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Occurrence, sources, and ecological risks of polycyclic aromatic hydrocarbons (PAHs) in the Amazon river

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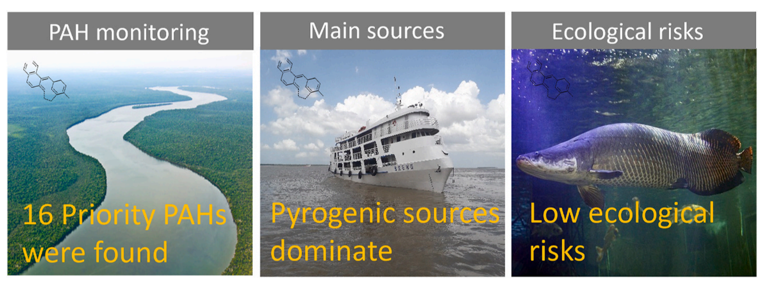
HIGHLIGHTS

- The presence of 16 priority PAHs was investigated in Amazonian surface waters.
- PAHs were found in all samples, with total concentrations up to 163 ng L^{-1}.
- Higher concentrations were found next to large urban areas.
- In most samples, PAH contamination was of pyrogenic origin.
- PAHs may not directly harm Amazonian freshwater ecosystems.

GRAPHICAL ABSTRACT



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ABSTRACT

The Amazon is the largest river by discharge volume and one of the most biodiverse biomes in the world. Lately, there has been a rapid increase of the urban population in the region, which has been translated into a growing emission of organic contaminants such as polycyclic aromatic hydrocarbons (PAHs) into surface water bodies. This study provides the most comprehensive evaluation of the PAH contamination levels in surface waters of the Amazon basin. We investigated the occurrence and potential sources of 16 priority PAHs and characterised their risks for freshwater ecosystems. For this, we took 40 water samples from different sites along the Brazilian part of the Amazon River, including three major tributaries, and smaller rivers crossing the main urban areas. The results of this study show that PAHs are widespread contaminants in rivers of the Brazilian Amazon. The sum of the total concentration of the 16 priority PAHs reached values of 134 ng L^{-1} in the Amazon River, and 163 ng L^{-1} near densely populated areas. On the other hand, the total PAH concentration was generally lower in the monitored tributaries. In most samples, the contamination pattern was dominated by high molecular weight PAHs, suggesting a major contribution of pyrogenic sources, although petrogenic contamination was also present in some locations near urban areas. We assessed ecological risks posed by PAH mixtures using a hazard index.

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The results indicated that PAH contamination is not likely to pose direct toxic effects for Amazonian freshwater organisms, however continued monitoring is recommended near densely populated areas.

List of abbreviations

AA-QS	Annual Average Quality Standard
Ace	acenaphthene
Acy	acenaphthylene
Ant	anthracene
BaA	benzo[*a*]anthracene
BaP	benzo[*a*]pyrene
BbF	benzo[*b*]fluoranthene
BghiP	benzo[ghi]perylene
BkF	benzo[k]fluoranthene
Chr	chrysene
DBahA	dibenz[a,h]anthracene
EQS	Environmental Quality Standards
Fl	fluoranthene
Flu	fluorene
GC	gas chromatography
HI	Hazard Index
HMW	High Molecular Weight
HQs	Hazard Quotient
IP	indeno[1,2,3-*cd*]pyrene
Kow	octanol/water partition coefficient
LMW	Low Molecular Weight
MS	mass spectrometry
Nap	naphthalene
PAHs	Polycyclic Aromatic Hydrocarbons
Phen	phenanthrene
PNEC	Predicted No Effect Concentrations
Pyr	pyrene
SDG	sustainable development goals
SIM	selected ion monitoring
SPE	solid-phase extraction

1. Introduction

In 2015, under the auspices of the United Nations, a new set of global sustainable development goals (SDG) were agreed upon internationally with the ambition to be accomplished by 2030. Among these, the 15th Goal aims to achieve the conservation, restoration, and sustainable use of freshwater ecosystems and their services, and to take action to reduce the degradation of natural habitats and halt the biodiversity loss (UN General Assembly, 2015). These objectives are of particular relevance for the Amazon region, as it represents the biggest drainage basin in the world, covering an area of about 7 million km^2 (Godinho and da Silva, 2018; Neves et al., 2018).

The Amazon is the most important tropical ecosystem, characterised by a large biodiversity of aquatic and terrestrial organisms (Paiva et al., 2020; Fidelis et al., 2023). Notwithstanding this, the Amazon region has become highly vulnerable to anthropogenic pressures, including agricultural expansion, urbanization, and trade (Castello et al., 2013). The rapid population growth and the lack of an appropriate wastewater management plan have resulted in significant water pollution problems. Recent studies have shown that Amazonian waters are contaminated with pharmaceuticals, personal-care products, pesticides, microplastics and other emerging contaminants, constituting an important threat for aquatic organisms (Sousa et al., 2020; Chaves et al., 2020; Fabregat-Safont et al., 2021; Rico et al., 2021, 2022, 2023). The intensification of human activities has also contributed to the emission of Polycyclic Aromatic Hydrocarbons (PAHs; Neves et al., 2018). PAHs are introduced into the environment both, from natural (forest fires, volcanic activity, biological synthesis) and from anthropogenic sources (incomplete combustion of fossil fuels and by industrial activities) (Abdel-Shafy and Mansour, 2016; Rizzi et al., 2021). According to the NASA's observation (NASA Earth Observatory, 2020), the Amazonian region is subject to intensive man-driven forest burning, accounting for about 15% of the total global fire emissions, which can be considered a major PAH source (Mishra et al., 2015). In addition to fires, intense vessel traffic, industries, hydroelectric power plants, untreated sewage and landfills along the Amazon River can contribute to the environmental release of PAHs (Rodrigues et al., 2018; Sousa et al., 2020; Lima et al., 2021).

