retention, and exhibits eutrophic conditions.<sup>16,17</sup> In contrast,

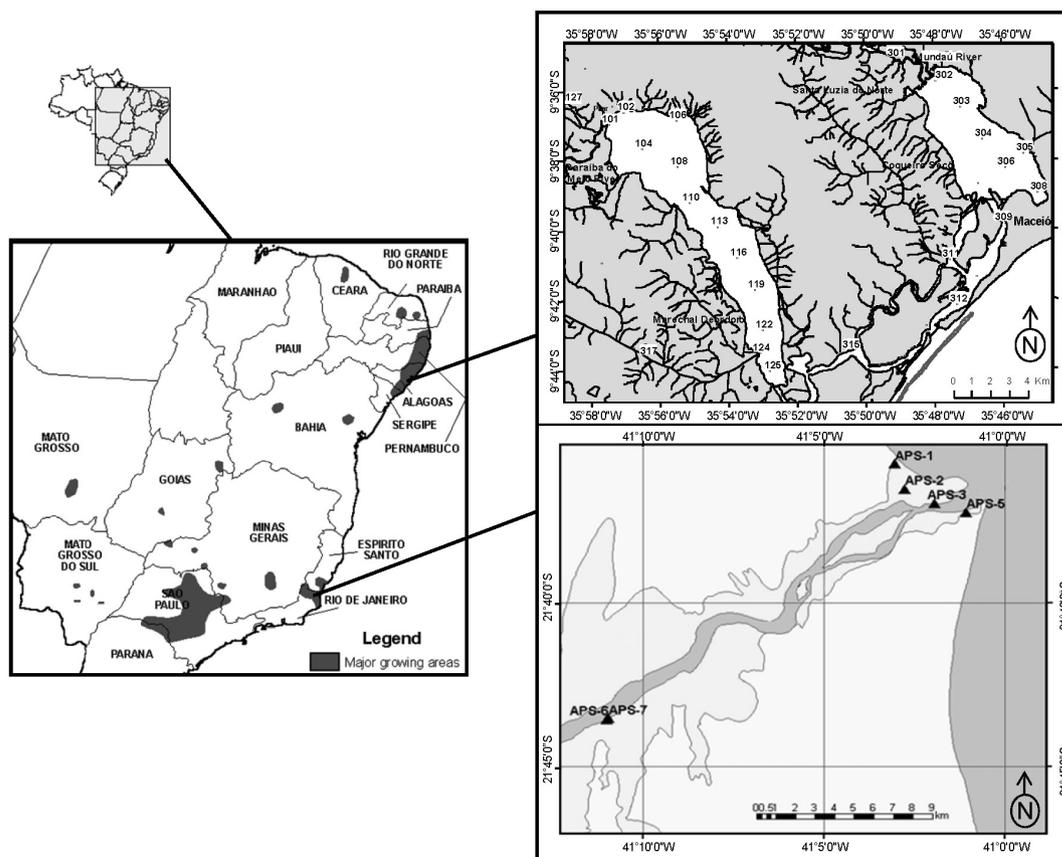


Figure 1. Map of the investigated areas including sampling stations.

the PSR estuary falls into the category of an estuarine-delta, fed by turbid river waters and is an exporter of materials to the coastal sea.

MMELS has a total surface area of 79 km<sup>2</sup> and a mean depth of around 2 m. It consists of three distinct compartments, the Manguaba (A = 43 km<sup>2</sup>) and the Mundaú (A = 24 km<sup>2</sup>) lagoons and a maze of mangrove-lined narrow channels (A = 12 km<sup>2</sup>) connected *via* a single 250 m-wide tidal inlet to the sea. The system of the watershed has an area of 7844 km<sup>2</sup> and the climate in the upper basin is semi-arid and the lower basin is tropical humid, with a precipitation of 1654 mm and distinct dry summer (November to March) and wet winter (May to August) conditions. Sugarcane waste effluents are transported by the rivers and urban sewage is introduced into Mundaú lagoon from the Maceió city (*ca.* 900,000 habitants) and a number of smaller cities into Manguaba lagoon.<sup>17</sup> Crop burning activities have been affecting the entire lower drainage basin and also Maceió city.

The PSR estuary is fed by the 1145 km long Paraíba do Sul River with a mean annual fresh water discharge of 868 m<sup>3</sup> s<sup>-1</sup> from a watershed of 55,400 km<sup>2</sup>, with access to the sea *via* a primary channel and a secondary channel lined by mangroves (Figure 1). The climate at the coast is tropical humid with an average annual precipitation of 1100 mm and wet summer (October to March) and dry winter (April to September) seasons. The river crosses three of the most important and developed states of Brazil (São Paulo, Minas Gerais and Rio de Janeiro). It supplies water for more than 11 million people of Rio de Janeiro, but it is also used as waste disposal for a very large number of industries along its course. Other human impacts arise from domestic/industrial effluents upriver, partially retained by a cascade of dams. Along its lower course in the coastal plains, it is affected by point and diffuse sources of sugarcane practices and domestic effluents. Ground water contamination by sugarcane effluents has been detected and crop burning practices have notoriously been affecting the medium-sized Campos dos Goytacazes City.<sup>18,19</sup>

#### *Sample collection*

A total of 25 sediment samples were collected from MMELS and 6 sediment samples were collected along the PSR (Figure 1). The samples were collected only once *per* site. Surface sediment samples (0-5 cm) were collected with a Van Veen type grab and kept in pre-cleaned aluminum foil containers. The sediments were kept in the refrigerator at -20 °C. Afterwards, they were sieved through 63 µm, subjected to lyophilization, extracted and analyzed. Surface

sediment samples from PSR were collected in July 2006 and from MMELS in August 2006.

