Article

Polycyclic Aromatic Hydrocarbons in Superficial Sediments of the Negro River in the Amazon Region of Brazil

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Polycyclic aromatic hydrocarbons (PAHs) were identified and quantified in samples of superficial sediments of the Negro River, in the Amazon region of Brazil, through analyses performed by GC/MS. Total PAH concentration that includes parent and alkylated PAHs ranged from 6.5 to 5348 ng g⁻¹ of dry weight. The Σ16 PAHs prioritized in environmental studies by the U.S. Environmental Protection Agency (USEPA) ranged from 5.6 to 1187 ng g⁻¹. The most contaminated places were those where muddy sediments were found, with the highest concentrations of organic matter, carbon and total nitrogen. The priority PAHs with high molecular weight represented 70% of the total abundance and showed that the main source of contamination of the sediments was pyrogenic. However, petrogenic PAHs coming from oil and derivatives input is also an important contamination source to be considered.

Keywords: Negro River, sediment, Amazon, PAHs

Introduction

The polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants with approximately 100 different types distributed in the environment.[1] These compounds are formed during the thermal decomposition of organic molecules with the subsequent recombinations.[2] Although PAHs may also be formed from natural sources, the burning of fossil fuels and the residues from industrial activities, in addition to chronic or accidental introduction of oil and its derivatives, contribute to their occurrence in the environment. Therefore PAHs have become an important class of xenobiotics accumulating in the soil and sediments.[3-6] The natural source can be associated to short term diagenetic degradation and to a direct biosynthesis by organisms.[7-9]

PAHs are classified as persistent toxic substances; even in low concentrations, they may jeopardize human health as well as the environment.[1] The U.S. Environmental Protection Agency (USEPA) has classified a group of 16 individual PAHs as primary pollutants due to their toxicity, mutagenicity, and carcinogenicity.[10-12] Among these 16 primary pollutant PAHs, seven are considered to be carcinogens: chrysene, benzo(a)anthracene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, benzo(b)fluoranthene, and benzo(k)fluoranthene.[13,14]

By analyzing the profiles of the PAHs found in an environmental matrix, it is possible to infer the main sources of these compounds (pyrolytic, petrogenic or diagenetic) because of the different PAH distribution pattern. For example, the low molecular weight (LMW) PAHs with 2 to 3 aromatic rings are predominant in petrogenic sources. The PAHs of high molecular weight (HMW), i.e., those with four to six aromatic rings, are most important in pyrogenic sources.[15] Some PAH isomers ratios can also be used to evaluate the sources.[16] However, those ratios should be used with caution, as their values may change during the environmental fate of these compounds. PAH distribution

in the environment are influenced by the different factors such as physicochemical properties of some PAH, and chemical or biological reactivity, that can modify the original composition of the source.[17-19]

In Brazil, the studies concerning the presence and accumulation of environmental pollutants have taken place mainly in the southeast area; in the north region, such studies are only incipient. In the rivers of the Amazon region, a few observations are mentioned in the literature indicating high concentrations of mercury,[20] the influence of the organochlorine insecticide DDT on aquatic animals and people living by the rivers[21] and the contamination of an aquifer by oil hydrocarbons.[22] For research studies concerning the presence of PAHs in the Amazon region, there are just few reports of studies carried out in the atmosphere,[23] in a dry land environment, and in flooded forests ("igapós") of the Amazon basin.[8,9,24] In the Amazon State, the Negro River, which flows along the edge of the Manaus city, has several ports, shipyards and petrol stations due to intense navigation, activity that has great economic importance for the region. This activity can contribute to the input of PAH in the environment. Thus, studies concerning the presence and accumulation of these compounds in sediment are important to mitigate environmental impacts and reduce the damage to human health.

With those facts in mind, this work aimed to determine the concentration and profile of PAHs in samples of superficial sediments of different regions of the Negro River as well as to indicate the main sources contributing to the entrance of those compounds into the environment.

Experimental

Methodology

The Negro River, located in the Amazon State of Brazil, is the largest tributary stream of the left bank of the Amazon River, with a length of 1.7 km and drains an area corresponding to 10% of the Amazon basin. Its formation is influenced by the weathering processes of sandy soils of the Central Amazon basin. The Negro River is characterized by dark waters, nutrient-poor sediments, significant quantities of dissolved humic substances, and an acidic pH, with values between 3.8 and 4.9.[20,25] Two different hydrologic seasons characterize the region: the dry period (from May to October) and the rainy season (from November to April). During the dry season, the river water level was once verified to be only 1 meter above sea level, whereas during the rainy season, that level was verified to be 29.97 meters above sea level.[26]

This study was carried out in three navigable regions of the Negro River (Figure 1, Table 1), encompassing six different localities: (*i*) close to the Tupé Sustainable Development Reserve (TR); (*ii*) the mouth of the São Raimundo basin (SR), modern Manaus port (MM) and Panair port (PA) located on the left bank and Iranduba (IR) on the right bank of the river; (*iii*) Ceasa port region (CE). The TR region is far from the Manaus urban center and is surrounded by native vegetation. In SR, domestic sewage from the São Raimundo upland stream and the activities of small fishing vessels are found. The sampling sites in MM and PA are located in the urban center of the Manaus city, in the vicinities of street markets with commercial activities and the presence of small, medium, and large ships. In IR, a region encircled by grasses, the influence of vessel activity is smaller, and there is no urban activity. The CE region is characterized by anthropic commercial activities, the presence of vessels of small and medium sizes and proximity to the Manaus industrial sector.

Sample collection

Three superficial sediment samples were taken in each locality during the period of August, October, and November, 2012 (regions 2 and 3) and May, 2013 (region 1) (Table 1). Samples were taken with the help of a stainless steel Van Veen dredger, with an area of 26 × 15 cm. The samples were kept at the temperature of −20 °C and then submitted to freeze-drying process for a period of 48 h.

Physicochemical analyses of the sediment

The lyophilized samples were used to determine granulometry by the pipetting dispersion method. The content of organic carbon (OC) was determined by organic matter oxidation with potassium dichromate in a sulfuric medium such as the method proposed by Walkley-Black.[27] To determine organic matter (OM), OC concentration was multiplied by 1.724. This factor was used because carbon contributes 58% to the mean composition of humus. The concentration of total nitrogen (TN) was determined following the procedure developed by Kjeldahl.[27] The results are presented in percentage.

