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Occurrence and Sources of Priority Polycyclic Aromatic Hydrocarbons in Sediment Samples along the Aurá River (Northern Brazil)

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Resumo

Hidrocarbonetos aromáticos policíclicos (HAP) são compostos orgânicos gerados pela combustão incompleta de matéria orgânica e há dezesseis PAHs (16 USEPA-HPA) considerados prioritários em estudos ambientais por parte da Agência de Proteção Ambiental dos Estados Unidos. Os objetivos deste trabalho foram determinar as principais variações de origem e espaciais do 16-USEPA-PAHs nos sedimentos do rio Aura, Estado do Pará, norte do Brasil. Ao norte do rio Aurá existe um aterro sanitário, atualmente desativado, que funciou de forma descontrolada e irregular por cerca de 24 anos. PAHs foram identificados e quantificados em sedimentos de 10 locais dentro do rio e em sua foz. As amostras foram analisadas por HPLC/UV-Vis-DAD para avaliar o grau de contaminação. Concentrações totais de PAH (ΣPAHs) variaram de 3 824,21-15 693,91 ng g-1. Em geral, observou-se um gradiente de concentração. As amostras de sedimentos foram classificadas como altamente contaminadas (ΣPAHs> 500 ng g-1). Em comparação com outras áreas, as concentrações de PAH no rio Aurá são relativamente semelhantes aos lugares altamente industrializados e poluídos. As razões de alto peso molecular / baixo peso molecular de PAHs (LMW/ HMW), indicam uma origem pirolítica, que demonstrou-se terem sido gerados principalmente a partir da combustão de resíduos.
Palavras-chave: hidrocarbonetos aromáticos policíclicos, rio Amazonas, cromatografia líquida de alta performance

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds generated by the organic matter incomplete combustion and there are sixteen PAHs (16-USEPA-PAHs) considered as priority in environmental studies by the Environmental Protection Agency of the United States. The aims of this work were to determine the major source and spatial variations of the 16-USEPA-PAHs in the sediments of Aurá river, State of Pará, northern Brazil. North of the Aurá river exists a landfill site, currently disabled, which operated in an uncontrolled and irregular manner for about 24 years. PAHs were identified and quantified in sediment from 10 sites inside the river and in its mouth. The samples were analyzed by HPLC/UV-Vis-DAD to assess the degree of contamination. Total PAH concentrations (ΣPAHs) ranged from 3 824.21 to 15 693.91 ng g^{-1}. In general, a concentration gradient was observed. The sediment samples were classified as highly contaminated (ΣPAHs > 500 ng g^{-1}). Compared to other areas, PAH concentrations in Aurá river are relatively similar to highly industrialized and polluted places. The ratios of low molecular weight/high molecular weight PAHs (LMW/HMW), indicates a pyrolytic origin, which have shown to be mostly from waste combustion.
Keywords: Polycyclic aromatic hydrocarbons. Amazon river. High performance liquid chromatography

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1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) include toxic organic compounds that can be found in wastewaters and sewages released from industrial and/or urban areas. These wastewaters and sewages are sometimes discharged untreated to stream waters and it can be a problem to human health. Though PAHs occur naturally in the environment, generated by forest fires and volcanic eruptions, but the largest amount of PAHs is released into the environment by human activities (King-Heiden *et al.,* 2011). Anthropogenic PAHs result mainly from pyrolytic processes, especially the incomplete combustion of organic materials during industrial activities, domestic waste burning, incineration and vehicle emissions, and as well as from petroleum cracking and refining in petrochemical industries (Porte *et al.,* 2006).

Due to their toxic, carcinogenic, and mutagenic characteristics, sixteen PAHs have been identified as priority pollutants by the United States Environmental Protection Agency (16-USEPA-PAHs) (Kayal & Connell, 1995). Two classes of PAHs can be distinguished based on their properties and molecular weight: first, the "low-molecular-weight" PAHs with two or three benzene rings and "high-molecular-weight" PAHs with four to six aromatic rings (Pereira Netto *et al.,* 2000). Sediments are often contaminated with complex mixtures of toxicants and represent sinks and potential sources for lipophilic pollutants (Brack, 2003). Pollutants of concern in sediments include moderately to strongly lipophilic chemicals such as PAHs (Villeneuve *et al.,* 2000, Brack *et al.,* 2005).