#### *Chemical standards*

Perdeuterated standard, pyrene-d<sub>10</sub> 98% was from Cambridge Isotope Laboratories (Andover, MA, USA). The reference mixture of PAHs (EPA 610) was from Supelco, Bellefonte, USA (part No. 4-8743) containing 100 mg L<sup>-1</sup> of anthracene (Ant), benzo[a]anthracene (BaA), benzo[a]pyrene (BaP), benzo[k]fluoranthene (BkF), chrysene (Chry), indeno[1,2,3-cd]pyrene (InP), phenanthrene (Phen) and pyrene (Py); 200 mg L<sup>-1</sup> of benzo[b]fluoranthene (BbF), benzo[g,h,i]perylene (BghiP), dibenzo[a,h]anthracene (DBA), fluoranthene (Flt), fluorene (Fluo); 1000 mg L<sup>-1</sup> of acenaphthene (Ace) and naphthalene (Nap) and 2000 mg L<sup>-1</sup> of acenaphthylene (Aceph). Perylene (Per) standard was from Sigma (USA). All solvents used for sample processing and analyses (dichloromethane, hexane) were chromatographic grade from Tedia Brazil (Rio de Janeiro, Brazil).

#### *Extraction and clean-up of samples*

About 10 g of lyophilized sediment was submitted to extraction by ultrasonication in 50 mL of dichloromethane for 20 min. The sample was centrifuged, the dichloromethane was extracted and the extraction process repeated two more times. The extracts (organic fraction) were combined and concentrated in rotary evaporator. The organic fraction was concentrated and fractionated using about 2.5 g of activated silica gel column (silica activated at 120 °C for 12 h). The column was eluted first with 10 mL of hexane to obtain the aliphatic hydrocarbon fraction. Further elution was with 10 mL of hexane/dichloromethane (8:2) to obtain the PAHs.<sup>11</sup> All the extracts were concentrated, transferred to an autosampler microvial (250 µL) and blow-down with N<sub>2</sub> to almost dryness. The PAH extracts were completed to 100 µL with pyrene-d<sub>10</sub> standard solution at 1 ng mL<sup>-1</sup>. The standard solution was added to the samples just before GC/MS analysis. This step was carried out only once *per* site (n = 1).

#### *Analytical methods*

Gas chromatographic/mass spectrometric analyses (GC/MS) were carried out on an Agilent Technologies (Palo Alto, CA, USA) GC/MS instrument with a gas chromatograph (GC), model 6890N equipped with a 7673 autosampler, coupled to a quadrupole mass spectrometer (MS), 5973 MSD. The capillary fused silica column was

a DB-5, 30 m, 0.25 mm i.d., with a 0.25- $\mu\text{m}$  film thickness (J & W Scientific). The column temperature for all analyses was programmed from 60 to 300 °C at a rate of 6 °C  $\text{min}^{-1}$  and held at 300 °C for 15 min. The injector was heated at 290 °C and 2  $\mu\text{L}$  sample volume was injected. Helium was used as carrier gas. Data acquisition was in electron impact (70 eV) and selected ion monitoring (SIM) mode was used. The standard PAH mixture was also analyzed in scan mode in the mass range of 50-400 Daltons. Two characteristic ions were selected for each parent PAH for their identification in SIM mode analyses together with their retention times. Before analysis, relevant standards (reference mixture of PAHs) were run to check column performance, peak height and resolution. With each set of samples to be analyzed, a solvent blank and a standard mixture were run in sequence to check for contamination, peak identification and quantification. Quality assurance procedures included control of the blank. This analytical method was validated and the quantification limit for PAHs was considered 0.1 ng  $\text{g}^{-1}$  based on previous studies.<sup>11</sup> External standard calibration curves were used for PAH quantification of the extracts in addition to the pyrene- $\text{d}_{10}$  internal standard. Calibration graphs for SIM mode were plotted using five to six points in the range of concentration 0.0025-4  $\mu\text{g mL}^{-1}$  for the standard solution mixture. The perylene calibration curve was constructed for quantification using the same protocol.

### TOC and TON

After removal of inorganic carbon by acidification with 1 mol  $\text{L}^{-1}$  HCl, sediment samples were dried at 40 °C and subsequently analyzed for total carbon and nitrogen with a Carlo Erba NA 2100 elemental analyzer. The samples were oxidized at 1100 °C and the oxidation products were transported by a carrier gas (He) through a reduction tube where NO<sub>x</sub> was reduced to N<sub>2</sub>. After removing water and halogens from the evolving CO<sub>2</sub> and N<sub>2</sub>, the gases were separated and quantified by a thermal conductivity detector. The relative standard deviation for the method was approximately 4.5%.<sup>20,21</sup>

## Results and Discussion

### Bulk organic composition of the sediments

The variability and contents of sedimentary PAHs are also controlled by the grain-size content and the origin of particulate organic matter of the sediments. Some insight on the surface sediment characteristics may be obtained from Table 1, which depicts the contribution of the fine fraction < 63  $\mu\text{m}$ , the content of total organic carbon (TOC) and C/N

ratios by weight. In general, the Manguaba and Mundaú lagoon compartments were near to entirely composed of fine organic-rich sediments with about 87 to 100% comprising of silt and clay. TOC concentrations from 2 to 4% reflected the material retainer potential in the lagoons. A larger contribution of terrestrial materials to the organic matter was found in the river-lagoon interfaces (Stations A-127, A-317, A-101, A-301, A-302), and exhibited C/N ratios about 13 to 21. The Mundaú and Manguaba lagoons of MMELS may be classified as highly organic-rich systems with C/N ratios varying from 7 to 10 in their central portion, suggesting the presence of autochthonous phytoplankton produced organic matter.