PAHs are highly persistent contaminants. They are characterised by a high octanol/water partition coefficient (Kow), low solubility in water and a high affinity for lipophilic matrices. Therefore, PAHs that reach aquatic ecosystems tend to adsorb to suspended particulate matter, sediments, and living organisms (Vijayanand et al., 2023), causing ecotoxicological hazards for many aquatic organisms. Moreover, PAHs have been proven to have mutagenic and carcinogenic properties (Barbosa et al., 2023; Kumar et al., 2020; Ambade et al., 2023), and due to this, the US-EPA has classified 16 PAHs as priority hazardous substances for human health. As reviewed by Honda and Suzuki (2020), PAHs can cause several kinds of toxic effects in the human population (i.e., reproductive disturbance, embryo deformity, endocrine disruption, and DNA damage). Furthermore, the presence of PAHs in the environment can have unforeseen ecological consequences, as different species show a varied range of sensitivities to the same congener or compounds within the same family (Sese et al., 2009). For example, it has been shown that the presence of benzo(*a*)pyrene in the water column can affect the structure of planktonic communities by causing a reduction in Cladocera abundance and subsequent dominance of rotifers (Ikenaka et al., 2013), while other studies suggest phytoplankton growth as the most sensitive endpoint (Othman et al., 2023).

Several studies have investigated the occurrence of PAHs in suspended particulate matter and sediments of specific locations of the Amazon basin (Lima et al., 2021; Sousa et al., 2020; Rodrigues et al., 2018). Rodrigues et al. (2018) evaluated the occurrence of PAHs in sediments of the northern Amazon River estuary and found total sediment concentrations between 22 and 159 ng g^{-1} dw. Sousa et al. (2020) found total PAH levels in suspended particulate matter of the Aurá River (northern Brazil), which is impacted by metropolitan region of Belém, up to 2500–2800 ng g^{-1} dw, while Lima et al. (2021) described concentrations of up to 33,000 ng g^{-1} dw in sediment samples taken near the urban area of Barcarena (Brazil). These studies point at petrogenic and fossil fuel consumption as the major sources of PAHs in the region. Moreover, they agreed upon the need to perform large scale monitoring studies to assess how the continued release of untreated sewage, and the increasing coal and biomass burning, industrial activities and vessel traffic in the region may be contributing to raise PAH levels and risks for Amazonian freshwater ecosystems.

Therefore, the objective of this study was to provide the first large-scale assessment of the environmental occurrence and spread of PAH pollution in the Amazon River basin, with focus on urban areas of the Brazilian Amazon, and to characterize their contamination sources and hazards for aquatic organisms. We assessed the exposure concentration of the 16 priority PAHs in water samples (dissolved and sorbed to suspended solids) collected along the Brazilian part of the Amazon River, in three major tributaries of the Amazon River, as well as in small rivers and streams crossing the urban areas of Manaus, Santarém, Macapá and Belém. This study contributes to the understanding of how the demographic increase and industrialization degree in the Amazon region can contribute to raise PAH levels in the largest river of the world and seeks for patterns of PAH contamination that should guide international chemical monitoring and management efforts.

2. Materials and methods

2.1. Sampling campaign

Water sampling was performed between November and December of 2019 in 40 sampling locations. Eleven samples were taken along the Amazon River, nine samples in three major tributaries (Negro River, Tapajos River, and Tocantins River), and twenty samples in smaller rivers crossing the urban areas of Manaus, Santarém, Macapá and Belém (Fig. 1). The samples were taken using a metal bucket from a water depth of 20–30 cm. Approximately 2 L of water were introduced into amber glass bottles and stored (at 4 °C) for a maximum of two days until extraction. A detailed description of the sampling campaign and locations is provided in Rico et al. (2021).

2.2. Chemical analysis

We analysed the concentration of PAHs dissolved in water and sorbed to suspended solids for the 16 PAHs priority substances listed by the US EPA: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phen), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[a,h]anthracene (DBahA), indeno[1,2,3-*cd*]pyrene (IP), benzo[ghi]perylene (BghiP).

Water samples were filtered using a 0.7 μm glass fibre filter. Afterwards, solid-phase extraction (SPE) was performed in groups of 4–8 samples. SPE was performed with Oasis HLB Waters (500 mg) cartridges preconditioned with 5 mL MeOH and 5 mL of ultra-pure water. 1 L of water was loaded into each SPE cartridge. After loading, 10 mL of ultrapure water was passed over the cartridges and were dried for 10 min. Afterwards, the loaded SPE cartridges were stored at −20 °C, and shipped to the University of Milano Bicocca (Italy), where they were eluted with 15 mL of n-hexane, 10 mL of n-hexane: methylene chloride (30:70), and 6 mL of ethyl acetate.

Glass fibre filters were lyophilized and extracted using an ultrasonic bath at 40 °C. The following extraction solvents were used: hexane (10 mL), followed by dichloromethane (10 mL), and ethyl acetate (10 mL). All extracts were concentrated to a volume of 0.05 mL by evaporation and introduced into amber glass vials.

PAHs were identified and quantified by gas chromatography (GC) - mass spectrometry (MS) using a mass data selective system (5977B) equipped with GC 8860 (Agilent Technologies, CA, USA) in selected ion monitoring (SIM) mode. Separations were performed by a GC-column HP-MS5, 30 m, 0.25 mm, 0.25 μm (Agilent Technologies) with a 1.5 mL min^{-1} of carrier gas flow (He). Prior to injection, 0.2 μL of internal standard (PCB141) was added to each calibration concentration and to each sample. Details of the instrumental parameters and detection limits are provided in the Supplementary Information file (Table S1).

Together with the samples, a field blank sample was prepared by passing 100 mL of ultrapure water over SPE cartridges. Traces of some PAHs were found in the field blanks and were used to correct the concentrations in the samples. The recovery efficiency was checked in three replicates at the fortification level of 10 ng L^{-1} for each selected compound. Compound recoveries ranged between 70% and 130% (see Table S2).