The Aurá river is located in the metropolitan area of Belém (capital of the State of Pará, northern Brazil) between the latitudes 01º02'30"S and 01º30'00"S and the longitudes 48º10'00"W and 48º30'00"W. It has, approximately, a total length of 10400 m. The climate of the area is characterized as "equatorial humid", according to the Köppen classification. The annual rainfall average is 2000 mm and the temperature average is 35°C (Ferreira & Costa, 2006). It is an area characterized by a diversity of environmental problems, including deforestation, erosion, flooding and water contamination (Siqueira & Aprile, 2013). North of the Aurá river exists a landfill site, currently disabled, which operated in an uncontrolled and irregular manner for about 24 years and approximately 1.4 km from the Aurá River there are the lakes Bolonha and Black Water, sources of water supply to the metropolitan region of Belém (Siqueira & Aprile, 2013).

The flood plains and rivers of the Amazon region are very sensitive to environmental pollution, especially the basins near to the coastal zone which sinuous channels associated with a large sedimentary material load carried by the flood pulse contribute to the residual accumulation process in this area (Matos *et al.,* 2011). The Aurá river is an important hydric source to the lakes where the water is collected to supply part of the Belém city.

Near the studied river there are a landfill site, currently disabled. Waste degradation products, as well as substances produced by its burning are potential sources of PAHs and these contaminants have as main final destination the river beds (Lima, 2004), the Aurá river in this case. The regional climate, characterized by constant and intense rains, allows the pollutants migration like a shaped plume moving through runoff toward the local rivers (Bahia *et al.,* 2006).

The present study, to our knowledge, is the first one to assess information about PAHs in the Aurá river. The aim of this work, therefore, was to determine the major source and spatial variations of 16-USEPA-PAHs in the sediments of this watercourse.

2. MATERIAL AND METHODS

Sediments were collected in 2014 at ten locations along the Aurá river (Fig. 1) and at its mouth inside the Guamá river. At each location, sediment was collected from the surface (0–10 cm) with a Petersen grab sampler and thoroughly homogenized in inert materials. Sediments were freeze-dried (Liotop, model 1101) and amounts of 4 g of the freeze-dried sediment were doped with 50 µL of an internal standard (500 ng g^{-1} Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10 and Chrysene-d12 solution in n-hexane HPLC grade). The PAHs were extracted in ultrasonic bath (Bandelin Electronic, model TK 30 Sonorex) during 30 min and 6 mL of dichloromethane (DCM) HPLC grade was used as solvent. This process is based on the method 3550C described by USEPA (2007).