Quantitative analysis of the polycyclic aromatic hydrocarbons (PAHs)

Sample extraction

The extraction procedure and the purification and separation methods used in the sediment samples were based on the United Nations Environmental Program[28] with
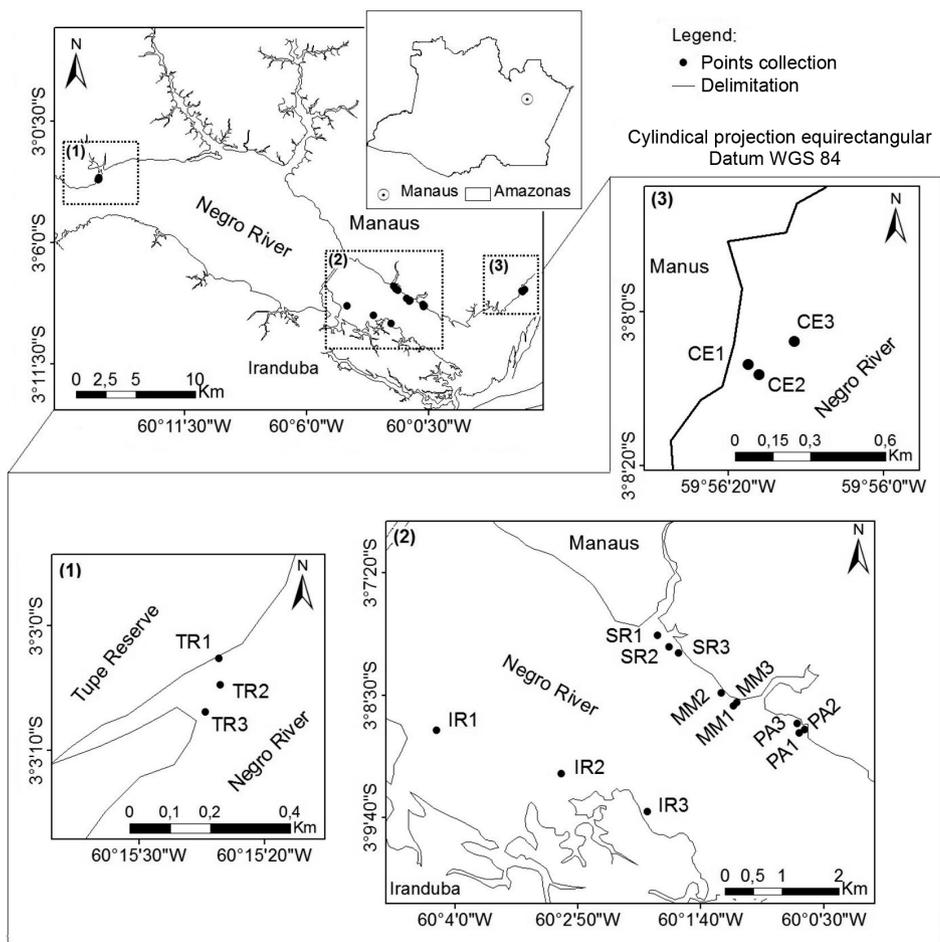
Figure 1. Sampling sites of superficial sediment in Negro River: (1) Tupé Reserve (TR), (2) São Raimundo basin mouth (SR), Modern Manaus port (MM), Panair port (PA) and Iranduba (IR), and (3) Ceasa port region (CE).

Table 1. Identification of the superficial sediment sampling sites

Region	Sampling site	Geographical position	Depth / m	Period (month/year)	Locality
	TR1	S 03°03'02.6" W 060°15'24.0"	4.62	May/2013	
1	TR2	S 03°03'04.7" W 060°15'23.9"	1.57	May/2013	Reserve Tupé
	TR3	S 03°03'06.9" W 060°15'25.1"	0.78	May/2013	
	SR1	S 03°07'55.2" W 060°02'05.3"	7.31	Aug/2012	
	SR2	S 03°08'05.45" W 060°01'53.02"	3.5	Oct/2012	São Francisco basin
	SR3	S 03°08'01.55" W 060°01'58.30"	2.51	Nov/2012	
	MM1	S 03°08'34.88" W 060°01'20.30"	9.83	Aug/2012	
	MM2	S 03°08'35.5" W 060°01'21.4"	2.77	Oct/2012	Manaus Moderna port
	MM3	S 03°08'28.1" W 060°01'28.9"	2.11	Nov/2012	
2	PA1	S 03°08'49.2" W 060°00'42.4"	11	Aug/2012	
	PA2	S 03°08'46.64" W 060°00'40.50"	7.74	Oct/2012	Panair port
	PA3	S 03°08'43.65" W 060°00'44.49"	2	Nov/2012	
	IR1	S 03°09'36.2" W 060°02'10.8"	7.28	Aug/2012	
	IR2	S 03°09'14.2" W 060° 02'59.8"	1.02	Oct/2012	Iranduba
	IR3	S 03°08'49.9" W 060°04'10.8"	1.36	Nov/2012	
	CE1	S 03°08'06.7" W 059°56'17.4"	6.38	Aug/2012	
3	CE2	S 03°08'08.15" W 059°56'16.04"	3.36	Oct/2012	Ceasa port
	CE3	S 03°08'04.0" W 059°56'11.2"	2.72	Nov/2012	

adaptations for studying environmental contaminants.[29] Amounts of 25 g of the sediment samples were used to extract the PAHs in a Soxhlet apparatus for 8 h using hexane/dichloromethane J. T. Baker, (Center Valley, PA, USA) (1:1, v/v). The solvent was concentrated in a rotary evaporator to a volume of 1 mL. The extract was fractionated by adsorption in an alumina column with silica gel when the aliphatic hydrocarbons were separated with 10 mL of *n*-hexane (fraction 1) and the PAHs (fraction 2) with 15 mL of dichloromethane/*n*-hexane 3:7 (v/v). Fraction 2 was concentrated in a rotary evaporator to a volume of 1 mL. Each fraction was analyzed by gas chromatography/mass spectrometry (GC/MS).

