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Metals, *n*-Alkanes, Hopanes, and Polycyclic Aromatic Hydrocarbon in Sediments from Three Amazonian Streams Crossing Manaus (Brazil)

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Received: 22 February 2020; Accepted: 13 April 2020; Published: 18 April 2020



Abstract: Pollution is increasing in the Amazon region and its real impact is still unclear. Since this region is of great interest to the global community, this study aimed to assess geochemical biomarkers and metals in sediments from three streams crossing Manaus, a Brazilian city of 2.1 million inhabitants located in the heart of the Amazon rainforest. The Mindu and Quarenta streams criss-cross the urban area of Manaus and receive domestic effluents from many heavily populated districts. In addition, the Quarenta stream is subjected to effluents from the industrial district of Manaus. The Tarumã-Açu stream is mostly covered by vegetation, although the region presents some occurrence of family farming, floating petrol station, marinas, and floating restaurants and bars. *n*-Alkanes were determined by Gas Chromatography with Flame Ionization Detection (GC-FID), whereas hopanes and polycyclic aromatic hydrocarbons (PAHs) were determined by Gas Chromatography coupled to Mass Spectrometry (GC-MS). The metals Ag, Cd, Cr, Co, Cu, Mn, Ni, Pb, and Zn were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) after microwave-assisted acid digestion. Concentrations of total PAHs and metals were higher in sediments from the urban streams Mindu and Quarenta because of the occurrence of more intense and diverse sources of pollution. In addition, some sediment samples from both these streams presented concentrations of fluoranthene, phenanthrene, and metals higher than the limits of low probability of adverse effects on biota established by the international guideline and by the Brazilian legislation. A similar total *n*-alkane concentration for sediments from all streams associated with profiles of *n*-alkanes with no odd/even hydrocarbon predominance suggests that biomass burning is an important source of hydrocarbons. Petroleum-derived products also represented a source for *n*-alkanes, as confirmed by the presence of α,β -hopanes, including an α,β -homohopane series from C₃₁ to C₃₅ with the presence of both 22*S* and 22*R* epimers. This is the first report on *n*-alkanes, PAHs, and hopanes in sediments from the Mindu, Quarenta, and Tarumã-Açu streams. The concentrations reported herein may be considered as baseline data in future monitoring programs of these streams.

Keywords: geochemical biomarkers; Mindu stream; Quarenta stream; Tarumã-Açu stream

1. Introduction

The Amazon basin stretches across 7.05 million square kilometers and is home to the iconic Amazon river, which, with its tributaries, contain 20% of world's fresh water [1]. However, since the beginning of the colonization of the Amazon region, anthropogenic actions have put pressure on water resources and created imbalances in the complex dynamics of the ecosystem [2]. Part of this complexity relies on the composition of the sedimentary organic matter (SOM) in waterbodies, which include compounds of autochthonous and allochthonous origin [3]. With this in mind, several classes of geochemical biomarkers and/or persistent organic pollutants have been addressed in order to study the short- or long-term impacts of natural or anthropogenic pressures on the Amazon waterbodies [4–9].

Classes of lipid biomarkers that represent different sources of organic matter (OM) have been widely employed as tracers and, among them, *n*-alkanes and hopanes play central roles [5,10–12]. Long-chain *n*-alkanes with an odd number of carbons (C_{27} – C_{35}) are derived from epicuticular waxes of superior plants, whereas those with short-chain (C_{15} – C_{19}) are derived from algae [3,13]. However, petroleum *n*-alkanes show no predominance of either odd- or even-numbered homologous [13]. Hopanes are lipid biomarkers with a pentacyclic triterpene structure, and originate from membranes of prokaryotes [14,15]. Such compounds are recalcitrant and therefore used to investigate oil and refined products in the SOM [14,15]. Hopanes occur as α/β (*R/S*) stereoisomers (positions C-17 and C-21) that possess different thermodynamic stabilities, and can vary from C_{30} – C_{35} as a quantity of carbon analogues [14,15]. Thus, petrogenic (petroleum and derived products) and biogenic sources (vascular plants, algae, and bacteria) tend to have distinct hopane profiles [14,15]. For example, the β,β -hopane configuration is biogenic, whereas the α,β -hopane configuration is more thermodynamically stable, and is therefore dominant in petroleum sources [14,15].

Persistent organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), are of great concern [16]. Three main sources of PAHs correspond to the following: I) pyrolytic that are emitted during the incomplete burning of coal, charcoal, oil-derivatives, gas, garbage, wood, biomass, and other organic materials; II) petrogenic that are formed in geological processes over long periods of time; and III) diagenetic that are derived from biogenic precursors, such as plants [17,18]. PAHs arose from atmospheric deposition, urban stormwater runoff, and domestic/industrial effluents accumulate in sediments [17,18]. Metals can reveal some harmful human activities near waterbodies, such as intensive agriculture, industry, mining, and urban pollution [19]. The concern regarding the metal levels is linked to the metals' toxicity and accumulative behavior [19]. Among the most toxic and harmful to the environment, the metals zinc, cadmium, lead, copper, nickel, and cobalt stand out in several studies [20–22].

The measurement of organic geochemical biomarkers, persistent organic pollutants, and metals in Amazonian waterbodies have been described in previous studies [5–9,22–26]. However, one of the most iconic urban centers of Brazil, and the biggest metropolis of the Amazon, Manaus, remains poorly studied in this respect [6,25,26]. According to the Brazilian Institute of Geography and Statistics—IBGE (2019) [27]—Manaus is an industrial city with 2,182,763 inhabitants. It is surrounded by a dense hydrographic network composed of rivers and streams that are called “igarapés” [9,28]. Igarapé, in the indigenous Tupi-Guarani language, means watercourse, and can be understood as a small waterbody, generally a tributary river or a canal that is navigable. In Manaus, some important tributaries flow into the Negro river and in a few kilometers into the Amazon river that is formed from the confluence with the Solimões river [9,28]. In this sense, contaminants released into the urban streams running through Manaus can reach the Negro river and, consequently, the Amazon river [9,28].

This study aimed to assess sediments from the three main streams of Manaus—Mindu, Quarenta, and Tarumã-Açu—in order to evaluate their sources of OM. For the purpose of identifying biogenic (aquatic and terrestrial) and anthropogenic (petroleum derivatives and biomass burning) OM, different classes of biomarkers were chosen. *n*-Alkanes, hopanes, and PAHs were determined and diagnostic ratios were calculated in order to investigate the SOM origin. In addition, concentrations of *n*-alkanes and PAHs determined herein will be useful as baseline data in future studies. Metals were included in

this study in order to investigate whether or to what point the industrial district of Manaus contributes as a source of contaminants.

2. Materials and Methods

2.1. Study Area and Sample Collection

Manaus (Amazonas state, Brazil) is situated in the western Brazilian Amazon (03°06' S, 60°01' W) (Figure 1). The city is criss-crossed by several streams that flow into the Negro river, which, after meeting the Solimões river is called the Amazon. Of these streams, Tarumã-Açu, Mindu, and Quarenta are the most important that cross Manaus [9,28]. The Mindu and Quarenta streams receive effluents from many heavily populated districts of the city [9,28]. Furthermore, the Quarenta stream receives effluents from the industrial district of Manaus [9,28]. The Tarumã-Açu stream is located in a peri-urban area and is mostly surrounded by vegetation. Although, activities such as family farming, boat repair, marinas, a floating petrol station, and floating bars and restaurants, exist in the region [9]. The study area and sampling stations are shown in Figure 1, and geographic coordinates are shown in Table S1 (see Supplementary Material). A total of twenty-six surface sediment samples (0–10 cm depth) were collected from the Mindu (São Raimundo basin) ($n = 9$), Quarenta (Educandos basin) ($n = 6$), and Tarumã-Açu (Tarumã-Açu basin) ($n = 11$) streams in March 2017 with a Van Veen sampler. All sediment samples were lyophilized, homogenized in a mortar with a pestle, and stored at room temperature until extraction.

