Brazilian Journal of Analytical Chemistry
Pre-publication – Accepted after peer review
doi: 10.30744/brjac.2179-3425.AR-188-2024

ARTICLE

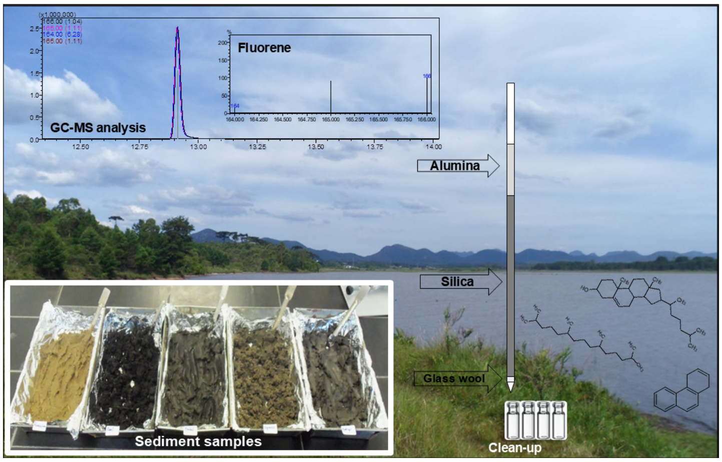
Geochemical Hydrocarbon Markers in River Sediments from a Densely Populated Area of Curitiba, Brazil

Lucélia Taverna[1], Fabricio Augusto Hansel[2], Cesar Alexandro da Silva[1,3], Vânia Ribeiro Ferreira[1], Emerson Luís Yoshio Hara*[1,3], Rafael Garrett Dolatto[1], Marco Tadeu Grassi[1]

[1]Grupo de Química Ambiental, Departamento de Química, Universidade Federal do Paraná. PO Box 19032, 81531-980, Curitiba, PR, Brazil

[2]Centro Nacional de Pesquisa de Florestas, Empresa Brasileira de Pesquisa Agropecuária. Estrada da Ribeira, Km 111, 83411-000, Colombo, PR, Brazil

[3]Laboratório de Geoquímica Ambiental e Poluição Marinha, Departamento de Oceanografia e Ecologia, Universidade Federal do Espírito Santo. Campus Goiabeiras, 29055-460, Vitória, ES, Brazil



Employing geochemical hydrocarbon markers, this work aimed to identify the sources of organic matter in water bodies in the Metropolitan Region of Curitiba, State of Paraná, Brazil. Also, a reduced scale protocol assisted by ultrasonic bath was developed and applied to extraction, fractionation, and clean-up of the aliphatic hydrocarbons (AH), polycyclic aromatic hydrocarbons (PAH), and sterols in sediment samples from the rivers Barigui, Iguaçu, and Timbu and from the water supply reservoirs Iraí and Passaúna. The total concentrations determined in all samples ranged from 1.15 to 509.65 μg g^{-1} for AH, between 97.3 and 440.65 ng g^{-1} for PAH, and from 1.73 to 747.92 μg g^{-1} for sterols. The highest concentration of the three markers was observed at the Timbu River, which is in an environmental protection area. About the samples from the Barigui River and both reservoirs, more than 95% of the molecules were classified as natural input. On the other hand, in the samples from the Iguaçu and Timbu rivers, densely urbanized area rivers, 53% and 88% of the markers, respectively, were classified as of anthropogenic origin. However, the ratios for PAH revealed the combustion of biomass as the main source of these compounds. The fecal marker coprostanol, which was detected in both the Iguaçu and Barigui rivers, shows contamination by domestic and industrial sewage, respectively. The ratios for sterols showed the presence of domestic sewage in rivers and reservoirs close to expanding urban areas. Thus, it was possible to conclude that the uncontrolled expansion of cities and their activities can compromise the integrity of the water bodies, their biota, and the supply of the population.