Conditions of the GC/MS

The analyses were performed using a gas chromatograph model 6890 attached to a mass spectrometer model 5973N (GC/MS) both pieces of equipment from the Agilent Technologies (Santa Clara, CA, USA). For the separation of the compounds, a capillary column (30 m × 0.25 mm, 0.25 μm film thickness) HP5MS (also from Agilent Technologies) was used. The temperature ramp for the analyses of the PAHs started at 40 °C with an increase in the warming rate from 20 °C up to 60 °C and at 5 °C min^{-1} up to 290 °C, where the temperature was held for 5 min, then increased at 10 °C min^{-1} up to 300 °C, where the temperature was kept constant for 10 min. Helium gas was used as the carrier. Acquisition of data was carried out using the selected ion monitoring (SIM). A volume of 1 μL of each sample was injected using the splitless method. The individual identification of the compounds was based on their retention time in comparison with those of the standards and on the ratio mass to charge (*m/z*) of the quantitation ion of each compound.

Internal standards and method validation

The PAH standards used as surrogates were the following: naphthalene-d$_{10}$, acenaphthylene-d$_{10}$, phenanthrene-d$_{10}$, chrysene-d$_{12}$, and perylene-d$_{12}$ from AccuStandard (New Haven, CT, USA). The recovery of the surrogate standards for all the samples ranged from 80 to 120% and correction was applied. The limit of detection (LOD) of the analytical method for the analyzed compounds was between 1.00 to 3.70 ng g^{-1}. The analytical curve was determined through the injection of the reference standards in at least five different concentrations. The monitored PAHs were: naphthalene (Nap), methylnaphthalene (Met-Nap), ethylnaphthalene (Etil-Nap), dimethylnaphthalene (Dimet-Nap), trimethylnaphthalene (Trimet-Nap),

acenaphthene (Ace), acenaphthylene (Acft), biphenyl (Bif), dibenzothiophene (DBT), methyldibenzothiophene (Met-DBT), dimethyldibenzothiophene (Dimet-DBT), anthracene (Ant), phenanthrene (Phe), methylphenanthrene (Met-Phe), fluorene (Fluo), methylfluorene (Met-Fluo), dimethylfluorene (Dimet-Fluo), fluoranthene (Flt), methylfluoranthene (Met-Flt), retene (Ret), pyrene (Py), methylpyrene (Met-Py), chrysene (Chry), methylchrysene (Met-Chry), dimethylchrysene (Dimet-Chry), benzo(a) anthracene (BaA), benzo(a)pyrene (BaP), benzo(e)pyrene (BeP), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(j)fluoranthene (BjF), benzo(c)phenanthrene (BcPhe), benzo(g,h,i)perylene (BghiP), benzo(b)chrysene (BbChry), dibenzo(a,h)anthracene (DBA), perylene (Per), indeno[1,2,3-cd]pyrene (InP) and coronene (Cor).

Data analysis

Individual parent and alkylated PAHs are listed in Table 3 as well as their sum (total $\sum$PAHs) and PAHs determined as priority by USEPA (Nap, Ace, Acft, Fluo, Phe, Ant, Flt, Py, BaA, Chry, BbF, BkF, BaP, InP, DBA, BghiP = $\sum$16PAHs).

Application of the diagnostic ratio (DR) index among PAHs

To indicate the main source of contamination, the following diagnostic ratios (DRs) were used: ratio of the low molecular weight PAH (Nap, Ace, Acft, Fluo, Ant and Phe = LMW) and high molecular weight PAH (Flt, Py, Chry, BaA, BaP, BbF, BkF, BghiP, DBA and InP = HMW) (LMW/HMW); between pairs of the isomers Flt and Py (MW 202) (Flt/[Flt + Py]), pairs of the isomers BghiP and InP (MW 276) (InP/[InP + BghiP]); relationship between the isomers 202 and the same alkylated C1Py (C$_0$/[C$_0$ + C$_1$] Flt/Py) and the sum of the parent PAHs with masses 128 (Nap), 178 (Ant, Phe), 202 (Flt, Py) and 228 (Chry, BaA) divided by these parent PAHs plus their related alkyl PAHs (Met-Nap, Etil-Nap, Dimet-Nap, Trimet-Nap, Met-Phe, Met-Flt, Met-Py, Met-Chry and Dimet-Chry) (Par/[Par + Alkyl]). The correlations between LMW/HMW *versus* InP/ (InP + BghiP), C0/[C0 + C1]Flt/Py and Par/(Par + Alkyl) were performed respectively and Flt/(Flt + Py) *versus* InP/ (InP + BghiP), C0/[C0 + C1]Flt/Py and Par/(Par + Alkyl) were also used with the same objective.[16,30-33]

Results and Discussion

Physicochemical composition of the superficial sediments

The data concerning the physicochemical aspects of the samples taken from the Negro River sediments are shown

in Table 2. A general result was that the sediment samples were essentially sandy (84.30 to 98.90%) excepting the SR1, PA1, PA2, CE1, CE3, and the three sites in Iranduba (IR), that presented predominance of mud (37.70 to 83.10%). Most of the sampling station showed low levels of OM, OC, and TN (Table 2), such as presented in literature data[20] that showed Negro River sediments as sandy and poor in nutrients. Sites situated along the Manaus city shore (SR1, CE3, CE1 and PA2) have heavy port activity and showed the highest concentrations of OM (6.23 to 11.06%), OC (3.62 to 6.43%), and TN (0.36 to 0.43%). These results may be associated with the entrance of organic matter (macro- and micronutrients) from several anthropic activities in that urbanized region. In addition, most of the watercrafts anchored at the river shore do not exhibit sewage treatment systems and can contribute with sewage to sediment. In the SR region, the sample collecting sites were at the São Raimundo basin mouth, one of the largest urban tributaries and receptors of domestic sewage in the Manaus city. This environment has already been classified as showing low levels of dissolved oxygen with values close to anoxia,[34] indicating the consumption of oxygen by aerobic bacteria of fecal origin. The amount of domestic sewage has a significant influence on the levels of organic carbon in the sediments, causing structural and quality alterations.[35,36] Two sampling sites in the Iranduba region (IR2 and IR3) also showed, respectively, considerable OM concentrations (4.36 and 4.1%), OC (2.54 and 2.39%), and TN (0.21 and 0.20%) (Table 2), most likely due to the verified entrance and deposition of plant material at those sample collecting sites. This material, after encountering the processes of leaching, conditioning, and fragmentation, makes nutrients available to the sediment.[37] The results indicate that the places with predominance of mud structure tend to store the largest concentrations of organic matter and nutrients, mainly when compared to the other sites, such as SR2, MM1, MM2, MM3, and PA3. These places,