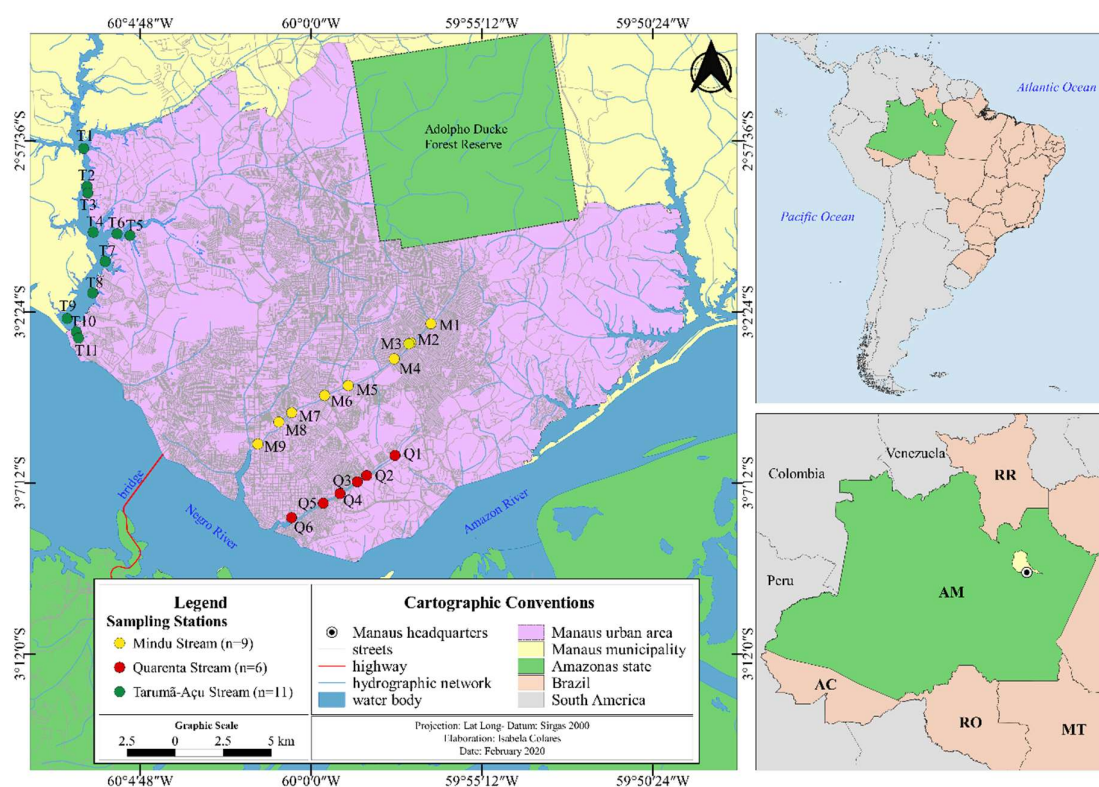


Figure 1. Study area and sampling stations in the Mindu (M), Quarenta (Q), and Tarumã-Açu (T) streams.

2.2. Chemicals and Reagents

High purity HNO_3 , HPLC-grade solvents (hexane, dichloromethane, and methanol) were purchased from Tedia (Mexico City, CMX, Mexico). The standard PAHs mixture (see Table S2 in Supplementary Material) was obtained from AccuStandard (New Haven, CT, USA). The standards n -hexadecane- d_{34} , n -triacontane- d_{62} , p -terphenyl- d_{14} , n - C_7 - $n\text{C}_{40}$ alkane mixture, and the certified

reference material CNS301 (trace elements in freshwater sediment) were obtained from Sigma-Aldrich (St. Louis, MO, USA). ICP multi-element standard solution IV CertiPUR was acquired from Merck (Darmstadt, HE, Germany). Silica gel (230–400 mesh) was bought from SiliCycle (Quebec, QC, Canada). Metallic copper was purchased from Dinâmica Química Contemporânea (Indaiatuba, SP, Brazil).

2.3. Sample Preparation

A total of 5.0 g of lyophilized sediment sample with 1.0 g of powdered metallic copper and the recovery standards was extracted with 15.0 mL of dichloromethane and methanol mixture (2:1, V/V). Extractions were carried out exhaustively (3×) for 15 min (each) in an ultrasonic bath, operating at a frequency of 40 kHz. Then, the combined extract was concentrated by roto-evaporation and a gentle nitrogen stream. The recovery standards were *n*-triacontane-*d*₆₂ (2.0 µg) for *n*-alkanes and *p*-terphenyl-*d*₁₄ (500.0 ng) for PAHs.

2.4. Extract Fractionation

The extracts were fractionated by column chromatography in 5.0 g of silica gel and 1.0 g of alumina. The combined extract was applied to the top of the column, and elutions were performed with 40.0 mL of hexane (saturated fraction, F1) and 70.0 mL of a mixture of hexane and dichloromethane (1:1, V/V) (aromatic fraction, F2).

2.5. Gas Chromatography Analysis

The *n*-alkanes (F1) were analyzed by Gas Chromatography with Flame Ionization Detection (GC-FID) model 2010 (Shimadzu, Kyoto, Japan) equipped with auto sampler model AOC-20s and auto injector model AOC-20i (Shimadzu, Kyoto, Japan). An SGE HT-5 capillary column (25 m, a 0.32-mm internal diameter, and a 0.10-µm film thickness) (Trajan Scientific and Medical, Ringwood, VIC, Australia) was used under the following conditions: nitrogen as the carrier gas (1.70 mL/min), splitless injection mode and temperature program: 60 °C (held for 5 min), increasing by 5 °C/min to 330 °C (held for 5.0 min). The injector and detector temperatures were kept at 280 and 330 °C, respectively. Hopanes (F1) and PAHs (F2) were analyzed by Gas Chromatography coupled to Mass Spectrometry (GC-MS) model QP2010 (Shimadzu, Kyoto, Japan) equipped with auto sampler model AOC-20s and auto injector model AOC-20i (Shimadzu, Kyoto, Japan). An RTX-5MS capillary column (30 m, a 0.25-mm internal diameter, and a 0.25-µm film thickness) (Restek, Bellefonte, PA, USA) was used to separate the compounds with a flow of helium at 1.00 mL/min. The injection (1.0 µL) was in the splitless mode with a temperature program of 60 °C (held for 5 min), increasing by 5 °C/min to 300 °C (held for 10.0 min). The injector, transfer line, and ion source temperatures were 280, 300, and 200 °C, respectively. The determination of PAHs was performed in the selected ion monitoring (SIM) analysis mode, considering the molecular ions listed in Table S2 (see Supplementary Material). Hopanes were monitored according to their molecular ions (*m/z* 370 (C₂₇), 384 (C₂₈), 398 (C₂₉), 412 (C₃₀), 426 (C₃₁), 440 (C₃₂), 454 (C₃₃), 468 (C₃₄), and 482 (C₃₅)) and fragments (*m/z* 191 and 177). In addition, the characteristic elution order of these biomarkers was considered in the identification.

2.6. Metal Determination

The quantitative determination of the metals was performed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using an optical equipment model iCAP 7600 Duo (Thermo Scientific, Waltham, MA, USA) with an ultrasonic nebulizer model U5000AT+ (Cetac Technologies, Omaha, NE, USA). Sample digestion was performed from 500 mg of sediment with 10.0 mL of HNO₃ in Teflon bombs using a microwave oven, model Mars 230/60 (CEM Corporation, Charlotte, NC, USA). The temperature of extraction rose to 165 ± 5 °C in 2 min, then rose to 175 ± 5 °C in 3 min, and remained at 175 ± 5 °C for 5 min. The digests were centrifuged at 3000 rpm for 10 min to clear the supernatant, which was diluted to 50.0 mL with deionized water and directly analyzed by ICP-OES to determine the concentrations of Ag, Cd, Cr, Co, Cu, Mn, Ni, Pb, and Zn.

2.7. Quantification and Quality Control

Quality assurance procedures, such as column performance checks and blank runs were performed for each sample set, and no interfering peaks/signals in the determination of the target compounds/metals were verified.

n-Alkanes were individually identified by matching the retention time observed for samples to those observed for a standard solution of *n*-C₇ to *n*-C₄₀ mixture. The quantitative determination of *n*-alkanes was performed through internal calibration using *n*-hexadecane-*d*₃₄ as internal standard. The calibration curves consisting of *n*-C₇ to *n*-C₄₀ alkane mixture at 1.0, 2.5, 5.0, 7.5, 10.0, 20.0, and 50.0 µg/mL, and 5.0 µg/mL of *n*-hexadecane-*d*₃₄ were constructed by plotting the analyte peak area/internal standard peak area versus the concentration of analyte. Each *n*-alkane was individually quantified by its respective calibration curve.

PAHs were identified by matching both molecular ion and retention time observed for samples to those observed for a standard solution, as listed in Table S2 (see Supplementary Material). The quantitative determination of PAHs was performed through internal calibration using deuterated homologous internal standards, as listed in Table S2 (see Supplementary Material). The calibration curves, consisting of the PAH mixture at 10.0, 50.0, 100.0, 150.0, 200.0, 400.0, 500.0, 600.0, 800.0, and 1000.0 ng/mL, and the deuterated PAH mixture at 500.0 ng/mL, were constructed by plotting the analyte peak area/internal standard peak area versus the concentration of analyte. Each PAH was individually quantified by its respective calibration curve and internal standard.