Cite: Taverna, T.; Hansel, F. A.; da Silva, C. A.; Ferreira, V. R.; Hara, E. L. Y.; Dolatto, R. G.; Grassi, M. T. Geochemical Hydrocarbon Markers in River Sediments from a Densely Populated Area of Curitiba, Brazil. *Braz. J. Anal. Chem.* (Forthcoming). http://dx.doi.org/10.30744/brjac.2179-3425.AR-188-2024

Submitted December 27, 2024; Resubmitted February 10, 2025; 2nd time Resubmitted April 14, 2025; Accepted April 14, 2025; Available online June, 2025.

Keywords: emerging contaminants, sample preparation, gas chromatography, polycyclic aromatic hydrocarbons, environmental chemistry

INTRODUCTION

The presence of elevated concentration levels of biogeochemical hydrocarbon markers, such as aliphatic hydrocarbons (AH), polycyclic aromatic hydrocarbons (PAH), and sterols in aquatic sediments, are frequently used as indicators of water pollution by persistent organic pollutants (POPs). Since sediments accumulate these POPs, the relative distribution or ratios are often used as an indicator of the origins and chemical/physical processes contributing to the pollution. Often, these POPs are continuously discharged into the water bodies through anthropogenic activities, worsened by deficiencies in the sewage collection and treatment services in municipalities from an emerging economy such as Brazil's.[1–6]

The analytical protocols to determine AH, PAH, and sterols, as well as other organic compounds in the sediment samples, comprise extraction, clean-up, and chromatographic determination. One of the most widely used extraction of organic compounds involves the use of the Soxhlet apparatus[7,8] and ultrasonic devices.[9,10]

Despite being efficient, the Soxhlet apparatus, which is recommended by the US EPA 3540C[11] method has disadvantages such as high consumption of organic solvents, significant waste generation, long extraction time, and considerable consumption of electrical power. To improve selectivity and minimize interferences, EPA 3540C recommends further purification procedures using alumina and silica gel chromatographic columns, as specified in US EPA 3610B[12] and US EPA 3630C[13] methods. However, these traditional clean-up methods have significant disadvantages, including high labor requirements, extensive solvent use, and substantial waste generation.

While these methods improve analytical precision, they inherently contradict the principles of green chemistry by increasing process inefficiencies and environmental burdens. Therefore, the development of alternative, eco-friendly purification strategies is crucial to minimizing solvent use, reducing waste production, and enhancing the sustainability of analytical methodologies. Ultrasonic devices have proven to be more attractive for routine analysis because they are an environmentally friendly alternative for extracting organic compounds from solid samples. These devices have a lower acquisition cost, require less time of use, allow reactions with smaller sample volumes, and, consequently, generate less waste generation[9,14–17] Due to these advantages, the EPA 3550C ultrasonic extraction method[18] has been widely adopted over the EPA 3540 method.

For instance, Martinez et al.[19] used an ultrasonic device to extract 16 PAHs in water, sediment, and mussel samples 30 mL of HX/DCM (1:1) in three sonication cycles of 10 min, clean-up was optimized using a solid-phase extraction cartridge filled with alumina. From the recovery experiments, the values ranged from 22% to 112%. According to the authors, due to its easier use and faster operation, ultrasonic extraction was chosen as the preferred option ahead of the standard Soxhlet method.[19]

Considering these aspects, the aim of determining the presence of PAH, AH, and sterols in sediments is to assess the environmental impacts of unregulated urban expansion, especially in developing countries like Brazil. Despite the economic growth observed in recent decades, sewage treatment has not followed at the same pace.[20,21]

The objective of this work was to modify and optimize an environmentally friendly sample clean-up and fractionation protocol for the determination of AH, PAH, and sterols. The modification was aimed at having the following advantages: minimizing the amounts of solvents and sorbents used in the extraction and clean-up steps, and reducing the total time of analysis, power consumption, and the quantities of waste generated. After the optimization of the method, it was validated and applied in the analysis of sediments from rivers and reservoirs of the Metropolitan Region of Curitiba, Brazil.