**Table 1.** TOC, C/N (by weight) obtained from the MMELS and PSR sediment

System	Site	Sample	Grain-size (%) < 63 $\mu\text{m}$	TOC / (%)	C/N
MMELS	Manguaba	127	64	1.36	11.5
		317	39	2.78	18.5
		101	52	0.73	10.7
		102	100	2.56	8.0
		104	100	3.8	9.6
		106	5	0.06	NA
		108	100	3.61	8.0
		110	100	3.88	9.1
		113	100	3.91	9.8
		116	100	3.79	9.7
		119	100	3.52	8.4
		122	87	4.33	9.1
	124	100	5.08	13.5	
	125	4.1	0.36	8.8	
	Channel	315	4	0.25	6.8
312		1	0.04	NA	
311		5	0.17	7.0	
309		24	0.82	7.8	
Mundaú	301	73	2.43	11.7	
	302	88	2.30	11.9	
	303	100	2.70	7.6	
	304	100	2.52	7.9	
	305	100	2.33	7.3	
	306	100	2.85	6.8	
	308	100	3.72	8.1	
PSR	Estuary	APS-1	66	0.92	11.5
		APS-2	52	0.54	9.0
		APS-3	45	0.38	9.5
		APS-5	79	1.09	10.9
	River	APS-6	17	0.65	21.7
		APS-7	49	2.34	26.0

In contrast, the PSR sediments exhibited a mixture of fine and large grained sediments and TOC values were by a factor of 3 to 5 lower than MMELS, except at the outlet of the sugarcane factory with TOC at 2.34% (APS 7). The C/N ratios at stations APS 6 and APS 7 were 21.7 and 26.0, demonstrating the presence of vascular plant material derived from the sugarcane effluents (*e.g.*, Vinasse). The estuarine sediments exhibited C/N ratios between 11 and 13, indicating the presence of phytoplankton and some terrestrial plant and/or mangrove materials. It is of a general consensus, that phytoplankton and its fresh derived detritus have typical C/N ratios by weight between 6 and 10, whereas vascular land plants have C/N ratios of 20 and greater.<sup>22</sup> However, the bulk C/N ratios cannot identify the exact nature of the composition of organic matter in the sediments. For example, C/N values of vascular plant remains between 30 and 40 may form part of the organic matter pool, but the bulk C/N signature remain at 15 when phytoplankton materials play a role. In general, the cellulosic land plants are better preserved, whereas the phytoplanktonic material is subject to enhanced degradation.<sup>23</sup> The predominance of fine organic-rich sediments with organic matter mainly derived from phytoplankton in MMELS, when compared with larger grained more organic-poor sediments with a higher contribution of terrestrial and/or mangroves materials in PSR, suggested that MMELS is more apt to degrade organic matter.

#### PAH concentrations

Quantitative results of PAH determination in sediments are shown in Table 2. Each system was subdivided. MMELS was divided into; 1) Manguaba lagoon, 2) Channel and 3) Mundaú lagoon. PSR was divided into; 1) Paraíba do Sul River and 2) Paraíba do Sul Estuary. The total PAH concentrations ( $\Sigma 16\text{PAH}$ ) in the sediments ranged from 2.9 to 84.0  $\mu\text{g kg}^{-1}$  in Manguaba lagoon and from 32.9 to 231.3  $\mu\text{g kg}^{-1}$  in Mundaú lagoon. In the Channel the concentration ranged from 7.53 to 35.1  $\mu\text{g kg}^{-1}$ . Despite the organic-rich nature of the MMELS sediments (*i.e.*, TOC 3-6% or more) and the presence of different anthropogenic sources, the data lie in the same range as observed in many previous studies of other Brazilian embayments such as Angra dos Reis (6.3-277.0  $\mu\text{g kg}^{-1}$ ),<sup>1</sup> São Sebastião (nd-257  $\mu\text{g kg}^{-1}$ )<sup>24</sup> and (20.4-200.3  $\mu\text{g kg}^{-1}$ ),<sup>25</sup> as well as, manifold other subtropical and temperate systems, such as the Seine River and estuary in France (4-36  $\mu\text{g kg}^{-1}$ ),<sup>3</sup> Gao Ping River in Taiwan (8-356  $\mu\text{g kg}^{-1}$ ),<sup>26</sup> Caspian Sea in Russia (6-345  $\mu\text{g kg}^{-1}$ ),<sup>13</sup> and Xiamen Harbor in China (98-309  $\mu\text{g kg}^{-1}$ ).<sup>27</sup>