Table 2. Physicochemical characterization of the superficial sediment samples from the Negro River, Amazon, Brazil

Region	Sampling site	Sand	Mud	OC / %	OM	TN
1	TR1	98.00	1.90	0.01	0.02	0.06
	TR2	98.50	1.50	0.01	0.01	0.06
	TR3	98.90	1.10	0.01	0.02	0.06
2	SR1	17.50	82.50	6.43	11.06	0.43
	SR2	94.50	5.50	0.09	0.15	0.04
	SR3	88.70	11.40	0.63	1.08	0.06
	MM1	97.40	2.60	0.11	0.18	0.06
	MM2	96.30	3.80	0.10	0.18	0.05
	MM3	94.10	5.90	0.40	0.69	0.05
	PA1	62.30	37.70	1.61	2.77	0.17
	PA2	45.10	54.90	3.62	6.23	0.36
	PA3	94.70	5.40	0.06	0.10	0.04
	IR1	26.00	74.00	0.17	0.30	0.09
	IR2	12.20	87.80	2.54	4.36	0.21
	IR3	20.70	79.30	2.39	4.10	0.20
3	CE1	20.50	79.50	4.55	7.82	0.34
	CE2	84.30	15.70	0.86	1.49	0.07
	CE3	17.00	83.10	4.80	8.25	0.30

notwithstanding the intense anthropic activity because of the port activity, showed low concentrations of OM, OC, and TN and sediments predominantly sandy in texture (> 84%) (Table 2).

PAH concentrations in superficial sediments

The concentration of the individual PAHs and the total concentration *per* sampling sites (total $\sum$PAHs, $\sum$16PAHs, and alkylated PAHs) are shown in Table 3. The concentration of total $\sum$PAHs *per* sampling station varied between 6.5 and 5348.3 ng g^{-1} of dry weight. The concentration of USEPA priority $\sum$PAHs varied between 5.6 and 1187 ng g^{-1}, and alkylated PAHs varied between 13.5 and 3780 ng g^{-1} (Figure 2).
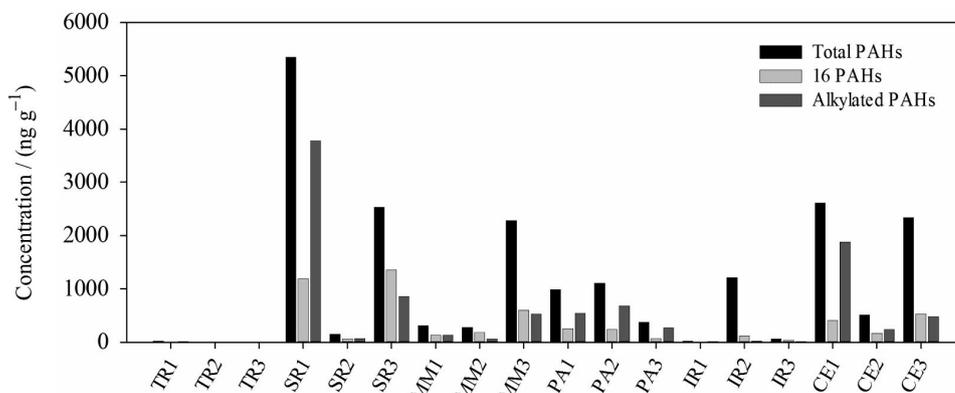

Figure 2. Polycyclic aromatic hydrocarbon (total PAH) concentrations, priority PAH according to USEPA ($\sum$16 PAHs) and alkyl-substituted PAHs (alkylated PAHs) in superficial sediments of the Negro River, Manaus, AM.

Table 3. PAH concentrations (ng g^{-1} of dry weight) in superficial sediments of the Negro River, Amazon, Brazil

Region	Site	Nap	Etil-Nap	Met-Nap	Dimet-Nap	Trimet-Nap	Bif	DBT	Met-DBT	Dimet-DBT	Ace	Acft	Ant	Phe	Met-Phe	Dimet-Phe	Fluo	Met-Fluo	Dimet-Fluo	Flt	Met-Flt	Py
1	TR1	9.1	nd	2.3	5.5	3.2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	2.5	nd	nd	nd	nd
1	TR2	nd	nd	nd	Nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
1	TR3	6.5	nd	nd	Nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2	SR1	169.2	34.8	64.3	165.7	663	18.4	17.5	87.1	196.6	nd	3.1	9.5	187.5	590.9	860.2	22.2	198.6	426.8	109.1	66.9	238.7
2	SR2	16.4	nd	2.2	3.6	7.2	2.2	nd	3.4	5.5	nd	nd	nd	5.2	11.5	15.3	nd	nd	6.4	5.6	2.6	8.4
2	SR3	178.8	13.7	49.7	57.5	123.8	9.3	8.4	31	50.1	4.5	4.2	9.7	76	112	125.4	7.9	26.7	63.5	170.9	49.7	153.1
2	MM1	19.5	nd	4.1	8.4	25.1	2.2	nd	4	7.7	nd	nd	nd	8.3	17.1	24.2	nd	5.4	13.3	16.1	6.1	18.4
2	MM2	19.6	nd	1.5	Nd	2.2	2.8	nd	1.6	3.1	nd	nd	nd	7.4	9.9	12	2.8	nd	4.4	30.9	5.5	27.6
2	MM3	28	4.7	7.5	16.5	73.7	2.8	2.1	19.5	45.6	nd	nd	2.8	17	69	134	2.8	19	58.9	18.2	13.3	26.3
2	PA1	49.2	6.8	17.4	28.9	84.4	5.8	3	16.1	35.9	nd	nd	2.7	25.3	68.9	115.2	3.1	19.4	50.3	24.7	14.2	33.2
2	PA2	11.3	7	11.6	27.8	119.2	3.4	3.2	19.8	47	nd	1.8	1.8	23.2	83.9	154.1	3.5	19.8	80.9	31.6	16.3	34.8
2	PA3	13.7	4.2	6.3	20.2	57.9	nd	nd	6.9	13.3	nd	nd	nd	10.5	33.3	51.6	1.6	12.7	32.6	7.3	4.7	14.4
2	IR1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	2.8	5.9	5.8	nd	nd	1.9	2.8	nd	nd
2	IR2	53.1	nd	nd	nd	nd	5.3	nd	nd	nd	nd	nd	nd	2.7	4.8	6.4	nd	nd	2	3.9	nd	6.1
2	IR3	22	nd	nd	nd	nd	1.9	2.4	nd	nd	nd	nd	2	nd	3.6	4.4	nd	nd	2.2	3.4	nd	5.3
3	CE1	69.2	50.3	98.8	204.7	301.5	16.8	8.7	34.6	53.3	nd	3.9	3.9	88.3	261.6	334.1	16	73.5	104.9	26.8	30.4	47.6
3	CE2	28.1	nd	2	6.5	29.2	nd	nd	9.1	20.1	nd	nd	nd	8.7	27.3	54.1	nd	3.9	27.4	13.4	7.7	16.4
3	CE3	28.3	3.8	5.3	13	78.4	1.9	2.4	18.9	44.5	nd	nd	2	16.7	61.9	103.4	2.8	22	52.3	16.3	12.2	22.1