MATERIALS AND METHODS

Reagents and standards

The organic solvents hexane (HX), dichloromethane (DCM), ethyl acetate (Et.Ac.), and methanol (MeOH) had a purity > 99% (Mallinckrodt, USA). The analytical standards androstanol (AND), cholestane (CLE), coprostanol (COP), epicoprostanol (ECOP), coprostanone (CTN), cholesterol (COL), cholestanol (CNL), stigmastanol (STN), stigmasterol (STR), and campesterol (CPL) as well derivatization reagent N,O-bis(trimethylsilyl)-trifluoro-acetamide trimethyl-chloro-silane (BSTFA/TMCS, 99:1) were purchased from same supplier (Sigma-Aldrich, USA).

To determine AH, a mixed solution of AH standards (n-C8 to n-C40, pristane, and phytane) was used for calibration, and deuterated standards n-C20D, n-C24D, and n-C30D from Accustandard, USA were used as surrogates.

A mixed solution of PAH: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Cry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indene[1,2,3-cd]pyrene (InP), dibenzo[a,h]anthracene (DahA) and benzo[g,h,i]perylene (BghiP) was used as analytical standard (Accustandard, USA).

A mixed solution of deuterated PAH containing naphthalene-D8 (NapD8), acenaphthene-D10 (AceD10), phenanthrene-D10 (PheD10), chrysene-D12 (CryD12), perylene-D12 (PerD12) which was used as internal standard (IS), and p-terphenyl-D14 (Accustandard, USA) as surrogate standard. Alumina (Al_2O_3), anhydrous sodium sulfate (Na_2SO_4), and copper powder were obtained from J. T. Baker, USA.

The purity of the gases (hydrogen, nitrogen, synthetic air, and helium) was 99.999% and supplied by White Martins, Brazil. Before using anhydrous sodium sulfate, it was heated at 400 °C for 4 h to purge humidity and organic contaminants. Copper was activated using HCl (6.0 mol L^{-1}) followed by MeOH rinsing, MeOH: DCM (1:1 v/v), and DCM. Silica and alumina gel, 70-230 mesh (Merck, Germany), were activated at 165 °C for 16 h and deactivated with ultra-pure water.

Assessing the efficiency of the extraction and clean-up steps

Extraction and clean-up steps were adapted from Mater et al.[22] Experiments of fortification and recovery related to extraction and clean-up steps were performed with standard solutions of AH, PAH, and sterols at the following concentrations of 10 µg, 96 ng, and 75 µg, respectively. To optimize the extraction step, 1.0 g of activated copper and 3.0 g of Na_2SO_4 were transferred into a glass conical tube, followed by the standard solutions of AH, PAH, and sterols.

The extractions were carried out in an ultrasonic bath (120 W, 25 kHz) using 7 mL of DCM: MeOH (2:1 v/v). Three cycles of extraction (20 min $cycle^{-1}$) were carried out and, after each one, the tubes were centrifuged (2000 rpm for 6 min) and the supernatants were transferred to a glass beaker. The extract was preconcentrated in a rotary evaporator (50 °C) and then submitted to clean-up.

Recovery was evaluated after the extract pre-concentration to approximately 100 µL followed by reconstitution in 1.0 mL of HX. Clean-up optimization was performed in glass columns (7 mm i.d. × 30 cm length) packed with silica gel, neutral activated alumina, calcinated Na_2SO_4, and activated copper standard solutions of AH, PAH, and sterols. Different amounts of alumina were evaluated, as well as the silica activation influence on the compound's fractionation (Table I).

The initial 5.5 mL eluted from the AH fraction (F1) and the final 1.0 mL (Experiments 1 and 2 of Table I) were collected into distinct beakers. In all experiments, F1 and PAH fraction (F2) have been pre-concentrated in a rotary evaporator up to 2 mL and then up to 1 mL under $N_{2\,(g)}$ flow. The sterols fraction (F3) was pre-concentrated to dryness and derivatized (40 µL BSTFA/TMCS, 70 °C for 1 h). Then, the derivatizing reagent was volatilized under N_2 flow and redissolved with 1 mL of HX.