2.3. Diagnostic ratios

Diagnostic ratios that involve pairs of PAH isomers and/or similar

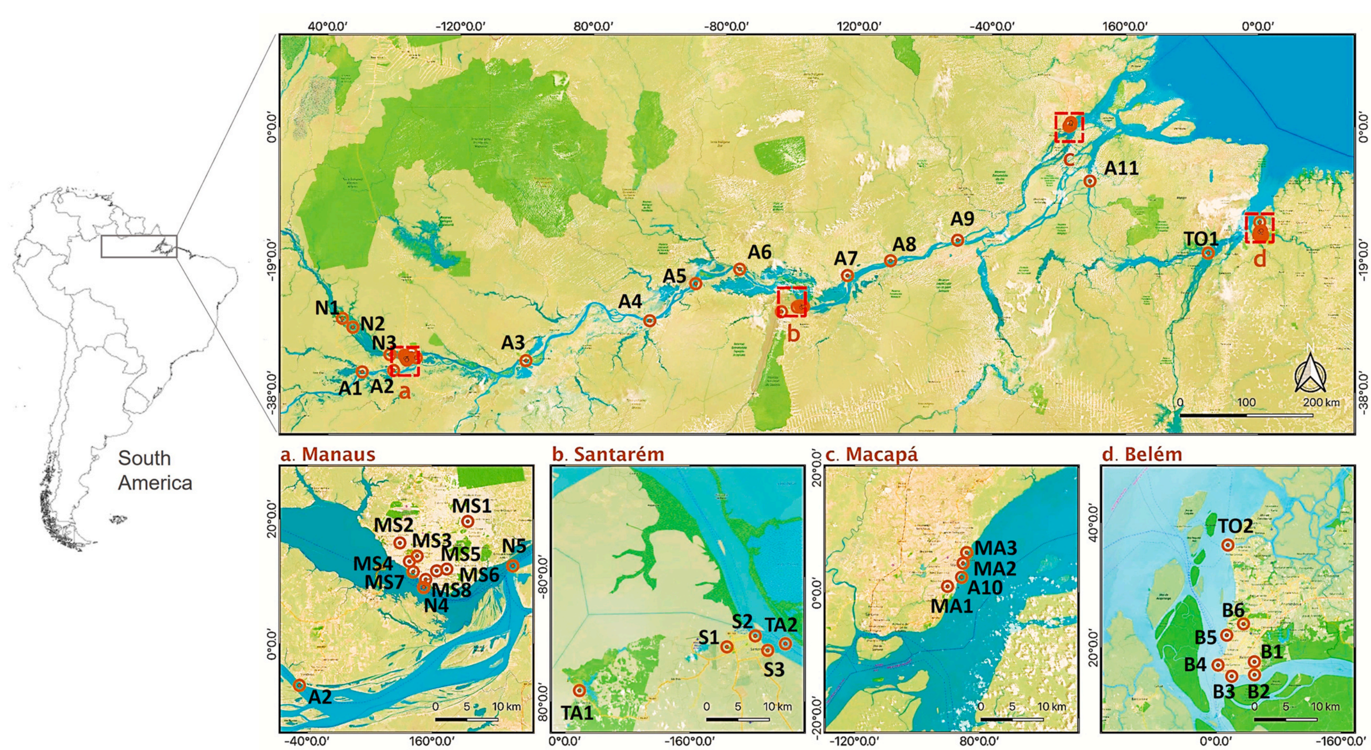

Fig. 1. Map of the study region and sampling locations. The sample codes correspond to: N: Negro River; M: Manaus; A: Amazon River; TA: Tapajos River; S: Santarém; MA: Macapá; Tocantins River; B: Belém. The figure has been adapted with permission from Rico et al. (2021).

physicochemical characteristics are widely used to discriminate between the PAHs origin (Yunker et al., 2002; Jiang et al., 2011). In this study, we used the following diagnostic rations to try to distinguish their main potential origin.

- anthracene/(anthracene + phenanthrene): Ant/(Ant + Phen) > 0.10 pyrogenic origin, <0.10 petrogenic origins (Yunker et al., 2002);
- fluoranthene/(fluoranthene + pyrene): Fl/(Fl + Pyr) > 0.5 grass, coal, or wood combustion, between 0.4 and 0.5 liquid fossil fuel combustion; <0.4 petrogenic sources (Yunker et al., 2002);
- benz[*a*]anthracene/(benz[*a*]anthracene + chrysene): BaA/(BaA + Chr) > 0.35 combustion sources and vehicle traffic, between 0.2 and 0.35 petrogenic origin or combustion; <0.2 petroleum sources (Hartwell et al., 2020);
- indeno [1,2,3-cd]pyrene/(indeno[1,2,3-*cd*]pyrene + benzo[ghi]perylene): IP/(IP + BghiP) > 0.5 combustions of biomass or coal; between 0.2 and 0.5 liquid fossil fuel combustion; <0.2 petrogenic sources (Syakti et al., 2015);
- High Molar Weight (HMW; 4–6 rings)/Low Molar Weight (LMW; 2–3 ring) PAHs: >1 pyrogenic source (Zheng et al., 2016).

2.4. Ecological risk assessment

Risks for Amazonian freshwater ecosystems were assessed based on the Hazard Index (HI), calculated as the sum of the Hazard Quotient (HQs) of each compound assuming additive effects for the PAH compounds contained in the mixture. HQs were calculated by dividing the total measured environmental concentration by the chronic Predicted No Effect Concentrations (PNEC) for each compound. PNECs were obtained from Wang et al. (2021) and were derived as the median Hazardous Concentration for the 5% of species obtained from Species Sensitivity Distributions built with experimental toxicity data (when available) or toxicity values derived with quantitative structure-activity relationship models (see Table S3). We assumed ecological risks may be expected when the calculated HI was higher than 1, which means that the PAH mixture will affect ≥5% of the species in the ecosystem after long-term exposure.

3. Results and discussion

3.1. PAH exposure levels

Table 1 shows the mean of the total PAH concentration (i.e. sum of the dissolved concentration and concentration in suspended solids) in the Amazon River and its tributaries (Tapajos, Tocantins, and Rio Negro), as well as in the small rivers and streams near urban areas. PAH contamination was found in all samples collected as part of this study in concentrations that range from few ng/L to hundred ng/L. PAH contamination was found in all samples, including the Anavilhanas National Park (samples N1 and N2; 4–10 ng L^{-1}), which has a great biodiversity of flora and fauna, and hosts protected mamifers such as the giant otter (*Pteronura brasiliensis*), the Amazonian manatee (*Trichechus inunguis*), or the Amazon river dolphin (*Inia geoffrensis*).

The mean PAH concentration in the Amazon River was 32 ng L^{-1}, with a maximum value of 134 ng L^{-1} in sample A4 (Fig. 2), which corresponds to a sampling point next to the harbour of the city of Parintins. The mean concentration in the three tributaries was generally lower as compared to the Amazon River. Among the tributaries, the Tapajos River was the most contaminated one, with a mean concentration of 20 ng L^{-1}, followed by the Negro River (14 ng L^{-1}), and the Tocantins River (12 ng L^{-1}). Water samples taken near Belém, the most densely populated city in northern Brazil, were found to be the most contaminated ones, with maximum concentrations reaching 63 ng L^{-1} and 163 ng L^{-1} in samples B3 and B5, respectively (mean concentration: 48 ng L^{-1}). Lower contamination levels were found in the urban areas of Santarem (mean concentration: 28 ng L^{-1}), Manaus (25 ng L^{-1}), and Macapá (18 ng L^{-1}).