The quantitative determination of the metals (Ag, Cd, Cr, Co, Cu, Mn, Ni, Pb, and Zn) was performed via external calibration, using the same acid matrix used for the sediment analyses. The calibration curves consisting of the mixture of metals at 1.0, 5.0, 10.0, 25.0, 100.0, 500.0, and 1000.0 ng/mL were constructed by plotting the metal signal area versus its concentration. Each metal was individually quantified by its respective calibration curve.

In order to evaluate the accuracy of the analyses, sediment samples were spiked with recovery standards (*p*-terphenyl-*d*₁₄ for PAHs and *n*-triacontane-*d*₆₂ for *n*-alkanes) prior to extraction. For both *n*-alkanes and PAHs, accuracy was calculated by comparing the concentration found for the respective recovery standard in the samples with its concentration in solvent. For metals, accuracy was evaluated by analyzing the certified reference material CNS301 (trace elements of freshwater sediment) in triplicate and comparing the concentrations found herein with those reported in the certificate of analysis.

In order to evaluate the precision of the analyses, a composite sample was subjected to the procedures described above in triplicate, and the concentrations found for *n*-alkanes, PAHs, and metals were used to calculate their relative standard deviations.

3. Results

3.1. Grain Size Distribution

The grain size distribution was similar for the sampling stations of each stream studied, with the sandy fraction predominant in all of them (Table S3). Sediments from the Mindu stream presented mainly medium and fine sand as the main fractions, whereas sediments from the Quarenta stream presented coarse and medium sand as the main ones. Sediments from the Tarumã-Açu stream varied mainly between very coarse and fine sand fractions. In the Mindu stream samples, M5 had the highest mud (silt + clay) fraction (5.34%), whereas in the Quarenta stream samples, Q6 presented the highest mud fraction (13.50%). All of the Tarumã-Açu sediment samples presented very low mud content (≤3.17%).

3.2. Aliphatic Hydrocarbons

The quantitative determination of the *n*-alkanes *n*-C₇-*n*-C₄₀ was performed by GC-FID and their individual concentrations are given in Tables S4–S6 (see Supplementary Material). The accuracy of

the results found for *n*-alkanes are represented by the recovery of *n*-triacontane- d_{62} , which was in the range of 73–94%.

Table 1 shows the total *n*-alkane concentrations for sediment samples from Mindu, Quarenta, and Tarumã-Açu streams.

Sediments from the Mindu stream presented total *n*-alkane concentrations which ranged from 3.02 (M6) to 4.74 $\mu\text{g g}^{-1}$ (M5), whereas, for the sediments from the Quarenta stream, total *n*-alkane concentrations ranged from 1.13 (Q3) to 6.49 $\mu\text{g g}^{-1}$ (Q6). In the Mindu and Quarenta stream samples, M5 and Q6 had the highest total *n*-alkane concentrations. Such accumulation may be related to the highest mud contents presented by these two samples. Total *n*-alkane concentrations showed a wider range from 2.23 (T8) to 10.51 (T9) $\mu\text{g g}^{-1}$ for sediments from the Tarumã-Açu stream. The highest total *n*-alkane concentration found for the sample T9 suggests a point-source of hydrocarbon in the area. The total *n*-alkane concentration did not show any pattern along the streams studied. Figure 2 shows the *n*-alkane distribution for two sediment samples from each stream studied.

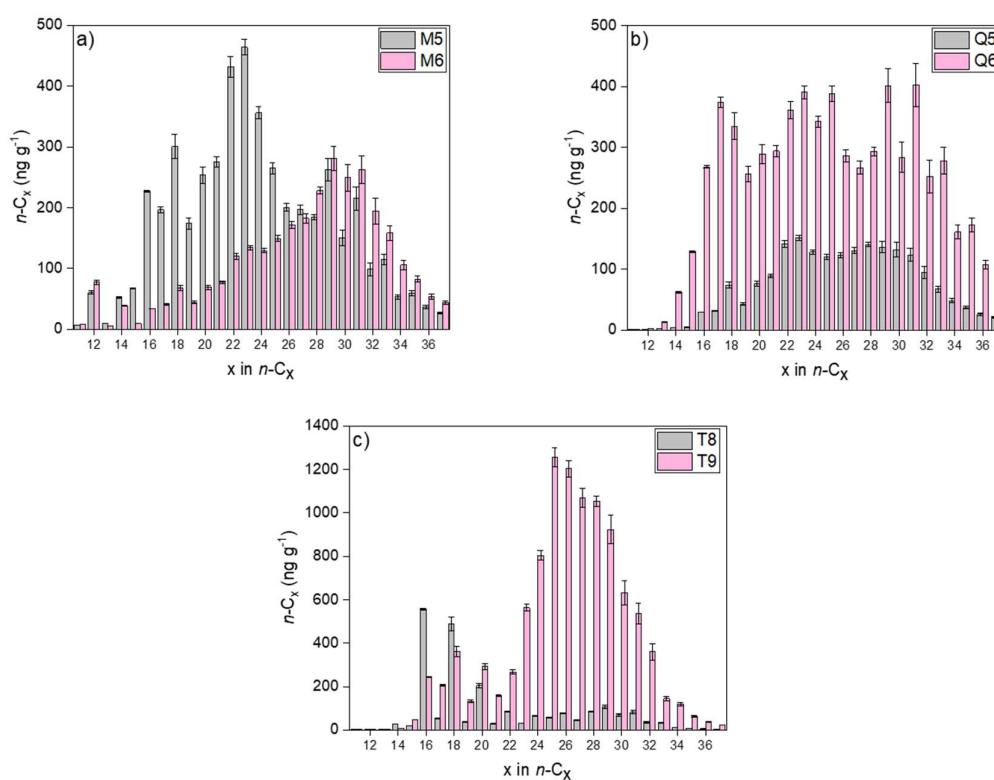


Figure 2. *n*-Alkane profiles for surface sediment samples from the (a) Mindu (M), (b) Quarenta (Q), and (c) Tarumã-Açu (T) streams.

Table 1. Concentrations and ratios of hydrocarbons in the sediment samples from the Mindu (M), Quarenta (Q), and Tarumã-Açu (T) streams.

	Total <i>n</i> -Alkanes μg g ⁻¹	CPI	C30 αβ/ββ	C31 αβ S/(S + R)	C32 αβ S/(S + R)	C33 αβ S/(S + R)	C34 αβ S/(S + R)	C35 αβ S/(S + R)	Total PAHs ng g ⁻¹	Fl (Fl + Py)	BaA (BaA + Ch)	BaA Ch
M1	2.26	0.96	1.15	0.53	0.54	0.59	0.59	0.60	351.69	0.76	0.33	0.49
M2	1.55	0.99	1.12	0.51	0.53	0.61	0.61	0.58	248.95	0.80	0.29	0.41
M3	2.41	0.94	1.23	0.54	0.61	0.62	0.60	0.59	259.09	0.73	0.28	0.39
M4	4.04	1.03	1.18	0.52	0.54	0.61	0.60	0.60	352.31	0.76	0.30	0.43
M5	4.74	1.26	1.22	0.53	0.56	0.65	0.60	0.63	441.58	0.71	0.23	0.30
M6	3.02	1.08	1.56	0.54	0.63	0.63	0.54	0.58	118.95	0.75	0.27	0.38
M7	2.83	0.95	1.14	0.54	0.55	0.64	0.59	0.60	200.60	0.75	0.34	0.51
M8	2.43	0.99	1.33	0.52	0.58	0.61	0.58	0.58	152.00	0.76	0.32	0.48
M9	3.05	1.06	1.25	0.53	0.54	0.64	0.59	0.59	230.18	0.76	0.37	0.59
Q1	3.68	0.93	1.25	0.53	0.61	0.62	0.61	0.57	249.82	0.73	0.41	0.69
Q2	3.81	1.22	1.32	0.51	0.54	0.60	0.60	0.58	234.70	0.73	0.40	0.67
Q3	1.13	0.99	1.18	0.53	0.59	0.63	0.61	0.60	240.93	0.75	0.37	0.67
Q4	4.84	0.94	1.18	0.52	0.54	0.62	0.59	0.66	209.63	0.75	0.40	0.58
Q5	1.98	1.00	1.12	0.53	0.57	0.59	0.58	0.60	227.39	0.77	0.36	0.66
Q6	6.49	1.27	1.47	0.53	0.55	0.63	0.60	0.61	380.12	0.56	0.16	0.56
T1	3.25	0.92	-	-	-	-	-	-	181.57	0.74	0.41	
T2	2.60	0.95	-	-	-	-	-	-	93.58	0.68	0.39	0.70
T3	3.76	0.89	-	-	-	-	-	-	106.09	0.76	0.44	0.65
T4	3.39	0.93	-	-	-	-	-	-	187.05	0.78	0.43	0.77
T5	2.97	0.85	-	-	-	-	-	-	108.94	0.72	0.42	0.76
T6	2.59	0.86	-	-	-	-	-	-	64.86	0.67	0.42	0.73
T7	4.56	0.90	-	-	-	-	-	-	72.57	0.61	0.37	0.72
T8	2.23	1.05	-	-	-	-	-	-	55.18	0.59	0.42	0.58
T9	10.51	1.06	3.29	0.48	0.66	0.60	-	-	123.65	0.73	0.41	0.71
T10	4.72	1.05	3.29	0.50	0.56	0.67	0.58	0.69	147.58	0.79	0.43	0.69
T11	4.99	0.93	2.18	0.52	0.61	0.61	0.68	0.53	196.81	0.80	0.41	0.74