Table I. Terms used in experiments to elute the AH, PAH, and sterols

Experiment	m of SiO_2	m of Al_2O_3[a]	V of HX (F1)	V of DCM:HX (F2)	V of Et.Ac.:MeOH (F3)
	g		mL		
1	2[b]	2	6.5	10 (3:2 v/v)	12 (3:1 v/v)
2	2[b]	1	6.5	10 (3:2 v/v)	12 (3:1 v/v)
3	2[b]	1	5.5	10 (4:1 v/v)	12 (3:1 v/v)
4	2[c]	1	5.5	10 (4:1 v/v)	12 (3:1 v/v)

[a] alumina was calcinated at 400 °C during 4 h and activated at 160 °C for 16 h; [b] silica gel activated at 160 °C, 16 h; [c] silica activated at 160 °C, 4 h, and then deactivated with 2% ultrapure water; F1: AH fraction; F2: PAH fraction, F3: sterols fraction; HX: hexane, DCM: dichloromethane, Et.Ac., ethyl acetate, MeOH: methanol.

Instrumental analysis

AH determination was performed using a gas chromatograph (Focus GC, Thermo Corporation, USA) with a flame ionization detector (GC-FID), equipped with a DB-5 capillary column (30 m length × 0.32 mm i.d. × 0.25 µm film thickness). The injector was set at 280 °C and operated in splitless mode. The detector temperature was set at 300 °C. The injection was performed (1.0 µL) by an autosampler (AS 3000, Thermo Corporation, USA). GC oven's initial temperature was 60 °C held for 1.5 min, 6 °C min^{-1} to 310 °C and held at 310 °C for 30 min. Nitrogen was used as carrier gas at a flow rate of 3 mL min^{-1}.

PAH determination was performed using a GC-MS (Focus-GC Polaris Q, Thermo Corporation, USA). The capillary column specifications were: 30 m length, 0.25 mm i.d., 0.25 µm film thickness (DB-5ms, Agilent, USA) and helium as carrier gas at 1.0 mL min^{-1}. F2 (1.0 µL) was injected in splitless mode. GC oven temperature was programmed from 50 °C (held for 5 min) to 230 °C at 5 °C min^{-1}, up to 250 °C at 2 °C min^{-1}, and finally to 300 °C at 5°C min^{-1} held for 8 min.

The mass spectrometer was operated in the electron ionization (EI) mode at 70 eV selected ion monitoring (SIM) mode, observing the ions in 3 segments: scan 1 (5-29 min): *m/z* 128, 136, 152, 154, 162, 164, 166, 178; scan 2 (30-47 min): *m/z* 178, 202, 228, 244; and scan 3 (47 min, until the end of run): *m/z* 228, 236 240, 252, 260, 264, 276, 277, 278, 279. The ion source and the transfer line temperatures were kept at 250 °C. A dwell time of 0.2 seconds was used for each *m/z*, resulting in 15 cycles/s for each SIM segment.

The injector temperature was kept at 270 °C. PAH quantification was performed by injecting a standard mixed solution containing 16 PAH and comparing their mass spectra to the NIST MS library.

Derivatized sterols were determined by injecting 1.0 µL of the sample in split mode (split ratio 1/20). The injector temperature was set up to 300 °C, and GC oven temperature was programmed: 60 °C to 250 °C at 15 °C min^{-1}, then up to 280 °C at 1 °C $min^{-1,}$ and finally up to 300 °C at 5 °C min^{-1}, holding for 5 min. The mass spectrometer was operated in the EI mode at 70 eV. The ion source and transfer line temperatures were set up at 200 °C and 280 °C, respectively. Mass spectra were obtained in full scan mode (50 and 550 *m/z*).

Quality assurance of the analytical method

Validation parameters and acceptance criteria used in our study were based on US EPA Method 8270E.[23] Blank sample extractions using sodium sulfate previously heated at 450 °C were performed. Calibration and linearity were measured by the correlation coefficient (R) obtained from analytical curves. The limit of detection (LOD) for PAH and sterols was calculated based on the parameters of the analytical curve: 3 times the ratio of the estimated standard deviation of the regression equation and the curve slope (Table S1 and S2).