In contrast to MMELS, the Paraíba do Sul Estuary values were higher ranging from 87.1 to 1380.0  $\mu\text{g kg}^{-1}$  and

in the upper two river sediments even attained 8513.8 and 9344.3  $\mu\text{g kg}^{-1}$ . The Paraíba do Sul Estuary results were in the same range as Tampa Bay in USA (200-4300  $\mu\text{g kg}^{-1}$ ),<sup>28</sup> Arcachon Bay in France (900-4100  $\mu\text{g kg}^{-1}$ ),<sup>4</sup> Daliao River in China (59.67-816.63  $\mu\text{g kg}^{-1}$ ),<sup>8</sup> Todos os Santos Bay (8-4163  $\mu\text{g kg}^{-1}$ ),<sup>29</sup> and Guanabara Bay in Brazil (91-8035  $\mu\text{g kg}^{-1}$ )<sup>30</sup> and (77-7751  $\mu\text{g kg}^{-1}$ ).<sup>11</sup> The highest PAH concentrations of the Paraíba do Sul River itself (Stations APS 6 and APS 7; Figure 1) were higher or in the same range found for Santos Bay (79.6-15389.1  $\mu\text{g kg}^{-1}$ ),<sup>31</sup> Patos Lagoon (37.7-11779.9  $\mu\text{g kg}^{-1}$ )<sup>32</sup>, and Rodrigo de Freitas Lagoon (405-11734  $\mu\text{g kg}^{-1}$ , including the alkylated PAH)<sup>33</sup> in Brazil, an elsewhere in the Persian Gulf Kuwait dominated by petroleum refineries (1300-17500  $\mu\text{g kg}^{-1}$ ),<sup>34</sup> Santander Bay in Spain (20-344600  $\mu\text{g kg}^{-1}$ ),<sup>35</sup> and Dar es Salaam in Tanzania (70.1-16474.3  $\mu\text{g kg}^{-1}$ ).<sup>36</sup>

In general, sediments may be classified as “highly contaminated” with total PAH concentrations beyond 500  $\mu\text{g kg}^{-1}$ , “moderately contaminated” at 250  $\mu\text{g kg}^{-1}$  to 500  $\mu\text{g kg}^{-1}$  of total PAHs, and “slightly contaminated” if total PAHs are below 250  $\mu\text{g kg}^{-1}$ .<sup>14,37</sup> All results observed in MMELS were below 250  $\mu\text{g kg}^{-1}$ . However, in PSR, four sites (including the two samples in the river) showed data higher than 500  $\mu\text{g kg}^{-1}$ .

With respect to the individual PAHs in the sediments, the composition was different between both systems. In the PSR, Flt and Py showed the highest concentrations at all sites, except for station APS-3 with high concentration of perylene. On the other hand, MMELS exhibited a distinct pattern for the biogenic PAH perylene, with high concentrations at all sites, except for sites A-312 and A-315 in the Channel, dominated by Phen, Flt and Py. The APS-6 and APS-7 sites (8513.76 and 9344.29  $\mu\text{g kg}^{-1}$ , respectively) in the Paraíba do Sul River located close to the point source of the industrial sugarcane processing plant (15 km upriver from the estuaries mouth) were governed by concentrations an order of magnitude higher, clearly indicating that its organic overloaded effluents (*e.g.*, Vinhasse) corresponded to the main PAH source of the river and, after dilution, also the estuary itself.

#### PAH source analysis

The PAH sources may be identified by individual PAH compound ratios based on the peculiarities in PAH composition and distribution patterns as a function of the emission sources.<sup>8,15</sup> The Ant/(Ant+Phen), BaA/(BaA+Chry), Flt/(Flt+Py), InP/(InP+BghiP) ratios have been applied to distinguish petrogenic and pyrogenic input.<sup>8,11,13,26,38</sup> These ratios are based on differences in heat of formation at the same molecular mass isomers. Pyrogenic