CPI: Carbon Preference Index = $2(\Sigma_{\text{odd } n\text{-C}_{25}\text{-}n\text{-C}_{33}})/[(\Sigma_{\text{even } n\text{-C}_{24}\text{-}n\text{-C}_{32}}) + (\Sigma_{\text{even } n\text{-C}_{26}\text{-}n\text{-C}_{34}})]$; Fl/(Fl + Py) = Fluoranthene/(Fluoranthene + Pyrene); BaA/(BaA + Ch) = Benzo[*a*]anthracene/Benzo[*a*]anthracene + Chrysene; BaA/Ch = Benzo[*a*]anthracene/Chrysene.

The *n*-alkane distributions shown in Figure 2 are representatives of the others for each stream studied. All the sediment samples from the Mindu stream showed *n*-alkane distribution profile similar to that of the sample M6, whereas only M5 showed a higher contribution of shorter homologous. Similarly, the sample Q6 is representative for the Quarenta stream, although Q4 had shown a higher contribution of shorter homologous. For the Tarumã-Açu stream, the sample T8 showed a *n*-alkane distribution profile similar to those of the samples T1-T5, T7, and T8, whereas the sample T9 is representative of the samples T6, T10, and T11. Sediment samples collected from the Mindu, Quarenta, and Tarumã-Açu streams showed the presence of *n*-alkanes ranging between *n*-C₁₁ and *n*-C₃₇, with no clear predominance of a specific *n*-alkane for the majority of them (Figure 2). Moreover, the *n*-alkane distribution showed no odd/even hydrocarbon predominance, as observed in sediments subjected to petroleum-derived OM [5,11]. The carbon preference index (CPI), defined as the odd to even carbon-number *n*-alkanes ratio in the range of *n*-C₂₅ to *n*-C₃₄ [10], varied between 0.85 and 1.26 (Table 1). Such values are considered as indicative of fossil origin for *n*-alkanes in the SOM [5,10,11]. In particular, some sediment samples from the Tarumã-Açu stream presented an unusual contribution of even-numbered short-chain *n*-alkanes, specifically *n*-C₁₆, *n*-C₁₈, and *n*-C₂₀. An unresolved complex mixture (UCM), which is generally associated with degraded or weathered petroleum residues [5,10,11], was only detected for the sample Q6.

Geochemical biomarkers of the hopane class were assessed in this study in order to corroborate the presence of petroleum-derived products, as suggested by the *n*-alkane profiles. A hopane series ranging from C₂₇ to C₃₅ was identified in all of the surface sediment samples from the Mindu and Quarenta streams and in a few of those from the Tarumã-Açu stream. Figure 3 shows three extracted ion chromatograms (*m/z* 191) for pentacyclic triterpanes to represent the streams studied.

Figure 3 shows that the more thermodynamically stable α,β -hopane configuration predominates over the biogenic β,β -hopane one, for example, for 17 α (H),21 β (H)-hopane (C₃₀), in the sediments from all of the three streams studied. Moreover, an α,β -homohopane series from C₃₁ to C₃₅ with the presence of both 22*S* and 22*R* epimers was observed in all of the sediment samples from the Mindu and Quarenta streams, and for a few of those from the Tarumã-Açu stream. The relative distribution of anthropogenic-related hopanes to biogenic ones is shown in Table 1. Values higher than 1.0 for the ratio of the hopane C₃₀ α,β to β,β configuration, and in the range between 0.51 and 0.66 for the ratio of α,β -homohopanes 22*S* to 22*R* + 22*S* are important to confirm the presence of petroleum-derived products in the streams studied.

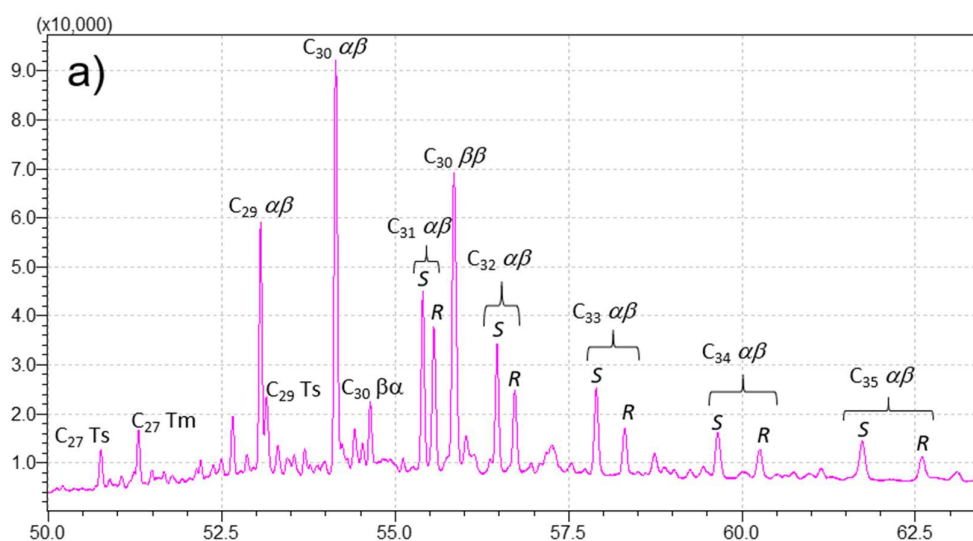


Figure 3. Cont.