Most PAH monitoring studies carried out in the Amazon region have focused on sediments (Souza et al., 2015; Rodrigues et al., 2018; Sousa et al., 2020; Lima et al., 2021). For example, Lima et al. (2021) found concentrations up to 312 ng g^{-1} d.w. near the city of Belém, while Sousa et al. (2020) reported values higher than 800 ng g^{-1} d.w. In the Aurà River, which flows through the municipality of Belém. Concentrations ranging from 22 to 159 ng g^{-1} d.w. were recorded in the urbanised edge of the Amazon River Estuary surrounding the city of Macapá (Rodrigues et al., 2018) and concentrations from 72 to 601 ng g^{-1} d.w. were found along the edge of the city of Manaus, in an area affected by urban and port activities (Souza et al., 2015). However, much lower values (6.5–9.1 ng g^{-1} d.w.) were quantified by Souza et al. (2015) in samples collected near the Tupé Sustainable Development Reserve, in the Negro River, a region upstream of Manaus and surrounded by native vegetation. Our results are in line with the outcomes of these studies, and point at large urban areas and their harbours as significant contamination hotspots in comparison to forested areas.

As shown in Fig. 2, the largest PAH concentrations were found in suspended particulate matter. However, some samples collected near the cities of Manaus (samples MS2, MS5, MS6, MS8), Macapá (MA1) and Belém (B1, B5) showed higher concentrations in the dissolved phase than in the sorbed phase (Fig. 2). Acenaphthene and fluorene were the compounds showing the largest concentration in the dissolved phase, which may be related to their lower log Kow (Mackay et al., 2006; Othman et al., 2023).

The PAH concentration profile, calculated as the ratio of a single PAH concentration to the sum of the 16 PAHs concentration, revealed that pyrene was the most abundant compound in all samples, representing 54–71% of the total PAH concentration in the Amazon River and its tributaries, and 17–58% in sampling sites near urban areas. In addition to pyrene, fluorene, fluoranthene, and chrysene dominated the

Table 1
Total concentration (ng/L) of the 16 analysed PAHs (sum of the dissolved concentration and concentration in suspended solids) in the different sample groups. nd: not detected.

Major sample group	Minor sample groups	Concentration ΣPAHs: mean (min-max)	Concentration Σ2 rings PAHs mean (min-max)	Concentration Σ3-4 rings PAHs mean (min-max)	Concentration Σ5-6 rings PAHs mean (min-max)
Amazon River and major tributaries	Amazon River (n = 11)	32 (4.2–134)	6.4 (nd – 70.5)	23.7 (2.6–71.8)	1.4 (nd – 4.7)
	Negro River (n = 5)	14 (4.4–31)	nd (nd – nd)	13.6 (4.4–30.4)	0.7 (nd – 2.1)
	Tapajos River (n = 2)	20 (15–25)	nd (nd – nd)	19.3 (15–23.7)	0.9 (nd – 1.7)
	Tocantins River (n = 2)	12 (2.8–22.0)	nd (nd – nd)	12.4 (2.9–21.9)	nd (nd – nd)
Urban areas	Manaus (n = 8)	25 (4.1–39)	nd (nd – nd)	22.7 (4.1–37.9)	2.1 (nd – 5.5)
	Santarem (n = 3)	28 (7.5–46)	nd (nd – nd)	27.1 (7.4–45.5)	0.8 (0.1–2.3)
	Macapa (n = 3)	18 (9.2–33)	4.7 (nd – 14.1)	12.8 (9.1–18.4)	0.6 (0.1–1.0)
	Belem (n = 6)	48 (5.1–163)	26.2 (nd – 157)	20.1 (4.0–58.1)	2.0 (nd – 5.0)

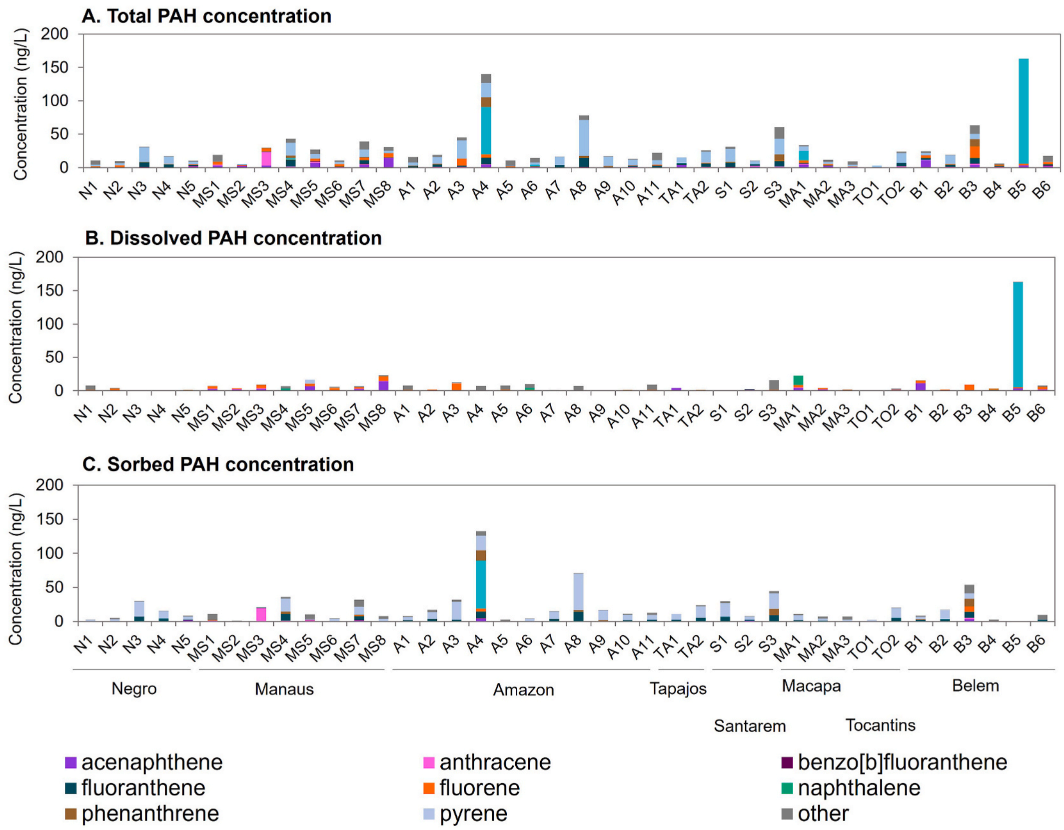

Fig. 2. Sum of PAH concentrations in the different samples and relative contribution of the different compounds to the sum. Only compounds with a concentration higher than 10 ng L^{-1} in at least one sample are shown, while the rest are grouped as Other. The individual PAH concentrations are provided in Table S4.