**Table 2.** PAH concentrations in MMELS and PSR sediments ( $\mu\text{g kg}^{-1}$ , dry wt.)

System	Site	Sample	Nap	Acft	Ace	Fluo	Phen	Ant	Flt	Py	BaA	Chry	BbF	BkF	BaP	InP	DBA	BghiP	$\Sigma 16\text{PAHs}$	Per
MMELS	Manguaba	127	ND	ND	ND	0.1	0.7	0.1	0.6	0.8	1.1	0.2	0.1	0.3	0.3	0.6	0.1	0.8	5.9	4.8
		317	ND	ND	ND	3.4	14.3	ND	13.6	11.2	2.3	4.9	ND	2.8	2.3	0.9	ND	2.9	58.4	6.4
		101	ND	ND	ND	0.1	0.5	0.1	0.3	0.2	0.3	0.2	ND	0.1	0.1	0.3	0.2	0.4	2.9	3.9
		102	ND	0.6	ND	1.0	8.1	0.7	11.3	17.5	1.1	1.0	0.5	1.3	1.3	0.5	ND	1.5	46.6	33.6
		104	ND	0.4	ND	1.1	9.9	1.3	15.1	17.2	1.9	3.2	2.8	3.1	2.5	1.5	0.1	4.1	64.0	103.7
		106	ND	ND	ND	0.7	1.1	0.7	1.0	ND	1.5	1.0	ND	0.9	0.1	1.5	0.8	2.1	11.4	30.2
		108	ND	0.4	ND	0.5	1.0	0.1	3.2	1.7	1.2	1.1	2.1	1.4	1.7	1.5	0.5	2.5	18.3	106.7
		110	ND	0.5	0.2	1.7	13.9	1.5	6.0	15.5	3.9	4.4	6.4	6.4	6.5	5.4	1.3	10.7	84.0	390.5
		113	ND	0.4	ND	0.5	0.4	0.0	1.2	1.5	1.1	1.0	2.0	1.2	1.7	1.4	0.3	2.3	14.6	44.0
		116	ND	ND	ND	0.1	0.8	0.1	1.5	1.4	0.5	0.2	ND	0.3	0.4	0.8	0.1	1.1	7.3	33.8
		119	ND	0.4	ND	0.5	0.3	0.0	0.2	0.4	0.7	0.6	1.3	0.7	0.9	0.9	0.1	1.4	8.0	12.5
		122	ND	ND	ND	2.4	6.7	1.2	1.9	ND	1.7	1.2	ND	2.2	0.7	1.5	1.2	2.3	23.1	15.8
	124	ND	0.5	ND	ND	0.5	0.0	0.5	0.6	1.0	1.0	1.6	1.0	1.5	1.1	0.4	1.6	10.9	11.6	
	125	ND	ND	ND	0.5	3.4	0.5	0.9	0.1	1.0	0.6	ND	0.5	0.2	1.2	0.4	1.1	10.4	7.0	
	Channel	315	ND	ND	ND	0.2	13.7	ND	4.5	3.8	0.2	0.9	ND	ND	ND	ND	0.0	ND	23.1	8.8
		312	ND	0.1	ND	0.4	7.8	0.1	8.9	11.1	1.5	1.3	ND	0.3	0.9	0.4	0.1	2.2	35.1	6.7
		311	ND	ND	0.3	0.3	2.2	0.4	0.7	0.0	1.1	0.4	ND	0.3	0.1	1.1	0.2	0.5	7.5	4.4
		309	ND	0.5	ND	0.6	2.9	0.1	3.4	2.7	2.3	3.0	3.0	2.8	3.1	2.0	ND	4.1	30.2	10.4
	Mundaú	308	ND	0.6	0.8	1.5	12.2	1.6	13.4	13.8	6.6	8.5	13.7	9.0	11.8	10.6	5.2	19.9	129.0	75.5
		306	ND	0.5	0.1	0.8	7.0	0.7	6.5	5.6	4.5	4.6	8.1	6.7	7.4	6.4	2.6	10.2	71.0	73.0
305		ND	0.5	0.1	0.8	6.5	0.5	7.5	3.9	3.2	3.7	6.3	5.2	4.5	4.4	0.9	7.3	54.6	107.6	
304		ND	0.5	0.1	0.8	3.1	0.4	0.6	6.0	2.5	2.6	3.4	2.7	4.2	1.9	ND	4.7	32.9	107.0	
303		ND	0.6	ND	1.1	22.4	1.6	ND	14.0	5.4	6.6	10.7	9.1	8.5	7.8	1.4	13.3	102.1	499.7	
302		ND	0.5	ND	0.9	11.9	1.1	12.1	11.1	4.1	5.4	7.0	6.1	5.8	5.0	1.8	9.2	81.3	65.4	
301		ND	1.7	0.6	2.6	37.0	4.5	49.8	29.1	16.7	11.6	13.3	11.3	16.7	12.8	2.0	22.1	231.3	207.3	
PSR	Estuary	APS-1	ND	3.6	ND	4.5	40.2	10.7	160.0	145.4	80.7	51.1	49.1	49.7	111.9	73.5	16.9	85.1	882.3	123.9
		APS-2	ND	1.7	ND	2.1	36.6	1.4	55.1	58.1	26.9	34.7	19.8	17.4	40.2	29.4	6.9	39.1	369.4	23.8
		APS-3	ND	0.4	ND	1.1	13.0	1.3	14.1	12.4	3.9	13.5	1.0	3.3	4.5	7.0	0.2	11.5	87.1	164.5
		APS-5	ND	1.9	0.3	4.0	30.8	11.0	234.4	184.6	132.1	148.4	22.7	96.1	189.2	121.9	21.2	181.4	1380.0	167.0
	River	APS-6	ND	44.1	ND	66.2	853.2	128.1	1618.6	1830.2	393.5	465.6	155.5	354.2	815.1	666.8	64.6	1058.0	8513.8	101.6
		APS-7	46.4	503.1	15.7	173.0	938.3	282.3	1813.9	3520.3	246.2	319.8	115.5	190.5	405.3	218.0	30.0	525.9	9344.3	80.8