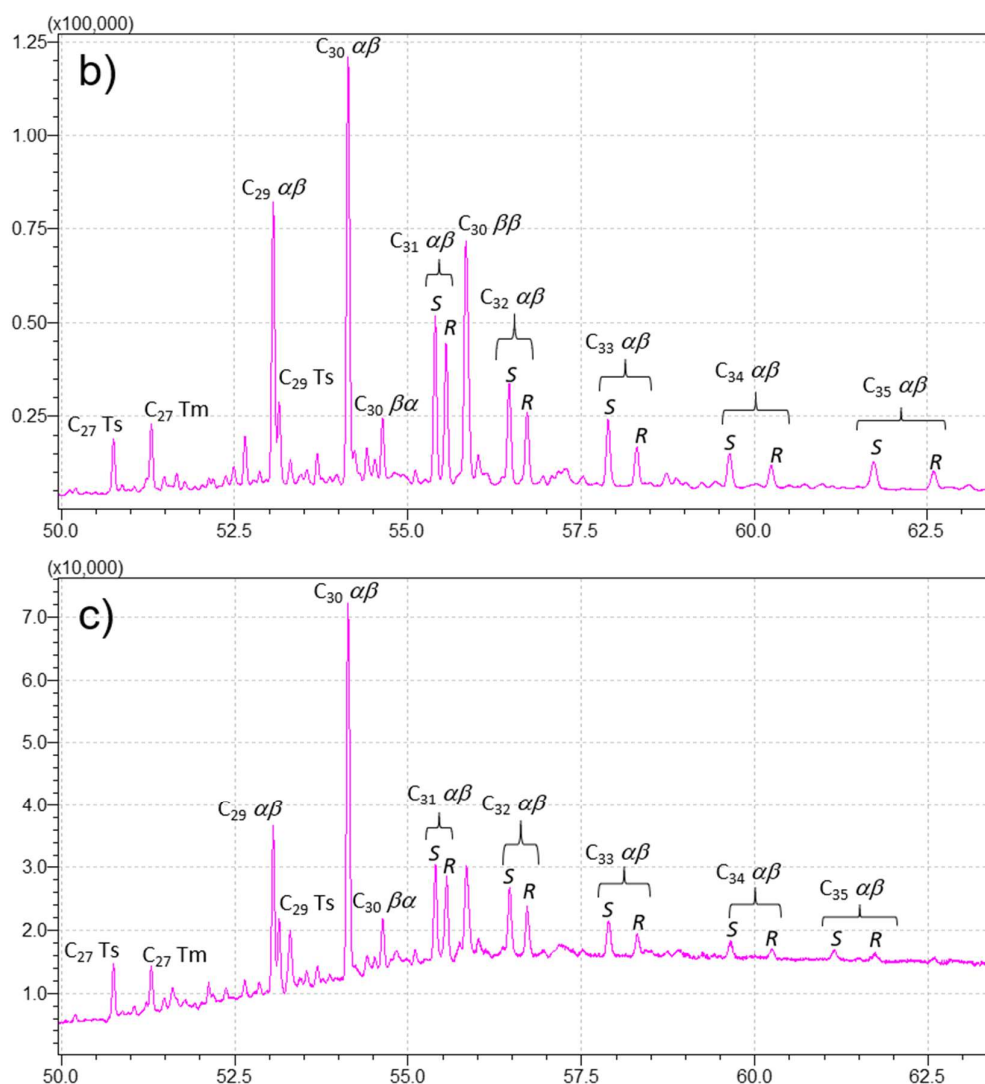


Figure 3. Extracted ion chromatograms (m/z 191) for pentacyclic triterpanes of sediment samples from the (a) Mindu, (b) Quarenta, and (c) Tarumã-Açu streams. C_{27} Ts: $18\alpha(H)22,29,30$ -trisorneohopane; C_{27} Tm: $17\alpha(H)22,29,30$ -trisnorhopane; C_{29} $\alpha\beta$: $17\alpha(H),21\beta(H)$ -30norhopane; C_{29} Ts: $18\alpha(H),21\beta(H)$ -30-norneohopane; C_{30} $\alpha\beta$: $17\alpha(H),21\beta(H)$ -hopane; C_{30} $\beta\alpha$: $17\beta(H),21\alpha(H)$ -hopane; C_{31} $\alpha\beta$ -S: $17\alpha(H),21\beta(H)$ -31-homohopane-22S; C_{31} $\alpha\beta$ -R: $17\alpha(H),21\beta(H)$ -31-homohopane-22R; C_{30} $\beta\beta$: $17\beta(H),21\beta(H)$ -hopane; C_{32} $\alpha\beta$ -S: $17\alpha(H),21\beta(H)$ -32-bis-homohopane-22S; C_{32} $\alpha\beta$ -R: $17\alpha(H),21\beta(H)$ -32-bishomohopane-22R; C_{33} $\alpha\beta$ -S: $17\alpha(H),21\beta(H)$ -33-tris-homohopane-22S; C_{33} $\alpha\beta$ -R: $17\alpha(H),21\beta(H)$ -33-tris-homohopane-22R; C_{34} $\alpha\beta$ -S: $17\alpha(H),21\beta(H)$ -34-tetrakis-homohopane-22S; C_{34} $\alpha\beta$ -R: $17\alpha(H),21\beta(H)$ -34-tetrakis-homohopane-22R; C_{35} $\alpha\beta$ -S: $17\alpha(H),21\beta(H)$ -35-pentakis-homohopane-22S; C_{35} $\alpha\beta$ -R: $17\alpha(H),21\beta(H)$ -35-pentakis-homohopane-22R.

3.3. Polycyclic Aromatic Hydrocarbons

The quantitative determination of PAHs was performed by GC-MS and their individual concentrations are given in Tables S7–S9 (see Supplementary Material). The accuracy of the results found for PAHs are represented by the recovery of p -terphenyl- d_{14} , which was in the range of 75–91%. Sediments from the Mindu stream presented total PAH concentrations from 118.95 to 441.58 ng g^{-1} for M6 and M5, respectively. In the same order of magnitude, sediments from the Quarenta stream presented total PAH concentrations from 209.63 to 380.12 ng g^{-1} for Q4 and Q6, respectively. The highest total PAH concentrations found for M5 and Q6 may be related to their higher mud contents. The total PAH concentrations ranged from 55.18 (T8) to 196.81 (T11) ng g^{-1} for sediments from the Tarumã-Açu

stream. The total PAH concentration did not show any pattern along the streams studied. In most of the sediment samples from the three streams studied, the highest concentrations were observed for the PAHs phenanthrene, fluoranthene, and pyrene. Investigations regarding the sources of PAHs in the environment were made by considering their relative proportion based on ring number and diagnostic ratios, as shown in Figure 4 and Table 1, respectively.

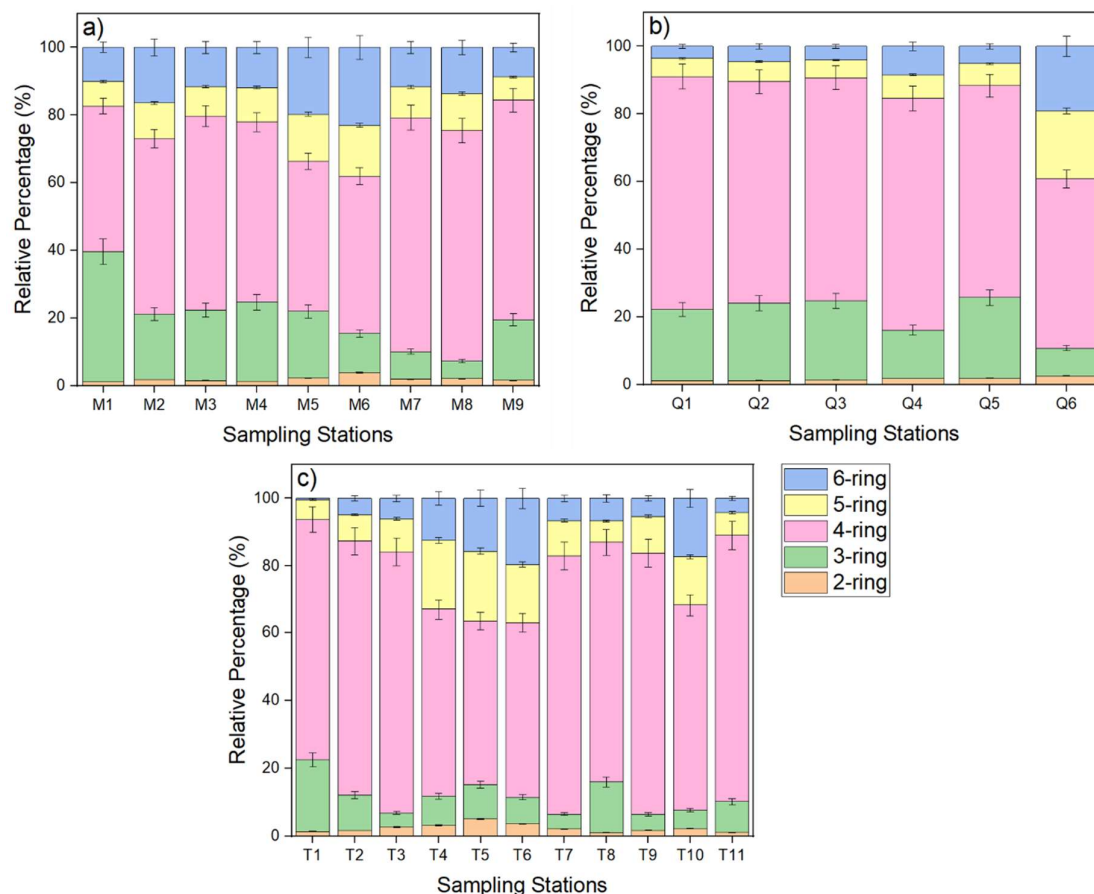


Figure 4. Relative percentage of PAHs based on their ring number for surface sediment samples from the (a) Mindu (M), (b) Quarenta (Q), and (c) Tarumã-Açu (T) streams.

Figure 4 shows that 4-ring PAHs were predominant in all sediment samples from the three studied streams, whereas 2-ring PAHs always presented a very low contribution. In addition, low molecular mass PAHs (sum of 2-ring and 3-ring PAHs) generally had about 20% of the contribution. In general, 3-ring PAHs presented a higher contribution in sediment samples from the Mindu and Quarenta streams in relation to those from the Tarumã-Açu stream. Ratios, such as Fluoranthene/(Fluoranthene + Pyrene) $\{Fl/(Fl + Py)\}$, Benzo[a]anthracene/(Benzo[a]anthracene + Chrysene) $\{BaA/(BaA + Ch)\}$, and BaA/Ch , are important for investigating the PAHs origin in the SOM [17,18]. The values of such ratios for the sediments under study are shown in Table 1. For surface sediment samples from the Tarumã-Açu stream, the ratio $Fl/(Fl + Py)$ ranged between 0.59 and 0.80, which indicates combustion as a principal source of PAHs. In addition, the ratio $BaA/(BaA + Ch)$ varied between 0.37 and 0.44, revealing the dominance of the isomer formed during combustion [17]. The diagnostic ratio $Fl/(Fl + Py)$ for surface sediment samples from the Mindu and Quarenta streams also indicated combustion as the principal source of PAHs. For these two streams, some sediments presented values for $BaA/(BaA + Ch)$ a little lower than 0.35—the limit for classifying the source as combustion [17]. In particular, the Q6 sample presented outlier values for both diagnostic ratios, 0.56 and 0.16 for $Fl/(Fl + Py)$ and $BaA/(BaA + Ch)$, respectively. The value found for $BaA/(BaA + Ch)$ indicates petroleum-derived products as the main source of PAHs in the area where Q6 sampling occurred [17].