concentrations profile of most samples, while naphthalene was the most dominant PAH in the most contaminated sites (A4 and B5). These results are in line with those reported by Sousa et al. (2020), who found pyrene, anthracene, fluoranthene and fluorene (formed during the combustion of fossil fuels) dominating the PAH exposure profile of sediment samples collected in the Aurá River, near Belém. On the other hand, Lima et al. (2021) found a higher prevalence of heavy and more persistent PAHs such as indeno[1,2,3-*cd*]pyrene and benzo[ghi]perylene in the majority of samples collected near Belém. A high prevalence of naphthalene in contaminated samples was also found by Rodrigues et al. (2018) and Wilcke et al. (2000). This compound, which is the most volatile PAH, is discharged into the environment by a variety of sources, including natural (such as forest fires) and anthropogenic (motor vehicles, fossil fuels burning, and industrial plants) sources, which may explain its high concentration in urban areas (e.g. sample B5) and in areas with high boat traffic (e.g. sample A4, harbour of Parintins).

3.2. Sources of PAHs

Diagnostic ratios allow the identification of the potential sources of PAH contamination in the environment (Yunker et al., 2002; Jiang et al., 2011). Nevertheless, as highlighted by several authors (Tobiszewski and Namiesnik, 2012; Ravindra et al., 2008; Zhang et al., 2005), this approach has some limitations due to the possible changes in concentrations suffered by some congeners during transport from the emission source to the sampling area, and the fate of the evaluated substances across the air, water and sediment compartments. The ratios Ant/(Ant + Phe) and BaA/(BaA + Chr) have been identified as the most sensitive to alterations due to atmospheric processes, while the FL/(FL + Pyr) and the IP/(IP + BghiP) ratios, and particularly the ratio between the high and low molar weight of the PAH congeners, have been considered more robust for the identification of PAH sources based on field observations (Zhang et al., 2005; Katsoyiannis et al., 2011; Yunker et al., 2002).

The calculated average PAH isomer pairs ratios are reported in Table 2. In almost all samples, the Ant/(Ant + Phen) ratio was >0.10 suggesting the dominance of PAHs of pyrogenic origin within the study area. Conversely, the diagnostic ratio Fl/(Fl + Pyr) ratio was generally <0.40, pointing at a petrogenic PAH origin, except for the city of Belém, which showed ratios above 0.50 in three samples (suggesting combustion of grass, coal, or wood) and between 0.40 and 0.50 in one sample, (indicating the combustion of oil products used by vehicles). However, the results of the Fl/(Fl + Pyr) ratio should be interpreted with caution, as it is highly influenced by the presence of pyrene (the most abundant compound).

Following Hartwell et al. (2020), a BaA/(BaA + Chr) ratio >0.35 is indicative of combustion sources and a possible indication of vehicle emissions, a ratio <0.20 hints towards petroleum sources, and a ratio of 0.20–0.35 may be related to either petrogenic or combustion sources. The results of this diagnostic ratio showed a varied range of possible sources, with some samples in the Amazon River, Tapajos River and in the surroundings of Manaus, Macapá, and Belém indicating a clear influence of vehicle combustion emissions.

Finally, an IP/(IP + BghiP) ratio <0.20 indicates a petrogenic source, and a ratio of 0.20–0.50 suggest liquid fossil fuel combustion, while values > 0.50 are characteristic of biomass or coal combustion (Syakti et al., 2015). The large number of non-detectable values for both congeners hampered the calculation of the IP/(IP + BghiP) ratio for many samples. When applicable, the ratio was <0.20 in the majority of samples from the Negro River and Macapá; <0.20 or between 0.20 and 0.50 in the main course of the Amazon River and higher than 0.50 in one sample from Tocantins and in the samples from the cities of Manaus and Belém, indicating liquid fossil fuel combustion or biomass/coal combustion.

The results of the application of the diagnostic ratios show that PAHs

Table 2
Mean (min-max) diagnostic ratios for each sample group. na: not available because some of the compounds were not detected.

Major sample group	Minor sample groups	Ant/(Ant + Phe)	Fl/(Fl + Pyr)	BaA/(BaA + Chr)	IP/(IP + BghiP)	ΣHMW/ΣLMW
Amazon River and major tributaries	Amazon River (n = 11)	0.73 (0.05–0.99)	0.18 (0–0.32)	0.37 (0.04–0.90)	0.27 (0.15–0.44)	7.4 (0.39–23.3)
	Negro River (n = 5)	0.97 (0.88–0.99)	0.17 (0.01–0.27)	0.18 (0.01–0.33)	0.19 (0.10–0.31)	8.46 (1.54–22.3)
	Tapajos River (n = 2)	(na – 0.99)	0.23 (0.22–0.24)	0.66 (na – 0.99)	na	8.25 (2.85–13.6)
	Tocantins River (n = 2)	0.99 (0.98–1)	0.13 (0–0.25)	(na – 0.99)	(na – 0.52)	6.83 (3.88–9.77)
Urban areas	Manaus (n = 8)	0.79 (0.23–1)	0.13 (0–0.34)	0.30 (0–0.98)	0.59 (0.15–0.99)	1.43 (0.04–6.09)
	Santarém (n = 3)	0.56 (0.08–0.99)	0.25 (0.25–0.26)	0.10 (0.01–0.25)	0.25 (0.14–0.35)	9.90 (2.20–20.9)
	Macapá (n = 3)	0.99 (0.99–1)	0.13 (0.01–0.21)	0.46 (0.17–0.94)	0.14 (0.08–0.18)	0.79 (0.44–1.20)
	Belém (n = 6)	0.82 (0.15–1)	0.51 (0.20–0.72)	0.59 (0.17–0.99)	0.84 (0.78–0.88)	2.36 (0.0–10.6)