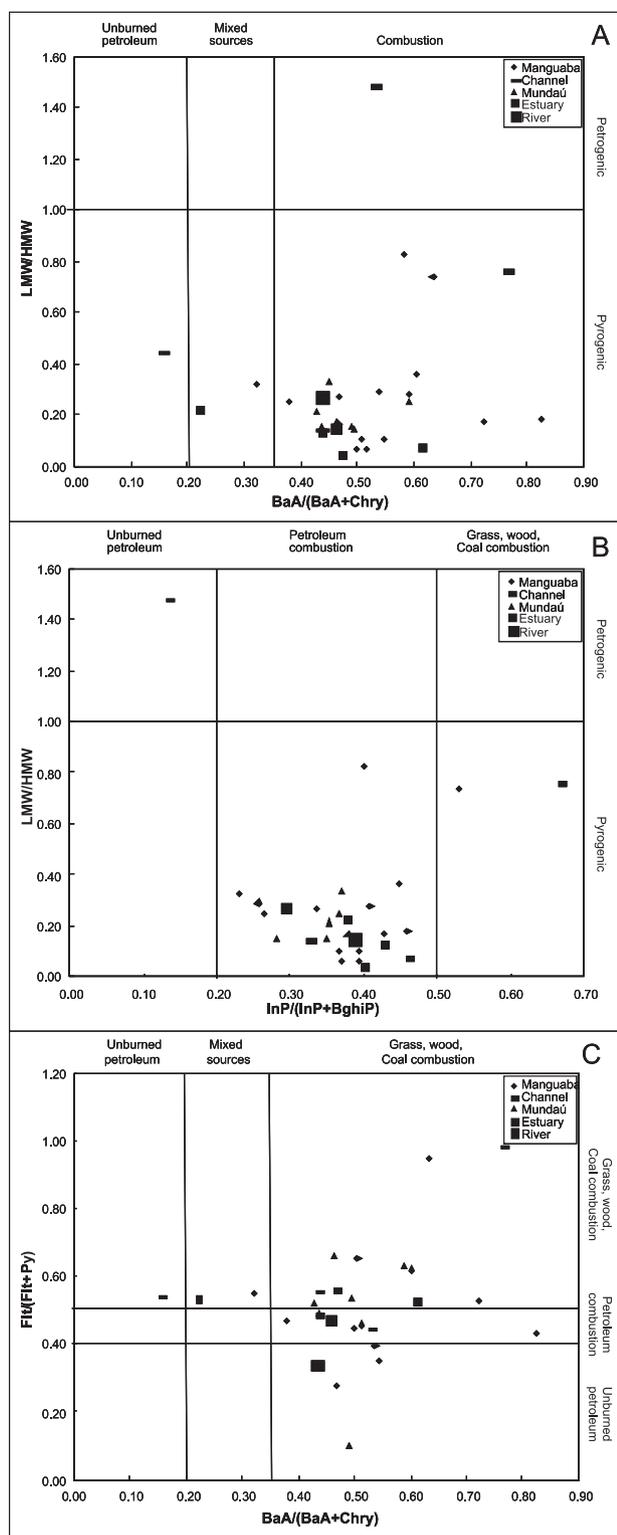
ND, not detected.

processes are fast reactions that form less stable isomers (the kinetic product). Diagenesis favors the most stable isomer (the thermodynamic product) by increasing the time of reaction.<sup>39</sup> Petrogenic inputs show  $\text{Ant}/(\text{Ant}+\text{Phen})$  values lower than 0.10 and pyrogenic inputs exhibit higher values.  $\text{BaA}/(\text{BaA}+\text{Chry})$  ratio of  $< 0.2$  suggests petrogenic input, and a ratio of  $> 0.35$  indicates pyrogenic processes, while a ratio between 0.2 and 0.35 is characteristic of combustion process.<sup>38</sup> Values of  $\text{Flt}/(\text{Flt}+\text{Py})$  ratios less than 0.4 correspond to petroleum pollution, and higher than 0.5 are characteristic of grass, wood or coal combustion.<sup>26</sup> Whereas,  $\text{Flt}/(\text{Flt}+\text{Py})$  ratios between 0.4 and 0.5 are more related to liquid fossil fuel combustion such as vehicle and crude oil. When  $\text{InP}/(\text{InP}+\text{BghiP})$  ratios show values lower than 0.20,

they highlight petroleum spill input; from 0.20 to 0.5 is characteristic of petrochemical fuel combustion and; values higher than 0.5 indicate grass, wood and coal combustion.<sup>26</sup> Petrogenic contamination is characterized by low molecular weight PAH predominance (LMW - two and three aromatic rings), while the high molecular weight (HMW - four, five and six rings) dominate in the pyrolytic origin. LMW/HMW ratios lower than 1 indicate pyrogenic contribution.<sup>14</sup>

In our study, PAH isomeric ratios from sediments indicated the combustion process as the main source.  $\text{BaA}/(\text{BaA}+\text{Chry})$  versus LMW/HMW ratios showed combustion and pyrogenic processes for PAHs in both systems, except at the Channel stations A-312 and A-315, the Manguaba lagoon station A-317 and at station APS-3 of

the Paraíba do Sul Estuary (Figure 2A). LMW/HMW *versus* InP/(InP+BghiP) showed pyrogenic sources originated by petroleum combustion, where only one sample indicated



**Figure 2.** PAH cross plots for: A) BaA/(BaA+Chry) *versus* LMW/HMW ratios; B) InP/(InP+BghiP) *versus* LMW/HMW ratios and; C) BaA/(BaA+Chry) *versus* FIt/(FIt+Py) ratios.

a petrogenic source (Figure 2B). On the other hand, BaA/(BaA+Chry) *versus* FIt/(FIt+Py) showed grass, wood and coal combustion for many sites, although BaA/(BaA+Chry) pointed to overall combustion (Figure 2C). These three ratios indicated that combustion is the main source of PAHs in these two Brazilian estuarine systems dominated by the sugarcane crop industry. Ant/(Ant+Phen) ratio indicated a petrogenic source for some sites, but this ratio is not recommended, as Ant usually is a low abundant peak in the chromatographic profile, thus leading to analytical errors and difficulties in quantification. The petrogenic contribution observed in some points of MMELS and PSR is less evident than found in Rodrigo de Freitas Lagoon,<sup>33</sup> located in the urban area of Rio de Janeiro City, Brazil. In general, no more than two PAH ratios are used to determine possible sources, as further ratios can lead to different and ambiguous interpretations.<sup>37</sup>