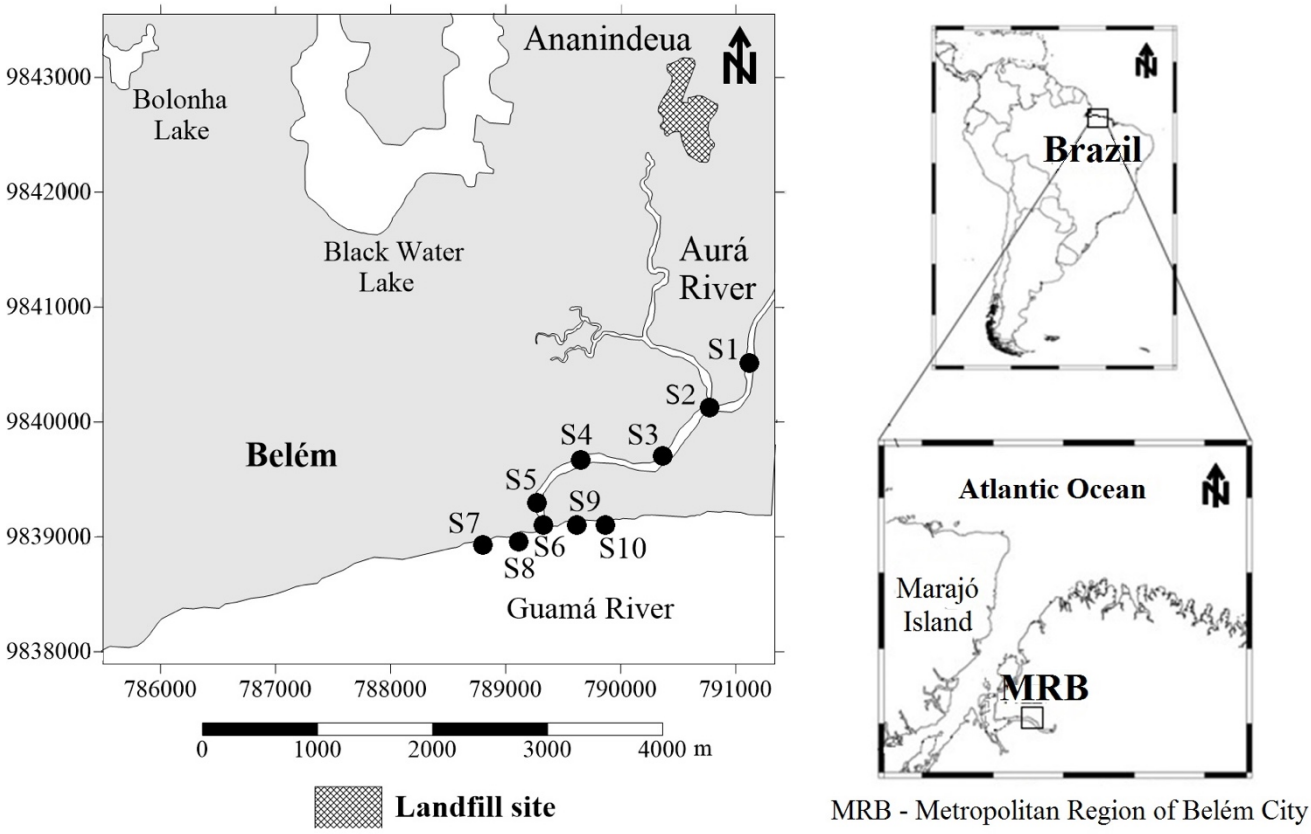

Figure 1. Aurá river map showing the 10 sampling sites near to the landfill and the lakes Bolonha and Black Water.

Empty extraction thimbles were subjected to the same extraction procedures and served as process controls. The extraction method recovery was calculated through values obtained for the internal standard. Afterwards the ultrasound extraction, the extract was cleaned up into a alumina/silica gel column using n-hexane and n-hexane/DCM solution (50:50; v:v) as mobile phase according to the method 3630C described by USEPA (1996).

The list of the 16 EPA priority PAHs was used, which often is taken as representative for the measurement of this substance class in environmental samples (Otte *et al.,* 2013). They are: naphthalene (Na), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flo), phenanthrene (Phe), anthracene (An), fluoranthene (Fl), pyrene (Py), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenzo[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP), indeno[1,2,3-*cd*]pyrene (IcdP).

Analysis of PAHs was carried out by high performance liquid chromatography with a diode array detector. HPLC equipment Dionex/Thermofisher Ultimate 3000 was used under the following operating conditions: C16 column (250 mm x 4.5 mm x 5 µm) from Acclaim; column temperature at 30°C; pump pressure between 2870-2980 psi; automatic injection of 20 µL; flow rate of 2 mL min^{-1}; elution system starting with 55% acetonitrile (ACN) and 45% Milli-Q water for 5 min, increasing to 85% ACN in 30 min, system stabilization in 85% ACN for 10 min, decreasing to 55% ACN and system stabilization in 55% ACN over 5 min. Readings were taken at wavelengths of 214, 254 and 263 nm.

External standard calibration curves were used for quantification of the extracts. Diagnostic rates of PAHs origin were used as tools for the interpretation of petrogenic or pyrolytic origin of these compounds (Gschwend & Hites, 1981, Budzinski *et al.,* 1997, Page *et al.,* 1999, Readman *et al.,* 2002, Yunker *et al.,* 2002). It can be calculated by the ratio of the sum of the low molecular weight PAHs total concentration (LMW) and the sum of high molecular weight PAHs total concentration (HMW) (Silva *et al.,* 2007).

3. RESULTS AND DISCUSSION

Recoveries for each individual PAHs studied in sediment samples were in the range of 99.4-100.3% (Table 1). According to the US Environmental Protection Agency (EPA) methods guidelines, acceptable recovery values should be in the range from 70 up to 130% (Ribani *et al.,* 2004). The calibration curves constructed were linear over the range of interest and correlation coefficients for the majority of compounds were greater than 0.99, indicating good performance of the chromatographic method. Good results were also observed for detection limits in the range 0.01 to 0.50 μg ml^{-1} and quantification limits 0.05 to 1.66 μg ml^{-1}.

Table 1. Concentration (ng g^{-1}) observed for each of the 16-USEPA-PAHs, ΣPAHs, LMW, HMW and the extraction method recovery percentage (%Rec) in the surface sediments of the 10 sampling sites along the Aurá river. ND = not detected.