are released into the Amazon River from mixed sources, which may include grass and wood burning, but also intensive vehicle and vessel traffic around the study area. Looking at the ΣHMW/ΣLMW ratio (Table 2), it can be concluded that most samples were characterised by a predominance of high molecular weight PAHs, which are usually associated with pyrogenic sources (Zheng et al., 2016). In the Amazon River, the ΣHMW/ΣLMW ratio was around 7, while in the Negro River and the other major tributaries the ratio ranged between 6.8 and 8.5, indicating a greater prevalence of heavier compounds. A predominance of HMW compounds in the Brazilian Amazon was also found by other authors (Lima et al., 2021; Pichler et al., 2021, Rodrigues et al., 2018). On the contrary, the ΣLMW and ΣHMW were very similar in samples collected close to the cities of Manaus and Macapá, with a ΣHMW/ΣLMW ratio of 0.8–1.4. In the samples with the highest total PAH concentration, taken near the harbour of Parintins and Belém (A4, B3, B5), the ratio was notably lower than 1 (0.01–0.6), indicating a petrogenic origin. These results indicate that PAH contamination in the Amazon River and its major tributaries is predominantly of pyrogenic origin, and largely influenced by the vessel traffic, as described by Dos Santos et al. (2016). On the other hand, in smaller rivers and streams next to urban areas, petrogenic contamination sources can also play an important role, potentially due to untreated sewage and oil spills from floating petrol stations and large ships.

3.3. Ecological risk assessment

The calculated HIs were lower than 1 in all samples (Fig. 3). The highest values were found in Manaus (MS1, MS5), Belém (B3), Santarém (S3) and in the Amazon River (A4), with HIs of about 0.4. The compounds contributing most to the calculated HIs were anthracene (in sample MS3), benzo[*b*]fluoranthene (in sample S3), dibenzo[a,h] anthracene (in sample MS5), indeno[1,2,3 -cd]pyrene (in sample B3), and benzo[*a*]pyrene (in many samples collected along the Amazon River and next to urban areas; Fig. 3). An additional comparison was made with the Environmental Quality Standards (EQSs) established for some individual PAHs for the implementation of the European Water Framework Directive (EC-SCHEER, 2023). Under this regulatory framework, the most critical EQSs are the AA-QS (Annual Average Quality Standard) of 8.2 ng L^{-1} for benzo[g,h,i]perylene, and the quality standard for secondary poisoning of 5.7 ng L^{-1} for benzo[*a*]pyrene. All measured concentrations in this study are far below the European EQSs. Therefore, our results indicate that the risks posed by the 16 priority PAHs to Amazonian freshwater organisms are low or insignificant. However, the presence of benzo[*a*]pyrene and naphthalene, which are considered powerful carcinogenic agents (IARC, 2010) should be continuously monitored in Amazonian surface waters. Moreover, the potential bioaccumulation of these compounds in large predatory fish species, such as peacock bass (*Cichla ocellaris*) or pirarucu (*Arapaimas gigas*), which serve as an important food source for the Amazonian population, should be investigated.

4. Conclusions

This study shows that PAHs are widespread contaminants in the Amazon River, with the highest concentrations occurring next to major urban areas, particularly near Belém and other important harbours. The results show a high prevalence of high molecular weight PAHs, which are indicators of pyrogenic sources of contamination, although petrogenic sources are also important in samples with high contamination levels. Notwithstanding the high levels of anthropogenic impact in some locations, current PAH exposure levels are expected to result in low or insignificant ecotoxicological hazards for Amazonian freshwater organisms exposed via water. However, the intense and unorganized development of the major urban areas in the Amazon could increase PAH exposure levels by uncontrolled chemical spills, freshwater runoff, and atmospheric deposition. Therefore, within the actions of the SDGs that aim to control and prevent the degradation of natural habitats that host large biodiversity, continued monitoring programs and bioaccumulation studies in aquatic animals are recommended. Such studies should also account for human exposure, as many local populations use the Amazon River as the main water source for human consumption.

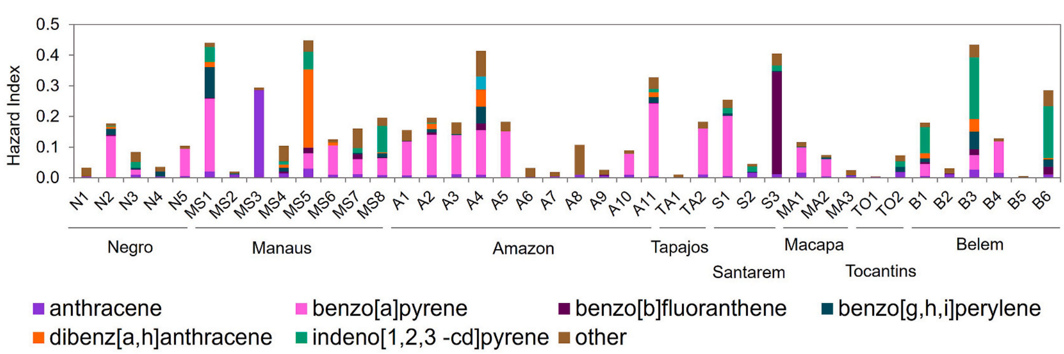

Fig. 3. Hazard Index (HI) calculated with chronic Predicted No Effect Concentrations (PNECs) for the PAH mixture found in the different water samples. Only compounds with an HI higher than 0.1 in at least one sample are displayed, while the rest are grouped as Other. An HI lower than 1 indicates low or insignificant risks in the sampling location due to the presence of PAH contamination.

Credit author statement

C. Rizzi: Investigation; Methodology; Formal Analysis; Writing - original draft. S. Villa: Investigation; Conceptualization; Writing - review & editing. M. Vighi: Conceptualization; Writing - review & editing. A.V. Waichman: Conceptualization; Investigation; Writing - review & editing. GS de Souza Nunes: Investigation; Writing - review & editing. R. de Oliveira: Conceptualization; Investigation; Writing - review & editing. A. Rico: Conceptualization; Formal analysis; Funding acquisition; Investigation; Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.139285.

References

Abdel-Shafy, H.I., Mansour, M.S., 2016. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. Egypt. J. Petrol. 25, 107–123. https://doi.org/10.1016/j.ejpe.2015.03.011.