Perylene is the main biogenic PAH found in sediments. It is formed by diagenetic transformation of marine precursors<sup>40</sup> and it is thought to be produced through in situ conversion of perylenequinone pigment by fungi.<sup>41</sup> The perylene concentrations ranged from 4.8 to 499.7  $\mu\text{g kg}^{-1}$ . These values were in the same range as rivers and an estuary from Shanghai in China (nd-588  $\mu\text{g kg}^{-1}$ ).<sup>42</sup> The presence of perylene above 10% of  $\Sigma 16\text{PAH}$  has been indicated as an important natural PAH contribution.<sup>9</sup> However, perylene is also formed by pyrolytic processes and could predominate in polluted areas that have anthropogenic potential.<sup>32</sup> All sites of MMELS showed perylene concentration values higher than 10% of  $\Sigma 16\text{PAH}$ . In the Paraíba do Sul River (stations APS-6 and APS-7), the observed perylene concentrations were 80.84 and 101.55  $\mu\text{g kg}^{-1}$ , less than 10% of 8513.76 and 9344.29  $\mu\text{g kg}^{-1}$  of  $\Sigma 16\text{PAH}$ , respectively. The analogous perylene concentration pattern observed for all sites in this study could be explained by the natural origin of this compound. As the Per concentrations detected lied in the same range, it may be assumed that the early diagenetic transformations were similar in all studied areas, except at the Channel of MMELS, where dilution processes with seawater occur. PAHs from the areas are mainly derived from sugarcane burning and/or also from vehicle emissions.

## Conclusions

PAH concentrations for the studied sites were low in the Channel of MMELS, intermediate in Manguaba lagoon and high in Mundaú lagoon. The Paraíba do Sul estuary exhibited lower concentrations in comparison to its river sites (APS 6 and APS 7). In all, MMELS has lower concentrations in comparison to the PSR, which was

highly contaminated. PAH source analysis suggested the predominance of pyrogenic input in both systems. More than two criteria could be used, leading to the conclusion that the main PAH source in these two Brazilian estuarine-systems dominated by sugarcane crops is the combustion source. The PAH ratios also indicated a possible mixed combustion source, e.g., from petroleum, grass, wood and/or coal combustion. Emissions of vehicles and fishing boats are possible sources of petrogenic hydrocarbons. PAH ratios suggested that PAHs could be also produced by sugarcane burning.

## Acknowledgments

The authors acknowledge CNPq, the Brazilian Research Council, for financial support (Process No. 590002/2005-8) and fellowships. We also would like to thank all professors, particularly Paulo P. Medeiros from LABMAR-UFAL and Carlos E. Carvalho and Carlos E. Rezende from CBB-UENF, and the students and technical staffs from the POLCAMAR Project that contributed to this part of the work and Gertrud Spörl from ZMT-Bremen, Germany, that performed the TOC and TON analyses.