3.4. Metals

The quantitative determination of metals was performed by ICP-OES, and their individual concentrations are given in Table 2. The accuracy for metals is represented by the recovery, which was calculated by comparing the concentrations found herein with those listed in the certified of the reference material CNS301 (trace elements of freshwater sediment).

In general, sediments from the Mindu and Quarenta streams showed higher individual concentrations for all metals in relation to those presented in the sediments from the Tarumã-Açu stream. In addition, metal concentrations did not show any pattern along the streams studied. Among the sediment samples collected in the Mindu stream, M5 was the one with the highest content of metals, followed by M7. These sampling stations are in an urban region, although they are not the closest to the most populated districts. None specific point-source of metals could be identified around the area of M5 and M7 stations. In particular, the sample Q6 differs by one order of magnitude for most metals in relation to the others. This may be justified by some characteristics of the sampling station, together with grain size distribution and the concentration of *n*-alkanes and PAHs, as discussed below. For the Tarumã-Açu stream, the metal concentrations did not vary a lot among samples. Figure 5 shows the relative percentage of metals in surface sediment samples from the three streams studied.

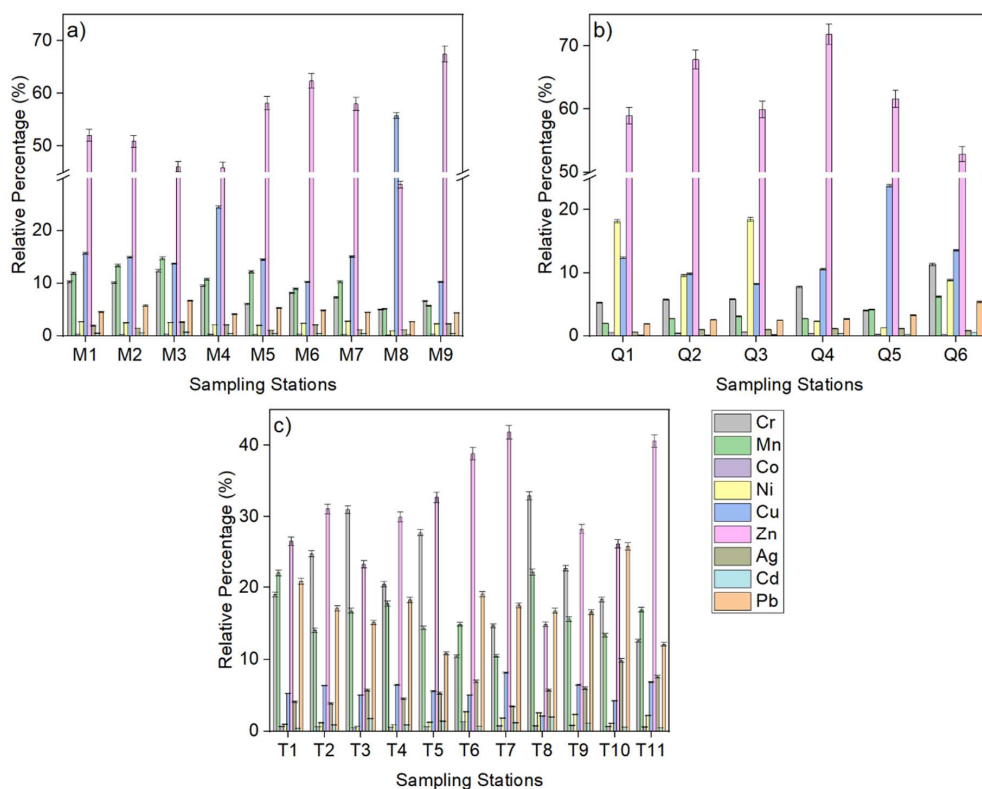


Figure 5. Relative percentage of metals in surface sediment samples from the (a) Mindu (M), (b) Quarenta (Q), and (c) Tarumã-Açu (T) streams.

The metal Zn was especially abundant in all of the sediment samples from the Mindu and Quarenta streams. In addition, Cu, Mn, and Cr presented considerable contribution in the sediments from both of these streams. The metal Cu was found in an outlier proportion in M8, whereas the metal Ni presented a higher contribution in sediments from the Quarenta stream, especially for the sampling stations near to the industrial district of Manaus. Sediments from the Tarumã-Açu stream presented a comparable contribution of metals, such as Zn, Pb, Mn, and Cr.

Table 2. Concentration of metals ($\mu\text{g g}^{-1}$) in surface sediment samples from the Mindu (M), Quarenta (Q), and Tarumã-Açu (T) streams.

Samples	Cr	Mn	Co	Ni	Cu	Zn	Ag	Cd	Pb
M1	3.62 ± 0.06	4.21 ± 0.08	0.12	0.95 ± 0.02	5.55 ± 0.05	18.38 ± 0.41	0.69	0.19 ± 0.003	1.61 ± 0.03
M2	6.53 ± 0.12	8.63 ± 0.16	0.20	1.61 ± 0.03	9.66 ± 0.09	32.83 ± 0.73	0.95	0.39 ± 0.006	3.72 ± 0.07
M3	4.68 ± 0.08	5.57 ± 0.11	0.15	0.97 ± 0.02	5.19 ± 0.05	17.42 ± 0.38	1.00	0.28 ± 0.004	2.54 ± 0.05
M4	4.89 ± 0.09	5.55 ± 0.11	0.17	1.11 ± 0.02	12.59 ± 0.12	23.60 ± 0.52	1.08	0.26 ± 0.004	2.15 ± 0.04
M5	11.84 ± 0.21	23.76 ± 0.45	0.51	3.96 ± 0.06	28.20 ± 0.27	113.09 ± 2.50	2.05	0.92 ± 0.02	10.32 ± 0.21
M6	3.08 ± 0.05	3.35 ± 0.06	0.15	0.89 ± 0.01	3.85 ± 0.04	23.38 ± 0.52	0.79	0.19 ± 0.003	1.81 ± 0.04
M7	8.33 ± 0.15	11.60 ± 0.22	0.34	3.23 ± 0.05	17.11 ± 0.16	65.66 ± 1.45	1.31	0.56 ± 0.009	5.08 ± 0.10
M8	3.76 ± 0.07	3.81 ± 0.07	0.15	0.73 ± 0.01	41.64 ± 0.40	21.46 ± 0.47	0.88	0.19 ± 0.003	2.01 ± 0.04
M9	1.72 ± 0.03	1.49 ± 0.03	0.11	0.61 ± 0.01	2.68 ± 0.03	17.58 ± 0.39	0.60	0.12 ± 0.002	1.15 ± 0.02
Q1	3.56 ± 0.06	1.36 ± 0.03	0.38	12.31 ± 0.20	8.40 ± 0.08	39.99 ± 0.88	0.43	0.12 ± 0.002	1.29 ± 0.03
Q2	4.25 ± 0.08	2.04 ± 0.04	0.33	7.07 ± 0.12	7.29 ± 0.07	50.30 ± 1.11	0.78	0.13 ± 0.002	1.94 ± 0.04
Q3	3.99 ± 0.07	2.14 ± 0.04	0.44	12.63 ± 0.21	5.65 ± 0.05	41.06 ± 0.91	0.69	0.14 ± 0.002	1.72 ± 0.03
Q4	3.14 ± 0.06	1.11 ± 0.02	0.17	0.94 ± 0.02	4.27 ± 0.04	29.01 ± 0.64	0.47	0.16 ± 0.003	1.09 ± 0.02
Q5	1.36 ± 0.02	1.40 ± 0.03	0.09	0.44 ± 0.01	7.94 ± 0.08	20.60 ± 0.46	0.40	0.09 ± 0.001	1.11 ± 0.02
Q6	37.54 ± 0.67	20.64 ± 0.39	0.76	29.26 ± 0.48	44.86 ± 0.43	174.86 ± 3.86	2.77	1.95 ± 0.03	17.85 ± 0.36
T1	0.50 ± 0.01	0.67 ± 0.01	0.03	0.09 ± 0.001	0.27 ± 0.01	1.62 ± 0.04	0.30	0.02 ± 0.001	0.48 ± 0.01
T2	0.74 ± 0.01	0.54 ± 0.01	0.03	0.05 ± 0.001	0.17 ± 0.01	1.05 ± 0.02	0.40	0.02 ± 0.001	1.04 ± 0.02
T3	2.21 ± 0.04	1.53 ± 0.03	0.08	0.23 ± 0.004	0.63 ± 0.01	2.76 ± 0.06	0.59	0.11 ± 0.002	1.62 ± 0.03
T4	3.78 ± 0.07	2.54 ± 0.05	0.09	0.30 ± 0.005	0.24 ± 0.01	1.71 ± 0.04	0.66	0.23 ± 0.004	1.93 ± 0.04
T5	2.52 ± 0.04	1.80 ± 0.03	0.13	0.31 ± 0.005	1.40 ± 0.01	7.16 ± 0.16	0.59	0.20 ± 0.003	3.00 ± 0.06
T6	0.46 ± 0.01	0.66 ± 0.01	0.06	0.12 ± 0.002	0.22 ± 0.01	1.72 ± 0.04	0.31	0.03 ± 0.001	0.85 ± 0.02
T7	1.65 ± 0.03	0.86 ± 0.02	0.04	0.07 ± 0.001	0.33 ± 0.01	1.95 ± 0.04	0.32	0.09 ± 0.001	0.65 ± 0.01
T8	1.30 ± 0.02	1.13 ± 0.02	0.04	0.06 ± 0.001	0.41 ± 0.01	1.91 ± 0.04	0.29	0.06 ± 0.001	1.17 ± 0.02
T9	2.99 ± 0.05	1.61 ± 0.03	0.05	0.07 ± 0.001	0.49 ± 0.01	2.24 ± 0.05	0.56	0.17 ± 0.003	1.46 ± 0.03
T10	1.80 ± 0.03	1.03 ± 0.02	0.05	0.09 ± 0.001	0.46 ± 0.01	2.27 ± 0.05	0.28	0.07 ± 0.001	1.25 ± 0.02
T11	2.72 ± 0.05	3.14 ± 0.06	0.10	0.14 ± 0.002	0.75 ± 0.01	3.77 ± 0.08	0.59	0.06 ± 0.001	2.98 ± 0.06
Recovery (%)	84–94	71–79	-	80–85	83–89	78–85	-	91–95	82–86
CV (%)	1.78	1.91	-	1.64	0.96	2.21	-	1.58	1.99