Ambade, B., Sethi, S.S., Chintalacheruvu, M.R., 2023. Distribution, risk assessment, and source apportionment of polycyclic aromatic hydrocarbons (PAHs) using positive matrix factorization (PMF) in urban soils of East India. Environ. Geochem. Health 45, 491–505. https://doi.org/10.1007/s10653-022-01223-x.

Barbosa Jr., F., Rocha, B.A., Souza, M.C.O., Bocato, M.Z., Azevedo, L.F., Adeyemi, J.A., Santana, A., Campiglia, A.D., 2023. Polycyclic aromatic hydrocarbons (PAHs): updated aspects of their determination, kinetics in the human body, and toxicity. J. Toxicol. Environ. Health, Part B 26 (1), 28–65. https://doi.org/10.1080/10937404.2022.2164390.

Castello, L., McGrath, D.G., Hess, L.L., Coel, M.T., Lefebvre, P.A., Petry, P., Macedo, M. N., Renò, V.F., Arantes, C.C., 2013. The vulnerability of Amazon freshwater ecosystems. Conserv. Lett. 6, 217–229.

Chaves, M.J.S., Barbosa, S.C., Malinowski, M.M., Volpato, D., Castro, Í.B., Franco, T.C.R. D.S., Primel, E.G., 2020. Pharmaceuticals and personal care products in a Brazilian wetland of international importance: occurrence and environmental risk assessment. Sci. Total Environ. 10, 139374 https://doi.org/10.1016/j.scitotenv.2020.139374, 734.

dos Santos, A.D.J., Costa, L.H.M., de Lima Braga, M., Velloso, P.B., Ghamri-Doudane, Y., 2016. Characterization of a delay and disruption tolerant network in the Amazon basin. Vehicular Comm 5, 35–43. https://doi.org/10.1016/j.vehcom.2016.09.002.

Fabregat-Safont, D., Ibáñez, M., Bijlsma, L., Hernández, F., Waichman, A.V., de Oliveira, R., Rico, A., 2021. Wide-scope screening of pharmaceuticals, illicit drugs and their metabolites in the Amazon River. Water Res. 200, 117251 https://doi.org/10.1016/j.watres.2021.117251.

Fidelis, E.G., Querino, R.B., Adaime, R., 2023. The amazon and its biodiversity: a source of unexplored potential natural enemies for biological control (predators and parasitoids). Neotrop. Entomol. 52, 152–171. https://doi.org/10.1007/s13744-022-01024-y.

Godinho, M.B.D.C., da Silva, F.R., 2018. The influence of riverine barriers, climate, and topography on the biogeographic regionalization of Amazonian anurans. Sci. Rep. 8, 3427. https://doi.org/10.1038/s41598-018-21879-9.

Hartwell, S.I., Lomax, T., Dasher, D., 2020. Characterization of sediment contaminants in Arctic lagoons and estuaries. Mar. Pollut. Bull. 152, 110873 https://doi.org/10.1016/j.marpolbul.2019.110873.

Honda, M., Suzuki, N., 2020. Toxicities of polycyclic aromatic hydrocarbons for aquatic animals. Int. J. Environ. Res. Publ. Health 17 (4), 1363. https://doi.org/10.3390/ijerph17041363.

Ikenaka, Y., Sakamoto, M., Nagata, T., Takahashi, H., Miyabara, Y., Hanazato, T., Ishizuka, M., Isobe, T., Kim, J.-W., Chang, K.-H., 2013. Effects of polycyclic aromatic hydrocarbons (PAHs) on an aquatic ecosystem: acute toxicity and community-level toxic impact tests of benzo[a]pyrene using lake zooplankton community. J. Toxicol. Sci. 38 (1), 131–136. https://doi.org/10.2131/jts.38.131.

International Agency for Research on Cancer, 2010. Some Non-heterocyclic Polycyclic Aromatic Hydrocarbons and Some Related Exposures, vol. 92. IARC Press, International Agency for Research on Cancer.

Jiang, Y.F., Wang, X.T., Wu, M.H., Sheng, G.Y., Fu, J.M., 2011. Contamination, source identification, and risk assessment of polycyclic aromatic hydrocarbons in agricultural soil of Shanghai, China. Environ. Monit. Assess. 183, 139–150. https://doi.org/10.1007/s10661-011-1913-1.

Katsoyiannis, A., Sweetman, A.J., Jones, K.C., 2011. PAH molecular diagnostic ratios applied to atmospheric sources: a critical evaluation using two decades of source inventory and air concentration data from the UK. Environ. Sci. Technol. 45 (20), 8897–8906. https://doi.org/10.1021/es202277u.

Kumar, A., Sankar, T.K., Sethi, S.S., Ambade, B., 2020. Characteristics, toxicity, source identification and seasonal variation of atmospheric polycyclic aromatic hydrocarbons over East India. Environ. Sci. Pollut. Res. 27, 678–690. https://doi.org/10.1007/s11356-019-06882-5.

Lima, E.A.R., Neves, P.A., Patchineelam, S.R., et al., 2021. Anthropogenic and natural inputs of polycyclic aromatic hydrocarbons in the sediment of three coastal systems of the Brazilian Amazon. Environ. Sci. Pollut. Res. 28, 19485–19496. https://doi.org/10.1007/s11356-020-12010-5.

Mackay, D., Shiu, W.Y., Ma, K.-C., Lee, S.C., 2006. Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. CRC Press.

Mishra, A.K., Lehahn, Y., Rudich, Y., Koren, I., 2015. Co-variability of smoke and fire in the Amazon basin. Atmos. Environ. 109, 97–104. https://doi.org/10.1016/j.atmosenv.2015.03.007.

Fires Raged in the Amazon Again in 2020, 2020. NASA Earth Observatory. https://earthobservatory.nasa.gov/images/147946/fires-raged-in-the-amazon-again-in-2020.

Neves, P.A., Colabuono, F.I., Ferreira, P.A.L., Kawakami, S.K., Taniguchi, S., Figueira, R. C.L., Mahiques, M.M., Montone, R.C., Bícego, M.C., 2018. Depositional history of polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and polycyclic aromatic hydrocarbons (PAHs) in an Amazon estuary during the last century. Sci. Total Environ. 615, 1262–1270. https://doi.org/10.1016/j.scitotenv.2017.09.303.

Othman, H.B., Pick, F.R., Hlaili, A.S., Leboulanger, C., 2023. Effects of polycyclic aromatic hydrocarbons on marine and freshwater microalgae–A review. J. Hazard Mater. 441, 129869 https://doi.org/10.1016/j.jhazmat.2022.129869.