## References

1. Azevedo, D. A.; Gonçalves, M. L.; Silva, D. B.; *Environ. Forensics* **2007**, *8*, 245.
2. Gao, X.; Chen, S.; Xie, X.; Long, A.; Ma, F.; *Environ. Pollut.* **2007**, *148*, 40.
3. Fernandes, M. B.; Sicre, M. A.; Boireau, A.; Tronczynski J.; *Mar. Pollut. Bull.* **1997**, *34*, 857.
4. Baumard, P.; Budzinski, H.; Garrigues, P.; *Mar. Pollut. Bull.* **1998**, *36*, 577.
5. Countway, R. E.; Dickhut, R. M.; Canuel, E. A.; *Org. Geochem.* **2003**, *34*, 209.
6. Stout, S. A.; Uhler, A. D.; Ernsbo-Mattingly, S. D.; *Environ. Sci. Technol.* **2004**, *38*, 2987.
7. Cheollee, B.; Shimizu, Y.; Matsuda, T.; Matsui, S.; *Environ. Sci. Technol.* **2005**, *39*, 7402.
8. Guo, W.; He, M.; Yang, Z.; Lin, C.; Quan, X.; Wang, H.; *Chemosphere* **2007**, *68*, 93.
9. Readman, J. W.; Fillmann, G.; Tolosa, I.; Bartocci, J.; Villeneuve, J. P.; Cattini, C.; Mee, L. D.; *Mar. Pollut. Bull.* **2002**, *44*, 48.
10. Beg, M. U.; Saeed, T.; Al-Muzaini, S.; Beg, K. R.; Al-Bahloul, M.; *Ecotoxicol. Environ. Saf.* **2003**, *54*, 47.
11. Silva, T. F.; Azevedo, D. A.; Aquino Neto, F. R.; *J. Braz. Chem. Soc.* **2007**, *18*, 628.
12. Azevedo, D. A.; Santos, C. Y. M.; Aquino Neto, F. R.; *Atmos. Environ.* **2002**, *36*, 2383.
13. Tolosa, I.; Mora, S.; Sheikholeslami, M. R.; Villeneuve, J. P.; Bartocci, J.; Cattin, C.; *Mar. Pollut. Bull.* **2004**, *48*, 44.
14. Soclo, H. H.; Garrigues, P. H.; Ewald, M.; *Mar. Pollut. Bull.* **2000**, *40*, 387.
15. Zhang, J.; Cai, L. Z.; Yuan, D. X.; Chen, M.; *Mar. Pollut. Bull.* **2004**, *49*, 479.
16. Oliveira, A. M.; Kjerfve, B.; *Estuar. Coast. Shelf Sci.* **1993**, *37*, 575.
17. Souza, W. F. L.; Machado, E. C.; Knoppers, B. A. In *Estuarine Systems of the Latin American Region and Estuarine Systems of the Arctic Region: Carbon, Nitrogen and Phosphorous Fluxes*; Camacho-Ibar, V.; Wulff, F.; Dupra, V.; Smith, S. V.; Marshall-Crossland, J. I.; Crossland, C. J., eds.; Loicz Reports and Studies: Netherlands, 2002.
18. Knoppers, B. A.; Ekau, W.; Figueiredo, A. G.; *Geo-Mar. Lett.* **1999**, *19*, 171.
19. Carvalho, C. E. V.; Salomão, M. S. M. B.; Molisani, M. M.; Rezende, C. E.; Lacerda, L. D.; *Sci. Total Environ.* **2002**, *284*, 85.
20. Jennerjahn, T. C.; Ittekkot, V.; Klöpffer, S.; Adi S.; Nugroho, S. P.; Sudiana, N.; Yusmal., A.; Prihartanto; Gaye-Haake, B.; *Estuar. Coast. Shelf Sci.* **2004**, *60*, 503.
21. Baum, A.; Rixen, T.; Samiaji, J.; *Estuar. Coast. Shelf Sci.* **2007**, *73*, 563.
22. Meyers, P. A.; Leenheer, M. J.; Eadie, B. J.; Maule, S.; *Geochim. Cosmochim. Acta* **1984**, *48*, 443.
23. Meyers, P. A.; *Org. Geochem.* **1997**, *27*, 213.
24. Zanardi, E.; Bicego, M. C.; Miranda, L. B.; Weber, R. R.; *Mar. Pollut. Bull.* **1999**, *38*, 261.
25. Medeiros, P. M.; Bicego, M. C.; *Mar. Pollut. Bull.* **2004**, *49*, 892.
26. Doong, R.; Linn, Y. T.; *Water Res.* **2004**, *38*, 1733.
27. Ou, S.; Zheng, J.; Zheng, J.; Richard, B. J.; Lam, P. K. S.; *Chemosphere* **2004**, *56*, 107.
28. Sherblom, P. M.; Kelly, D.; Pierce, R. H.; *Mar. Pollut. Bull.* **1995**, *30*, 568.
29. Venturini, N.; Tommasi, L. R.; *Mar. Pollut. Bull.* **2004**, *48*, 97.
30. Meniconi, M. F. G.; Gabardo, I. T.; Carneiro, M. E. R.; Barbanti, S. M.; Silva, G. C.; Massone, C. G.; *Environ. Forensics* **2002**, *3*, 303.
31. Medeiros, P. M.; Bicego, M. C.; *Mar. Pollut. Bull.* **2004**, *49*, 761.
32. Medeiros, P. M.; Bicego, M. C.; Castela, R. M.; Del Rosso, C. D.; Fillmann, G.; Zamboni, A. J.; *Environ. Int.* **2005**, *31*, 77.
33. Stefens, J.; Santos, J. H. Z.; Mendonça Filho, J. G.; Peralba, M. C. R.; *J. Environ. Sci. Health, Part A* **2007**, *4*, 399.
34. Fowler, S. W.; Readman, J. W.; Oregione, B.; Villeneuve, J. P.; Mckay, K.; *Mar. Pollut. Bull.* **1993**, *27*, 171.
35. Viguri, J.; Verde, J.; Irabien, A.; *Chemosphere* **2002**, *48*, 157.
36. Gaspere, L.; Machiwa, J. F.; Mdachi, S. J. M.; Streck, G.; Brack., W.; *Environ. Pollut.* **2009**, *157*, 24.

37. Notar, M.; Leskovsek, H.; Faganeli, J.; *Mar. Pollut. Bull.* **2001**, *42*, 36.
38. Yunker, M. B.; McDonald, R. W.; Vingarzan, R.; Mitchell, R. H.; Goyette, D.; Sylvestre, S.; *Org. Geochem.* **2002**, *33*, 489.
39. Jeanneau, L.; Faure, P.; Montarges-Pelletier, E.; Ramelli, M.; *Sci. Total Environ.* **2006**, *372*, 183.
40. Bouloubassi, I.; Fillaux, J.; Saliot, A.; *Mar. Pollut. Bull.* **2001**, *42*, 1335.
41. Jiang, C.; Alexander, R.; Kagi, R. I.; Murray, A. P.; *Org. Geochem.* **2000**, *31*, 1545.
42. Liu, Y.; Chen, L.; Jianfu, Z.; Qinghui, H.; Zhiliang Z.; Hongwen, G.; *Environ. Pollut.* **2008**, *154*, 298.

*Received: November 3, 2009*

*Web Release Date: April 22, 2010*