4. Discussion

Mud fraction versus total *n*-alkane and total PAH concentrations showed weak correlation, which indicates that grain size was not the main factor influencing the accumulation of such compounds in the study area. However, the two samples with the highest fine contents (M5 and Q6) were also the ones with the highest total *n*-alkane, total PAH, and metal concentrations. Both samples M5 and Q6 were collected near densely populated districts of Manaus. The sample M5 was collected in an urban region, although it was not the closest to the most populated districts. A specific point-source pollution in the M5 sampling station was not identified. Notably, the Q6 sampling station is located in the Educandos Bay, which is an area of weak current and subject to frequent stormwater flooding in the Amazonian rainy season. In this sense, dissolved and particulate OM coming from the headwaters of the Quarenta stream becomes stagnant in the Educandos Bay area, and accumulates to a greater degree.

In general, sediments from the Tarumã-Açu stream presented lower concentrations of total PAHs and metals in relation to both the Mindu and Quarenta streams. However, total concentrations of *n*-alkanes were similar for all of the three streams studied. Both the Mindu and Quarenta are important streams that criss-cross the most urbanized areas of Manaus and receive effluents from many heavily populated districts of the city. The Quarenta stream also receives effluents from the industrial district of Manaus, where industries producing two-wheeler vehicles, electronics, optical, and chemical products are located. The Tarumã-Açu stream is located in a peri-urban area and is mostly bordered by vegetation. However, this waterbody may be influenced by family farming activities, intense traffic (canoe, boats, and yachts), the presence of marinas, and floating bars and restaurants on its right margin. Moreover, there is a floating petrol station in the Tarumã-Açu stream, which may explain the highest total *n*-alkane concentration found for the sample T9. A similar total *n*-alkane concentration for sediments from all streams suggests that the navigability potential of the Tarumã-Açu stream contributes to the input of petroleum-derived products in this peri-urban waterbody. Nevertheless, PAH and metal sources seem to be more intense and diverse in the urbanized area of Manaus, as revealed by their higher concentration in the Mindu and Quarenta streams. These findings may be related to the high concentrations of coprostanol (a marker of domestic sewage) observed in sediments from the Mindu and Quarenta streams [9]. Therefore, the high concentration of metals observed for these urban waterbodies must be, in part, introduced into the environment by the discharge of domestic sewage.

A comparison of the total *n*-alkane concentrations found herein with other Brazilian waterbodies is shown in Table S10 (see Supplementary Material). The total *n*-alkane concentrations observed for the Amazonian streams studied were similar to those found for other Brazilian areas, such as the São Francisco river (SE) ($0.22\text{--}2.72\ \mu\text{g g}^{-1}$) [29], the Imbé, Urubu and Ururá rivers (RJ) ($1.2\text{--}4.3\ \mu\text{g g}^{-1}$) [30], and the Santos bay and estuary (SP) ($0.10\text{ to }14.56\ \mu\text{g g}^{-1}$) [31]. However, the total *n*-alkane concentrations found herein were slightly lower than those reported for the Sergipe river estuarine system (SE) ($9.9\text{--}30.8\ \mu\text{g g}^{-1}$) [32], three mangroves in southern Brazil (SC) ($1.9\text{--}55.6\ \mu\text{g g}^{-1}$) [12], and for the Itajaí-Açu estuarine system (SC) ($0.5\text{--}69.7\ \mu\text{g g}^{-1}$) [10]. It is important to highlight that the sediments of those areas usually presented much higher fine-grain content than those observed in this study [10,29,31,32].

The profiles of *n*-alkanes with no odd/even hydrocarbon predominance associated with CPI values close to 1.0 found for all sediments suggest the presence of petroleum-derived products, such as lubricating oils [5,11,13]. The presence of the thermodynamically stable α,β -hopanes in most sediments corroborates the occurrence of a fossil origin for *n*-alkanes [5,10]. However, microorganisms, recycled OM, and OM from biomass burning emissions should not be discarded as sources of *n*-alkanes with no odd/even hydrocarbon predominance [33,34]. A previous study has reported that direct emission samples of Amazonian biomass burning in the flaming and smoldering phases showed *n*-alkane profiles without odd/even hydrocarbon predominance [35]. Most sediment samples from the Tarumã-Açu stream presented a profile of *n*-alkanes with no odd/even hydrocarbon predominance in the range between *n*-C₂₄ and *n*-C₃₇. Moreover, an unusual profile with a high predominance of the

even homologues was observed for the short-chain *n*-alkanes, specifically for *n*-C₁₆, *n*-C₁₈, and *n*-C₂₀. The predominance of short-chain and even carbon-numbered *n*-alkanes has also been reported as a result of the thermal degradation of biomass [33,34].

The total PAH concentrations found in this study for surface sediments from the Mindu, Quarenta, and Tarumã-Açu streams were mostly in the range 100–1000 ng g^{−1}, which is considered to be a moderate level of contamination [36]. Possible ecotoxicological risks of PAHs present in the Amazonian streams studied were evaluated by comparing their concentrations with those established by the Brazilian legislation (CONAMA 454/2012) [37] and the widely used Sediment Quality Guideline [38]. Some sediment samples from the Mindu and Quarenta streams presented concentrations of fluoranthene and phenanthrene higher than the threshold effect level (TEL) of the guideline [37] and the level 1 (limit of low probability of adverse effects on biota) established by the Brazilian legislation [36]. Therefore, adverse effects on the benthic communities that live in these waterbodies are expected to occur eventually in the streams studied [37].