Paiva, P.F.P.R., de Lourdes Pinheiro Ruivo, M., da Silva Júnior, O.M., et al., 2020. Deforestation in protect areas in the Amazon: a threat to biodiversity. Biodivers. Conserv. 29, 19–38. https://doi.org/10.1007/s10531-019-01867-9.

Pichler, N., de Souza, F.M., dos Santos, V.F., Martins, C.C., 2021. Polycyclic aromatic hydrocarbons (PAHs) in sediments of the amazon coast: evidence for localized sources in contrast to massive regional biomass burning. Environ. Pollut. 268, 115958 https://doi.org/10.1016/j.envpol.2020.115958.

Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos. Environ. 42, 2895–2921. https://doi.org/10.1016/j.atmosenv.2007.12.010 submitted for publication.

Rico, A., de Oliveira, R., de Souza Nunes, G.S., Rizzi, C., Villa, S., Lopez-Heras, I., Vighi, M., Waichman, A.V., 2021. Pharmaceuticals and other urban contaminants threaten Amazonian freshwater ecosystems. Environ. Int. 155, 106702 https://doi.org/10.1016/j.envint.2021.106702.

Rico, A., de Oliveira, R., de Souza Nunes, G.S., Rizzi, C., Villa, S., De Caroli Vizioli, B., Montagner, C.C., Waichman, A.V., 2022. Ecological risk assessment of pesticides in urban streams of the Brazilian Amazon. Chemosphere 291, 132821. https://doi.org/10.1016/j.chemosphere.2021.132821.

Rico, A., Redondo-Hasselerharm, P.E., Vighi, M., Waichman, A.V., de Souza Nunes, G.S., de Oliveira, R., Singdahl-Larsen, C., Hurley, R., Nizzetto, L., Schell, T., 2023. Large-scale monitoring and risk assessment of microplastics in the Amazon River. Water Res. 232, 119707 https://doi.org/10.1016/j.watres.2023.119707.

Rizzi, C., Villa, S., Chimera, C., Finizio, A., Monti, G.S., 2021. Spatial and temporal trends in the ecological risk posed by polycyclic aromatic hydrocarbons in Mediterranean Sea sediments using large-scale monitoring data. Ecol. Indicat. 129, 107923 https://doi.org/10.1016/j.ecolind.2021.107923.

Rodrigues, C.C.S., Santos, L.G.G.V., Santos, E., Damasceno, F.C., Corrêa, J.A.M., 2018. Polycyclic aromatic hydrocarbons in sediments of the Amazon River Estuary (Amapá, Northern Brazil): distribution, sources and potential ecological risk. Mar. Pollut. Bull. 135, 769–775. https://doi.org/10.1016/j.marpolbul.2018.07.053.

Sese, B., Grant, A., Reid, B.J., 2009. Toxicity of polycyclic aromatic hydrocarbons to the nematode Caenorhabditis elegans. J. Toxicol. Environ. Health, Part A 72, 1–13. https://doi.org/10.1080/15287390903091814.

Sousa, L.C., Rodrigues, C.C.S., Mendes, R.A., Corrêa, J.A.M., 2020. PAH profiles in suspended particulate matter from an urbanized river within the Brazilian amazon. Bull. Environ. Contam. Toxicol. 105, 86–94. https://doi.org/10.1007/s00128-020-02912-y.

Souza, H.M.L., Taniguchi, S., Bícego, M.C., Oliveira, L.A., Oliveira, T.C.S., Barroso, H.S., Zanotto, S.P., 2015. Polycyclic aromatic hydrocarbons in superficial sediments of the Negro River in the amazon region of Brazil. J. Braz. Chem. Soc. 26 (No. 7), 1438–1449.

Syakti, A.D., Asia, L., Kanzari, F., Umasangadji, H., Lebarillier, S., Oursel, Garnier, C., Malleret, L., Ternois, Y., Mille, G., Doumenq, P., 2015. Indicators of terrestrial biogenic hydrocarbon contamination and linear alkyl benzenes as land-base pollution tracers in marine sediments. Int. J. Environ. Sci. Technol. 12, 581–594. https://doi.org/10.1007/s13762-013-0430-x.

Tobiszewski, M., Namiesnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environ. Pollut. 162, 110–119. https://doi.org/10.1016/j.envpol.2011.10.025.

Transforming Our World: the 2030 Agenda for Sustainable Development, 2015. UN General Assembly, 21 October 2015, A/RES/70/1, available at: https://www.refworld.org/docid/57b6e3e44.html. (Accessed 17 November 2022).

Vijayanand, M., Ramakrishnan, A., Subramanian, R., Issac, P.K., Nasr, M., Khoo, K.S., Rajagopal, R., Greff, B., Wan Azelee, N.I., Jeon, B.-H., Chang, S.W., Ravindran, B., 2023. Polyaromatic hydrocarbons (PAHs) in the water environment: a review on toxicity, microbial biodegradation, systematic biological advancements, and environmental fate. Environ. Res. 227 https://doi.org/10.1016/j.envres.2023.115716.

Wang, Y., Liu, M., Dai, Y., Luo, Y., Zhang, S., 2021. Health and ecotoxicological risk assessment for human and aquatic organism exposure to polycyclic aromatic hydrocarbons in the Baiyangdian Lake. Environ. Sci. Pollut. Res. Int. 28 (1), 574–586. https://doi.org/10.1007/s11356-020-10480-1.

Wilcke, W., Amelung, W., Martius, C., Garcia, M.V.B., Zech, W., 2000. Biological sources of polycyclic aromatic hydrocarbons (PAHs) in the amazonian rain forest. Z. Pflanzenernähr. Bodenk 163, 27–30.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org. Geochem. 33, 489–515. https://doi.org/10.1016/S0146-6380(02)00002-5.

Zhang, X.L., Tao, S., Liu, W.X., Yang, Y., Zuo, Q., Liu, S.Z., 2005. Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios: a multimedia approach. Environ. Sci. Technol. 39 (23), 9109–9114. https://doi.org/10.1021/es0513741.

Zheng, B., Wang, L., Lei, K., Nan, B., 2016. Distribution and ecological risk assessment of polycyclic aromatic hydrocarbons in water, suspended particulate matter and sediment from Daliao River estuary and the adjacent area, China. Chemosphere 149, 91–100. https://doi.org/10.1016/j.chemosphere.2016.01.039.