16-USEPA-PAHs	SAMPLING SITES									
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Na	1 079.96	1 079.10	1 066.42	1 063.34	1 062.98	1 089.86	1 074.11	ND	1 082.82	1 152.86
Acy	1 444.76	1 442.43	ND	ND	ND	1 447.02	ND	ND	ND	ND
Ace	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Flo	999.87	998.68	998.02	ND	996.53	ND	ND	ND	ND	ND
Fhe	973.23	973.14	970.02	968.63	967.54	973.33	974.78	974.69	ND	ND
An	1 061.05	1 074.49	1 069.24	1 066.49	1 064.60	1 079.76	ND	ND	ND	ND
Fl	1 167.08	1 166.87	1 166.85	1 163.55	1 163.39	1 169.81	ND	1 167.49	ND	ND
Py	1 446.49	1 438.03	1 435.44	1 432.27	1 432.05	1 451.16	1 452.29	1 450.91	ND	ND
Chr	1 119.32	1 109.84	1 108.71	1 108.08	1 108.01	ND	1 144.05	1 143.44	ND	ND
BaA	1 092.22	1 089.65	1 089.07	1 089.06	1 088.82	ND	1 089.06	ND	ND	ND
BbF	146.95	148.69	147.41	151.85	153.08	ND	ND	ND	ND	ND
BkF	1 194.97	1 193.32	1 191.86	1 191.89	1 189.41	1 219.32	1 219.07	1219.37	1 189.82	1 213.93
BaP	ND	ND	1 335.77	1 334.05	ND	ND	ND	ND	ND	ND
DahA	1 290.99	ND	ND	ND	ND	ND	ND	ND	ND	ND
IcdP	1 400.59	1 399.99	1 396.71	1 396.24	1 396.10	1 475.42	1 477.05	1 468.22	1 399.34	1 457.41
BghiP	1 276.43	1 276.00	1 275.24	1 274.20	1 273.18	ND	ND	1 305.19	1 275.25	ND
LMW	5 558.86	5 567.85	4 103.70	3 098.46	4 091.64	4 589.98	2 048.88	974.69	1 082.82	1 152.86
HMW	10 135.05	8 822.40	10 147.06	10 141.19	8 804.05	5 315.72	6 381.52	7 754.61	3 864.41	2 671.35
ΣPAHs	15 693.91	14 390.25	14 250.76	13 239.64	12 895.69	9 905.70	8 430.40	8 729.30	4 947.23	3 824.21
%Rec	99.6	99.4	99.8	99.7	100.2	99.9	99.8	100.0	100.2	100.3

The concentration ranges of individual and total PAHs in sediment samples from Aurá river are shown in Table 1. The average total 16 PAHs concentration (ΣPAHs) from the 10 samples ranged from 3824.21 ng g^{-1} at sampling site 10 (S10) to 15693.91 ng g^{-1} at S1. In general, a concentration gradient was observed. The highest concentrations were detected in the northern portion of the Aurá river, close to the local landfill and a decreasing in the values of the ΣPAHs was detected toward the mouth of the Aurá river. The typical high rainfall index in the region may have significantly contributed to an increase in the river flow leading to PAHs distribution from the pollution source.

Samples may be classified as "highly contaminated" if total PAH concentrations (ΣPAHs) are higher than 500 ng g^{-1}, "moderately contaminated" at 250 ng g^{-1} to 500 ng g^{-1} ΣPAHs, and "slightly contaminated" if ΣPAHs are below 250 ng g^{-1} (Soclo *et al.,* 2000). Our data demonstrates that all the sediment samples along the Aurá river are classified as highly contaminated. On the other hand, the concentration of individual PAHs was also lower than the sediment quality criteria proposed by USEPA (1993) for **Flo** (3000 ng g^{-1}), **Ace** (2400 ng g^{-1}) and **Phe** (2400 ng g^{-1}). It is noteworthy that the sampling sites S3 and S4 were the only ones where there was observed the PAH **BaP** (1335.77 ng g^{-1} and 1334.05 ng g^{-1}), this compound is the most studied among the 16-USEPA-PAHs due to their extremely toxic properties. According to Garcia (2004), **BaP** is mainly found in areas close to runoff and mixed wastewater (domestic and industrial) discharge and close to the oil industry such as refineries and gasoline stations.

BkF and **IcdP** were observed in all studied sites. **Py** was the PAH with greater concentration detected, 1446.49 ng g^{-1} in S1. Among the PAHs with low molecular weight, the **Ace** was not detected in any of sample sites. While **Na** was observed throughout the sampling area, except in S8. Generally, there was a slight sinking in the individual light PAHs detection from S1 to S10; the total amount ranged from 5558.86 to 974.69 ng g^{-1}. All 10 high molecular weight PAHs were detected in at least one

sampling point. **IcdP** was observed in every studied site, representing an average of 23% of HMW. The average HMW from the 10 samples ranged from 2671.35 at S10 to 10135.05 ng g^{-1} at S1.