Region	Site	Met-Py	Chry	Met-Chry	Dimet-Chry	BaA	BbF	BjF	BkF	BeP	BaP	BcPhe	Per	InP	DBA	BbChry	BghiP	Cor	ΣPAH (with Per)	ΣPAH (without Per)	Σ16PAH	ΣPAH alkylated
1	TR1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	22.6	22.6	9.1	13.5
1	TR2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
1	TR3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	6.5	6.5	6.5	nd
2	SR1	89.4	135	168.6	168.1	24.3	26.5	12.1	13.6	107.6	59	2.8	74.5	60.6	16.2	4.6	112.9	47.8	5348.3	5273.8	1187	3780.9
2	SR2	3.6	5.6	5.5	3.6	2.1	nd	nd	nd	5.3	4.3	nd	7.1	3.4	1.1	nd	4.4	1.3	145.5	138.4	56.4	70.4
2	SR3	44.4	113.6	72.9	33.7	75	54.2	20.8	25.3	142.1	168.1	4.3	68.1	140.8	38.6	24.5	133.3	26.2	2528.5	2460.5	1354	854
2	MM1	5.7	14.5	7.7	3.3	11.3	4.9	2.2	2.4	11.3	14.7	nd	7.9	10.2	3.2	1.9	9.3	1.3	307.4	299.5	133	132
2	MM2	5.6	19.6	8.9	3.1	10.3	5.6	3.1	3.3	19.1	21	nd	7.4	16.8	4.3	2.3	16	2	280.3	272.9	182	57.7
2	MM3	15.7	16.6	24.9	25.9	6.4	2.7	1.8	2	12.9	4.2	nd	1017.6	194.6	65.9	8.5	213.5	54.5	2283.4	1265.8	601	528
2	PA1	17.6	23.8	42.8	21.4	10.4	5.6	3.2	3.4	23.1	17.5	nd	90.7	18.9	5.7	1.4	26.4	11.1	983.4	892.7	250	539.2
2	PA2	25.1	27.3	41.2	22.8	10.9	8	2.3	2.6	23.7	22.4	nd	108.5	21.6	5.3	2.5	25.6	7.4	1103.9	995.5	232	676.4
2	PA3	7.5	6	10.5	4.3	2.3	1.6	nd	nd	5.4	4.6	nd	18.7	4.3	1.1	nd	4.8	1.8	376.8	358.2	72.1	265.9
2	IR1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	22.8	22.8	5.6	13.7
2	IR2	nd	1.7	1.7	nd	nd	nd	nd	nd	nd	nd	nd	1066.3	16.2	6.6	nd	25.9	4.7	1208.8	142.5	116	14.9
2	IR3	nd	1.7	1.9	nd	nd	nd	nd	nd	1.4	nd	nd	10.1	1.3	nd	nd	1.7	nd	60.3	50.2	35.2	12
3	CE1	73.6	49.7	128.2	130.3	19.2	6.4	2.9	3.5	32.1	24.9	1.4	239.6	15.9	9.4	4.2	22	6.6	2614.9	2375.3	407	1879.6
3	CE2	11.7	16.4	19.6	13.7	6.8	5.2	2.2	2.6	22.2	20	nd	70.7	17.3	5.5	2.3	22.8	4.2	508.3	437.6	163	232
3	CE3	14.9	17.2	27.2	23.6	5.8	4.2	nd	1.6	13.7	3.3	nd	1218.7	150.5	57.9	5.7	200.7	34.4	2332.6	1113.8	529	481.2

nd: not detected.

The highest concentrations of total PAHs were observed in port regions such as SR1 (5348.3 ng g^{-1}), CE1 (26149 ng g^{-1}), SR3 (2528.5 ng g^{-1}), CE3 (2332.6 ng g^{-1}), MM3 (2283.4 ng g^{-1}) and PA2 (995.5 ng g^{-1}). These same places, with the exception of PA2, also showed the highest concentrations of USEPA priority Σ16 PAHs, thus confirming that those sites are the most impacted by contamination by PAHs: SR1 (1187 ng g^{-1}), SR3 (1354 ng g^{-1}), MM3 (601 ng g^{-1}), CE3 (529 ng g^{-1}), and CE1 (407 ng g^{-1}). The alkylated PAHs were high at SR1 (3780.9 ng g^{-1}), CE1 (1879.9 ng g^{-1}), and SR3 (854 ng g^{-1}) and PA2 (676.4 ng g^{-1}). Sites TR1, TR2 and TR3 showed the lowest concentrations of the different groups of analyzed PAHs (6.5 to 22.6 ng g^{-1}). At TR2, these compounds were not found (< LOD). The sampling sites in Iranduba also showed relatively low concentrations of PAHs at IR1 (5.6 to 22.8 ng g^{-1}) and IR3 (12.0 to 60.3 ng g^{-1}), with the exception of IR2, with a concentration of 1208 ng g^{-1} of total ΣPAHs, but the PAH that contributed most to the significant concentration in IR2 was perylene, a PAH of biogenic or diagenetic origin.[7,38,39]

The Σ16 PAH concentrations found in the sediments of the Negro River region, which is under a heavy influence of urban and port activities, can be compared with those reported by other studies performed in fluvial systems where similar anthropic activities are routinely carried out (Table 4).