A comparison of the total PAH concentrations found herein with other riverine and/or estuarine environments is shown in Table S10 (see Supplementary Material), which provides a general overview of such compounds in Brazilian areas. The total parent PAH concentrations observed for the Amazonian streams were similar to those reported for other Brazilian areas, such as the Patos Lagoon (RS) (7.3–92.8 ng g^{−1}) [39], the Sergipe river estuarine system (SE) (not detected–127.3 ng g^{−1}) [40], the Amazon river estuary (AP) (22.2–158.9 ng g^{−1}) [8], and the Capibaribe estuarine system (PE) (not detected–497.6) [41], but lower than those reported for areas of intense ship traffic, petroleum refinery, and intense urbanization and industrialization, such as the Itajaí-Açu estuarine system (SC) (28.4–1237.2 ng g^{−1}) [10], the Cocó and Ceará rivers (CE) (3.04–2234.76 ng g^{−1}) [42], and the Santos bay and estuary (SP) (60–8680 and 79.6–15389.1 ng g^{−1}) [31,43]. The total parent PAH concentrations observed for the streams studied were also compared to those reported previously for sediments of the Negro river (AM), where ports, shipyards and petrol stations are located [6]. Most sediments from the Negro river presented total PAH concentrations similar to those found for the three streams of study [6].

The prevalence of high molecular mass PAHs in relation to the low ones, with the dominance of 4-ring PAHs, is indicative of pyrolytic sources [17]. Such an origin is corroborated by the values found for Fl/(Fl + Py), which were higher than 0.5, which is a value that indicates that PAHs are mostly from combustion [17]. Moreover, most sediment samples showed values for BaA/(BaA + Ch) higher than 0.35, confirming dominance of the isomer formed during combustion [17]. It is important to highlight that some samples presented values for BaA/(BaA + Ch) slightly smaller than 0.35, suggesting another contribution pattern. In this sense, the ratio BaA to Ch was calculated in order to investigate the specific source of combustion-derived PAHs. The values found herein were compared to those reported for the certified reference material SRM 1650 (Diesel Particulate Material) (0.30), automobile exhaust (0.53), and wood (0.79) [18]. Sediments from the Tarumã-Açu stream presented values for the ratio BaA to Ch, which were a little higher than others, indicating the prevalence of forest fires/wood burning (0.79) and lower input of PAHs from automobile exhaust (0.53) in this peri-urban area [18]. Both of the streams located in the more urbanized area showed values raging between 0.30 and 0.69, indicating mixed sources with a higher contribution of automobile exhaust-derived PAHs [18].

Regarding metals, sediments from the Tarumã-Açu stream presented notably lower concentrations in relation to both the Mindu and Quarenta streams. The outlier concentrations of Ni in sediments from the Quarenta stream are probably due to the incorrect discharge of wastewater from industries located in the industrial district of Manaus. Sediments from the Tarumã-Açu stream presented a comparable contribution of the metals Zn, Pb, Mn, and Cr, whereas the Mindu and Quarenta streams showed an increased proportion for the metals Zn, Cu, and Ni. This distribution pattern suggests a higher contribution of sources such as domestic effluents, industrial activities, and automobile exhaust emissions. A comparison of the metal concentrations found herein with other riverine and/or estuarine

environments is shown in Table S11 (see Supplementary Material), which provides a general overview of the contamination degree of the streams studied in relation to other Brazilian areas.

Compared with sediments of black and whitewater rivers within the Itacoatiara city (AM), Central Amazon, metal concentrations were higher for sediments of the Mindu and Quarenta streams [23]. Compared with estuarine environments, such as the Itajaí-Açu estuarine system (SC) [44] and the São Marcos bay and Anil river estuary (MA) [45], sediments from the Mindu and Quarenta streams presented a comparable concentration for most metals. It is important to mention that those both estuarine systems are also port regions [44,45]. Compared with the polluted and eutrophic Rodrigo de Freitas Lagoon [46], the Mindu and Quarenta streams presented slightly lower concentrations for most metals. Only the metals Mn and Pb were found in much lower concentrations herein compared to all of the systems cited [23,44–46]. The Quarenta and Mindu streams also presented slightly lower concentrations for most metals than those reported for the Xingu and Fresco rivers [22] and the Furo da Laura estuary [24], which are Amazonian waterbodies located in the Pará state. Only the metal Cu was observed in a higher concentration in the streams studied herein [22,24]. Compared with the highly polluted Tietê river (SP) [47], sediments from the Mindu and Quarenta streams presented very lower concentrations for all of the metals. The metal concentrations observed for the Quarenta stream were quite distinct of those reported in two previous studies [25,26]. Such differences may be due to the sampling year, sampling stations, and/or the methodologies used. The metal concentrations found for sediments from the Tarumã-Açu stream were much lower than those reported in all the studies cited above [44–47].

Possible ecotoxicological risks associated with metals being present in the studied Amazonian streams were evaluated by comparing their individual concentrations with those established by the widely used Sediment Quality Guideline proposed by Macdonald, Ingersoll, and Beger (2000) and with those established by the Brazilian legislation (CONAMA 454/2012) [37,38]. The sediment samples from the Tarumã-Açu stream presented concentrations lower than the lowest effect level (LEL) for all of the metals listed in the guideline [38]. Therefore, sediments from the Tarumã-Açu stream are considered to be clean to marginally polluted, and no adverse effects on the majority of sediment-dwelling organisms are expected [38]. Similarly, sediments from the Tarumã-Açu stream showed metal concentrations lower than those established by the Brazilian legislation as level 1, which is the limit of the low probability of adverse effects on biota [37]. For the Mindu stream, only the sediment samples M5, M7, and M8 showed metal concentrations that could cause any adverse effects [38]. The sample M7 presented the metal Cu in a concentration above LEL, whereas the samples M5 showed it in a concentration above the minimal effect threshold (MET) [38]. The sample M5 also presented the metal Cd in a concentration above the threshold effect level (TEL) [38]. The sample M8 presented the metal Cu in a concentration higher than both TEL and level 1 of the Brazilian legislation [37,38]. Although the sample M5 had shown metal concentrations in one-order of magnitude higher than the others, adverse effects on biota are not expected to occur frequently in this sampling area. Nevertheless, sediments of Mindu stream are also considered to be clean to marginally polluted [38]. For the Quarenta stream, only the sample Q6 showed concentrations that could cause any adverse effects [37,38]. For this sample, the metals Zn, Cu, Ni, and Cd were found in concentrations above the level 1 established by the Brazilian legislation (CONAMA 454/2012) [37]. The concentration of the metals Cr, Ni, Cu, and Cd were found to be above TEL, whereas the concentration of Zn was above MET. In spite of the highest metal concentrations found for the sample Q6, sediments from this sampling area are considered to be marginally polluted [38]. Therefore, none of the streams studied could be classified as heavily polluted according the Sediment Quality Guideline [38] and/or above level 2 (limit of high probability of adverse effects on biota) according the Brazilian legislation [37]. However, the highest concentrations of metals observed for the Mindu and Quarenta streams show that anthropogenic activities are strongly influencing these waterbodies. The results found herein indicate the need for implementing effective programs of environmental management and monitoring, as well as stricter and well-enforced legislation.

5. Conclusions

Concentrations of total *n*-alkanes, total PAHs, and metals did not show significant correlation with the fine-grain fraction, revealing that grain size is not the main factor that influences the accumulation of those contaminants in the Mindu, Quarenta, and Tarumã-Açu streams. A similar total *n*-alkane concentration was found for sediments from all streams, whereas metals and PAHs were found in higher concentrations in the urban streams because of the occurrence of more intense and diverse sources, including industrial and domestic effluents, and automobile exhaust emissions. The profiles of *n*-alkanes with no odd/even hydrocarbon predominance associated with CPI values close to 1.0 suggest that biomass burning is an important source of hydrocarbons. Although, fossil-derived products also represent a source for *n*-alkanes, as confirmed by the presence of the α,β -configuration for the pentacyclic triterpenes, including an α,β -homohopane series from C₃₁ to C₃₅ with the presence of both 22*S* and 22*R* epimers. Some sediment samples from the Mindu and Quarenta streams presented concentrations of fluoranthene, phenanthrene, and metals higher than the limits of the low probability of adverse effects on biota.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2624-8549/2/2/18/s1>, Tables S1–S9.

Author Contributions: Conceptualization, G.A.B. and H.H.F.K.; methodology, M.G.d.M., L.G.d.C. and L.A.R.; formal analysis, M.A.B. and É.S.J.; investigation, F.M.A.d.S.; data curation, G.d.S.C.; writing—original draft preparation, G.A.B. and H.H.F.K.; writing—review and editing, J.d.S.C.; project administration, G.A.B.; funding acquisition, G.A.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research has been financially supported by CNPq (grant number 428435/2016-5) and by MCTIC (project 7.05 Proesp Ufam).

Acknowledgments: M.G. de Melo would like to thank CAPES for the MSc Scholarship. All authors thank to the funding agencies CNPq, CAPES, FAPEAM and FINEP. We also thank Central Analítica (UFAM) for the instrumental support.

Conflicts of Interest: The authors declare no conflict of interest.

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