The analysis and comparison of the total sedimentary PAH levels in this study with other Brazilian sediments and worldwide data shows that the Aurá river has PAHs rates similar to highly industrialized and contaminated locations (Table 2).

To find the origin of the pollution in the Aurá river sediment samples, we used the LMW/HMW ratios criteria, as demonstrated in Fig. 2. All samples in this study yielded LMW/HMW ratios lower than 1, indicating a pyrolytic origin for the PAH contaminants (Silva *et al.,* 2007). Usually, no more than two criteria are used to determine possible sources, because using more criteria can lead to different and ambiguous interpretation of the results. Petrogenic contamination is characterized by the predominance of the low molecular weight while the high molecular weight PAHs dominates the pyrolytic PAH distributions (Soclo *et al.,* 2000, Magi *et al*., 2002). The probable origin of these contaminants, based on LMW/HML ratios, are emissions from the regular burning of solid waste (intentional or not) in the landfill close to the Aurá river.

Table 2. Concentration of total PAHs in selected Brazilian and worldwide sediments.

Region	Total PAHs (ng g^{-1})	Reference
Low Levels		
Chesapcake Bay-USA	1 - 180	Dickhut *et al.* (2000)
Lowland Region, Manaus-Brazil	13 - 58	Wilcke *et al.* (2003)
Laja Lake, Bío Bío-Chile	46 – 359	Queiroz *et al.* (2005)
Santana Harbor, Santana-Brazil	101 – 554	Lima (2009)
Intermediate Levels		
Caspian Sea, Europe	1 – 1 600	Tolosa *et al.* (2004)
Cocó River, Fortaleza-Brazil	721 – 2 233	Cavalcante *et al.* (2008)
Guanabara Bay, Rio de Janeiro-Brazil	83 – 2 427	Silva *et al.* (2007)
Todos os Santos Bay, Bahia-Brazil	8 – 7 221	Rocha *et al.* (2012)
High Levels		
Aurá River, metropolitan region of Belém city-Brazil	**3 824 – 15 694**	**This work**
Santos Estuary, São Paulo-Brazil	23 – 68 130	Bícego *et al.* (2006)
Lagoa dos Patos Estuary, Rio Grande do Sul-Brazil	38 – 11 780	Medeiros *et al.* (2005)
Portland Harbor, Portland-USA	860 – 20 644	Stout *et al.* (2001)
South Paraíba River, Rio de Janeiro-Brazil	182 – 35 082	Nudi (2005)

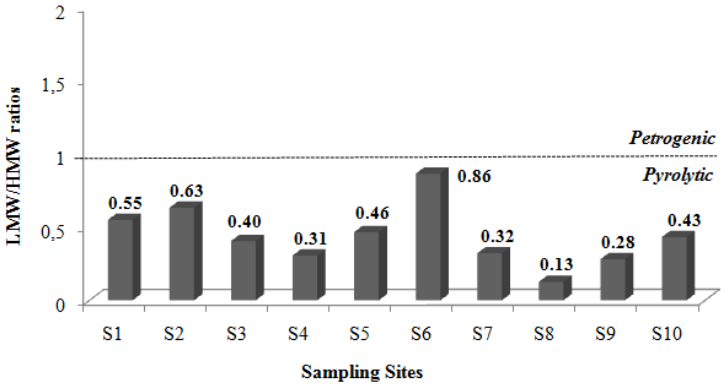

Figure 2. Plot of LMW *versus* HMW for sediment samples in the 10 sampling sites in Aurá river.

4. CONCLUSION

The present work represents the study of the distribution and origin of 16-USEPA-PAHs in surface sediments of the Aurá river, this is an important source of water supply to the metropolitan region of Belém city. For the sediment samples collected, ΣPAHs ranged from 3824.21to 15693.911 ng g^{-1} and are dominated by higher molecular weight compounds.

Furthermore, based on selected PAH ratios, it was observed that sediments present a dominant pyrolytic inputs. Therefore, the results suggest that PAHs in the Aurá river study area are derived, primarily, from burning of solid waste (intentional or not) in the landfill. The values found in this study suggest an important environmental impact and possible toxic effects on organisms inhabiting the sediment along the sampling grid, it shall be investigated in further studies. Compared to other urbanized areas worldwide, the measured PAH content of the Aurá river would indicate it to be highly contaminated.

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