The Iguaçu River Basin sediment samples showed concentrations between 131 and 1713 ng g^{-1}.[40] In the state of South Carolina, USA, the Cooper River,[41] close to urban areas, showed a variation of 1460 to 1840 ng g^{-1} and the Arc River in France showed concentrations between 151 and 1257 ng g^{-1},[42] that are close to the values reported in this work. However, research observations in several places on the globe reveal PAH concentrations still higher, such as the concentrations found in the River Dalião in China (103-2790 ng g^{-1}),[43] and Ashley (3950-2790 ng g^{-1}), in South Carolina (USA).[41] In Brazil, the studies were undertaken at various locations: at the basin of the Paraiba do Sul River (4955-5354 ng g^{-1}),[44] in the Guandu River in the state of Rio de Janeiro (15 to 8156 ng g^{-1}),[5] rivers, swamps, and waterfalls in the vicinity of the National Parks of the Southeast region (4-2430 ng g^{-1}),[45] and the Paraiba do Sul River (5113 to 40.773 ng g^{-1})[5] (Table 4). All these places are exposed to domestic or industrial sewage in addition to the vehicular activity of the great cities and, in some cases, plant burning for agricultural purposes, factors capable of maximizing the deposition of PAHs in sediments.

The degree of sediment contamination may be evaluated based on the concentration of the 16 priority PAHs, as determined by the USEPA. Environments may be classified as "highly contaminated" when their concentration of Σ16 PAHs is above 500 ng g^{-1}, "moderately contaminated" when that concentration is between 250 and 500 ng g^{-1}, and "weakly contaminated" when that observed concentration is below 250 ng g^{-1}.[15,43,46-48] Among the samples evaluated in this study, four sites were classified as highly contaminated (SR1, SR3, MM3, and CE3), two as moderately contaminated (PA1 and CE1) and seven as weakly contaminated (IR2, SR2, PA2, PA3, MM1, MM2, and CE2). The sampling sites in TR and IR were not used to assess the degree and source of contamination (except IR2) because they have very low concentrations of Σ16 PAHs. All of the environments classified as highly and moderately contaminated are situated on the shore of the Manaus city and show high navigation activity with direct contamination sources of little spillages of oil derivatives and fossil fuel combustion processes that produce and liberate PAHs that, in association with organic particles in suspension, tend to accumulate in the sediments. The Captaincy Fluvial in the Western Amazon has a total of 13.676 vessels registered for the river activity around the city of Manaus, a fact that contributes to PAH entry in this region. The sites showing the lowest PAH levels are those with lowest anthropic input.

Table 4. Comparisons between PAH values (ng g^{-1} of dry weight) detected in Brazilian rivers and those of rivers of other parts of the world

Location	Anthropic activity	PAHs / (ng g^{-1})	Reference
Negro River, Amazon, Brazil	Urban areas, port region and conserved area	5.6-1187 (16)[a]	This study
Arc River, Southeast France	Urban and industrial areas	151-1257 (17)[a]	42
Iguaçu River basin, Paraná, Brazil	Urban and industrial areas	131-1713 (16)[a]	40
Daliao River, China	Urban and industrial areas	103-3420(18)[a]	43
Rivers, swamps and dams, Southeast Brazil	Proximity of national parks	4-24430 (13)[a]	45
Reservoir, Paraíba do Sul River, Brazil	Urban and industrial areas	4955-5586 (16)[a]	44
Paraíba do Sul River, Southeast Brazil	Urban and industrial areas	5113-40.773 (16)[a]	5
Guando River, Rio de Janeiro, Brazil		15-8156 (16)[a]	
Ashley River, South Carolina, USA	Urban and industrial areas	3950-2790 (24)[a]	41
Cooper River, South Carolina, USA		1460-1840 (24)[a]	

[a]Number of PAHs analyzed.

Sites PA2, PA3, MM1, MM2, and CE2 did not present high concentrations but it is possible to attribute PAH input to port activity and urban sewage.

Based on a general view of the PAH concentrations in the study area, it was possible to observe that the stations SR1, SR3, CE1, and CE3, which displayed the highest PAH concentrations, were also the sites with the highest concentrations of OM, OC, and TN. The organic matter content of the sediments is one of the main factors determining the levels and distribution of PAHs.[5,49,50] In the sites mentioned, the sediments are composed mainly by mud, thus showing that granulometry is also an important factor influencing the PAH concentration in environmental samples. Several studies confirmed the hypothesis that the PAH concentration tends to be higher in soil and sediments with predominance of mud presented relatively higher concentrations of PAH.[49,51] Samples with predominance of sand in their composition, such as PA3, MM1, MM2, and CE2, were classified as weakly contaminated with the exception of PA2, where the texture was mixed, and this observation is also in agreement with the literature. However, there were predominantly sandy regions in the Negro River such as SR3 and MM3 (88 and 94% sand, respectively), which also showed high priority PAH contamination. Among other factors, the proximity to polluting sources may be even more important than the concentration of total carbon and granulometry to explain the variability in the PAH concentrations.[44] In addition, the mineral composition of the surface of the particles found in sediments may be a factor that favors the accumulation of PAHs.[51]

PAH profile

Among the PAHs examined, perylene was the most abundant (19.9%), followed by Dimet-Phe (9.9%), Trimet-Nap (7.8%), and Met-Phe (6.8%). Perylene is a diagenetic PAH, resulting from biological processes in the initial stages of diagenesis in sediments or starting from terrestrial plants[38,39,47] and has also been mentioned as a good indicator of the biological synthesis of PAHs.[45] In studies concerning environmental contamination, perylene concentration should therefore be discarded. In this work, most of the sampling sites did not show significant differences between the total $\sum$PAHs with perylene and total $\sum$PAHs without perylene, with the exception of MM3, IR2, and CE3 (Table 3). According to the literature,[49] the occurrence of perylene at levels > 10% of total $\sum$PAHs is attributed to natural sources as observed in sites IR2 (88.2%), CE3 (53.2%), MM3 (44.6%), IR3 (16.8%), and CE2 (13.9%), mainly because of plant material such

as grasses in the margins of the Porto da Ceasa region, shrubbery in Iranduba, and floating macrophytes close to the margins of the Manaus Moderna Port found in those regions.

The methylated PAH compounds of low molecular weight are known to be constituents of fossil fuels.[13] The abundance of those compounds in sediment samples from some sampling sites is another indication that there was recent contamination by spillage of oil derivatives. In this study, some sites classified as highly contaminated (SR1, CE1, and SR3) showed high concentrations of alkylated PAHs (854 to 3780.9 ng g^{-1}). These sites have port activity and the presence of several vessels anchored to the Negro River shore, and these circumstances may have resulted in eventual oil spillages.

Among the 16 priority PAHs as defined by the USEPA, the most abundant were BghiP (15.35%), Nap (13.52%), InP (12.59%), Py (12.29%), Phe (9.0%), and Chry (8.40%). High molecular weight PAHs (four to six aromatic rings) that are part of the priority pollutants as determined by the USEPA and that are the most persistent in the environment represents nearly 70% of the total PAHs found in this work. The sites classified as highly impacted in this study (SR1, SR3, MM3, and CE3) showed considerable levels of BghiP (112.9 to 213 ng g^{-1}) and InP (60 to 194.6 ng g^{-1}). Compounds such as BghiP, DBA, and InP are predominantly found in areas under intense urban and industrial impact, mainly because of the combustion of oil products.[40] In urban areas, soil drainage systems also contribute to significant increments in PAH sources such as asphaltic surfaces and tire wear.[16,40,48] The high molecular weight PAHs are of pyrolytic origin, formed mainly during combustion processes and transferred to the aquatic environments by runoff water or atmospheric deposition,[48] such as occurred in the study area that showed PAHs coming from combustion of oil derivatives, vehicle and vessel activities and input from urban effluents. The Nap and Phe are classified as petrogenic, whereas Py and Chry usually result from pyrolysis processes.[4] The presence of Phe, Fluo, Py, and Nap may also be due to contamination of the sediments by domestic sewage.[36] In this study, environments receiving high amounts of domestic sewage such as SR1 and SR3 were also the environments presenting the highest concentrations of Nap (169.2 to 178.8 ng g^{-1}), Phe (76 to 187.5 ng g^{-1}) and Py (153.1 to 238.7 ng g^{-1}).

PAHs and contamination sources

PAH sources in the environment can be identified using DRs.[15,16,19] The use of DRs has been utilized and indicated by to be helpful in many researches that analysed PAHs in several matrices, such as particulate matter in water[52] or

river,[30,31,46] lagoon,[53] marine[54] sediments and atmosphere.[55] However, it is required have knowledge of PAH sources and fate around the study area for a more robust interpretation.[16] Thus, DRs used in this study aimed to enter the different classes of PAHs mentioned in the results and some isomers, for accurate distinction between the indication petrogenic or pyrogenic sources for the different sampling sites.

The ratio LMW/HMW with indices < 1 indicates a pyrogenic contribution and indices > 1 indicates a petrogenic contamination.[15] For the diagnostic ratio Flt/(Flt + Py), values < 0.40 correspond to pollution by oil and > 0.50 are characteristic of grass, wood or coal combustion. However, the values between 0.40 and 0.50 are related to the combustion of oil products employed by vehicles. For the relationship between InP/(InP + BghiP) values with indices lower than 0.20 indicate large amounts of spilled oil. Values from 0.20 to 0.50 characterize the combustion of petrochemical fuels; values larger than 0.50 indicate combustion of wood, plants or coal.[16] The ratio C0/(C0 + C1)Flt/Py use the isomers with mass 202. Values > 0.50 indicate grass, wood or coal combustion, and values below 0.50 for petrogenic source.[16,32,33] For Par/(Par + Alkyl), values < 0.30 are indicative of petrogenic source and values > 0.50 are indicative of petroleum burning, coal and wood combustion.[33] The index results previously mentioned for the determination of the main sources of PAH contamination in sediments of the Negro River are described in Table 5.

Making use of the ratio LMW/HMW,[15] it was possible to observe that all the environments receive a larger contribution of pyrogenic contamination. Using the ratio Flt/(Flt + Py),[16] most of the sampling sites indicated vehicle combustion of fossil fuels (values between 0.40 and 0.50), with the exception SR1, PA3, and CE1 that showed petrogenic sources as the most important source of contamination. However, the sampling sites SR2 and MM3 indicated grass, wood and coal combustion. The ratio InP/(InP + BghiP)[16] showed pyrogenic sources of

contamination in all of the environments, mainly by the combustion of fossil fuels, except SR3, MM1, and MM2, which were characterized by biomass burning (wood, plant or coal), possibly influenced by urban activities. The ratio C0/(C0 + C1)Flt/Py[16] showed values higher than 0.50, indicating predominance of pyrogenic sources in all locations. However, the values obtained by the ratio Par/(Par + Alkyl)[33] show the existence of petrogenic input, result also indicated to the sampling sites SR1, PA3 and CE1 by ratio Flt/(Flt + Py) (Tabela 5).

The analysis of cross plot using LMW/HMW and DRs showed that most of the sampling sites indicated PAH from pyrogenic sources (Figures 3a and 3b). However, the ratio of LMW/HMW PAHs *versus* Par/(Par + Alkyl) provided an indicated of petrogenic sources of contamination to some sampling sites (Figure 3c). Among Flt/(Flt + Py) and other DRs applied, the majority of stations presented the range of 0.40 to 0.50 (Figures 3d and 3e), corresponding to the combustion of oil, but the ratio of Flt/(Flt + Py) with Par/(Par + Alkyl) also provides an indication of petrogenic sources (Figure 3f). Most of the indices examined showed the pyrogenic source of the predominant source of contamination. However, the contribution of alkylated PAH in some sampling sites may be associated with oil input coming from urban and portuary activity around of the city of Manaus.

Conclusions

The presence of PAHs in superficial sediments of the Negro River can be attributed to sites that showed the influence of mud predominance as well as the accumulation of organic matter, carbon, and total nitrogen. The study area receives PAH input mainly from pyrogenic sources related to oil combustion but petrogenic PAH introduction, represented by alkylated compounds, coming from oil and derivatives input is also an important contamination source to be considered.

Table 5. Diagnostics ratios found in the literature and in this work

|	PAH source				Sampling site												
	Reference	Petrogenic	Pyrogenic	G. w. c.[a] combustion	Combustion of fossil fuel	IR2	SR1	SR2	SR3	MM1	MM2	MM3	PA1	PA2	PA3	CE1	CE2	CE3
LMW/HMW	15	> 1.00	< 1.00	–	–	0.92	0.49	0.62	0.26	0.26	0.17	0.09	0.47	0.22	0.56	0.80	0.29	0.10
Flt/(Flt + Py)	16	< 0.40	–	> 0.50	0.40-0.50	0.39	0.31	0.40	0.53	0.47	0.53	0.41	0.43	0.48	0.34	0.36	0.45	0.42
InP/(InP + BghiP)	16	< 0.20	0.20-0.50	> 0.50	–	0.38	0.35	0.43	0.51	0.52	0.51	0.48	0.42	0.46	0.47	0.42	0.43	0.43
C0/(C0 + C1)Flt/Py	16	< 0.50	–	> 0.50	–	1.00	0.80	0.79	0.88	0.86	0.91	0.74	0.77	0.73	0.74	0.50	0.72	0.72
Par/(Par + Alkyl)	33	< 0.30	–	> 0.50	–	0.84	0.23	0.44	0.53	0.46	0.70	0.23	0.29	0.22	0.21	0.16	0.34	0.24

[a]G.w.c. = grass, wood and coal combustion.
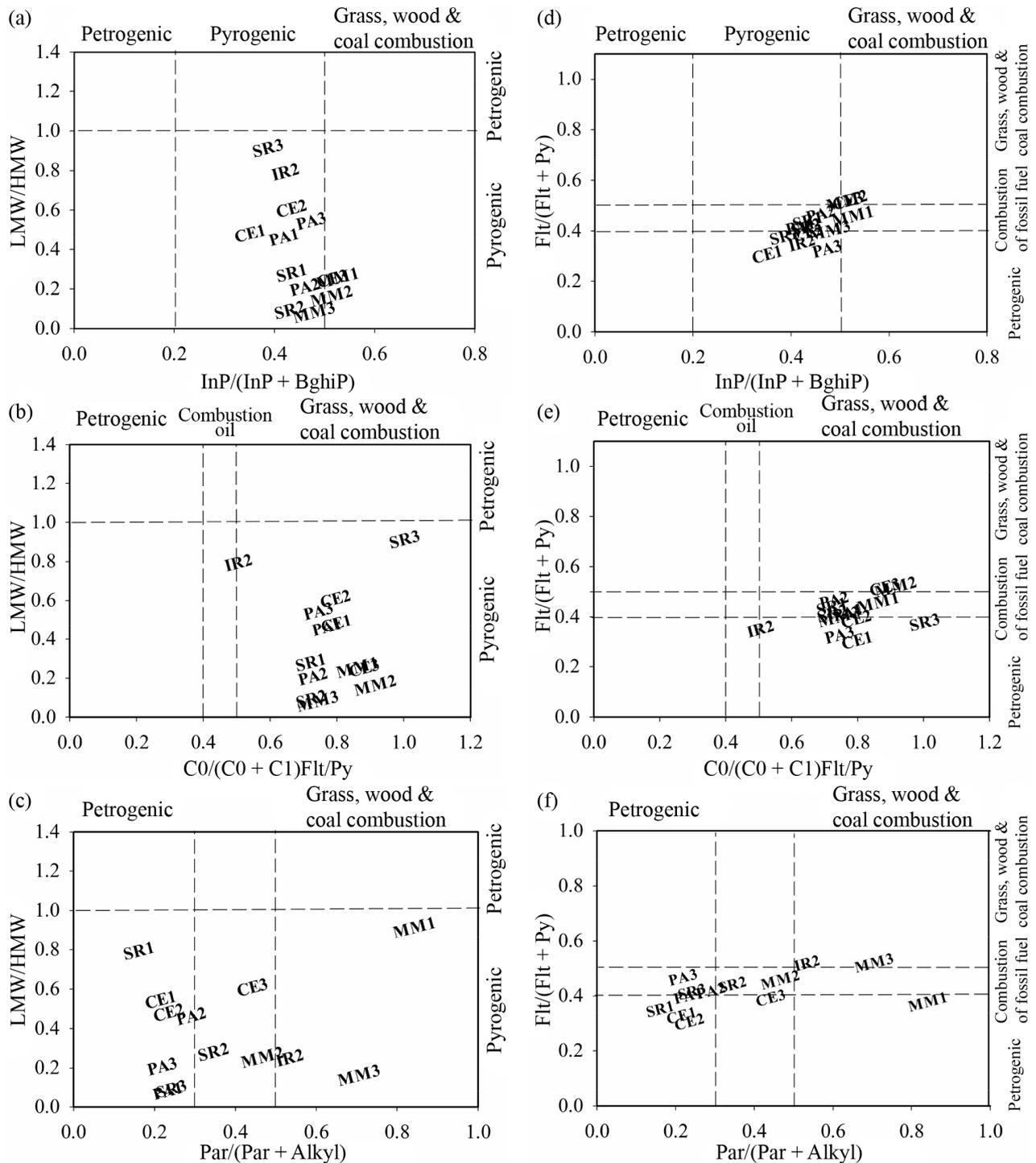
Figure 3. Cross plots of the LMW/HMW *vs.* InP/(InP + BghiP) (a), C0/(C0+C1)Flt/Py (b) and Par/(Par + Alkyl) (c). Cross plots of the Flt/(Flt + Py) *vs.* InP/(InP + BghiP) (d), C0/(C0+C1)Flt/Py (e) and Par/(Par + Alkyl) (f).

Acknowledgment

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