To quantify AH, analytical curves (n=3) were plotted to range from 0.3 to 25 µg mL^{-1} using n-C16D (10 µg mL^{-1}) as internal standard and the concentration of surrogate standards (n-C20D, n-C24D, and n-C30D) ranged from 1 to 25 µg mL^{-1} (Table S3); analytical curves were used to obtain the response factor (RFx), which was used to determine the AH concentrations (C_{HA}) according to Equation 1.

$$C_{HA}=\left(\frac{A_X}{A_{IS}}\right)\left(\frac{C_{IS}}{RF_X}\right) \qquad \text{(Equation 1)}$$

where A_x and A_{IS} correspond to area values obtained for target AH and C16D, respectively; C_{IS} corresponds to n-C16D concentration in the extract, and RFx is the response factor of target AH.

For PAH, linear analytical curves (n=3) were plotted to range from 4.9 to 490 ng mL^{-1} using a mixed solution of deuterated PAH containing NapD8, AceD10, PheD10, CryD12, PerD12 was used as internal standard (IS) at 102.4 ng mL^{-1} (Table S1). Besides, linear analytical curves (n=3) for the surrogate standard p-terphenyl-D14, whose concentrations ranged from 9.6 to 200 ng mL^{-1}, were plotted. To quantify sterols, linear analytical curves were plotted ranging from 0.24 to 15 µg mL^{-1} (COP, ECOP, CTN, COL, CNL, STR, and STN) and 0.4 to 20 µg mL^{-1} for CPL using CLE as IS (15 µg mL^{-1}) (Table S2). Efficiency extraction was determined using AND as a surrogate standard, and analytical curves (n=3) ranged from 2 to 20 µg mL^{-1}. Concentrations of sterols were obtained from RF according to Equation 1.

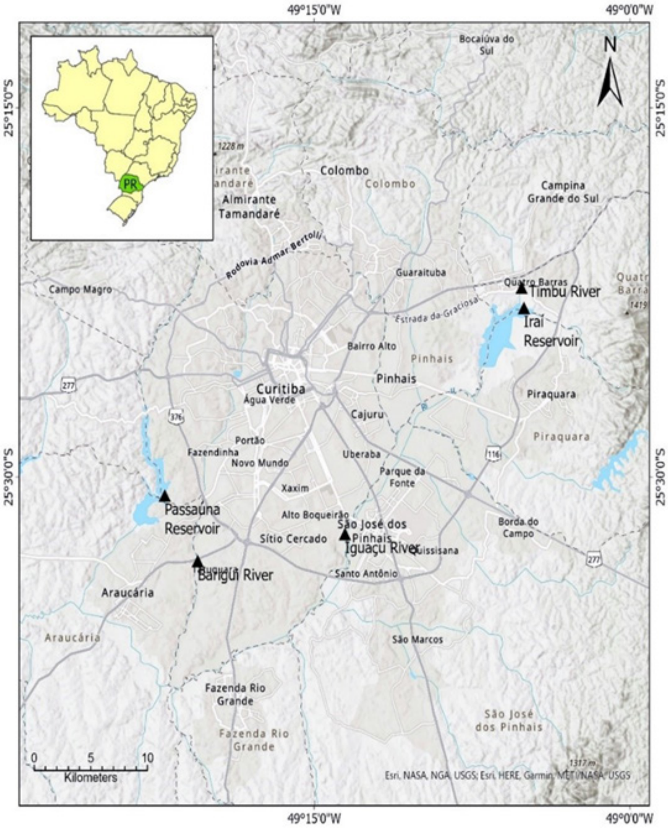
The LOD values for AH were calculated based on the signal-to-noise ratio: 3 times the ratio of the lowest concentration of the calibration curve and the signal-to-noise ratio regarding the point of least concentration of the calibration curve (Table S3). The limit of quantification (LOQ) for the three classes of compounds was considered as the ratio of the lowest concentration of the calibration curve and the sediment mass.

Due to the absence of sediment certified containing sterols, the accuracy of the method was verified from recovery experiments using a sediment reference prepared in the laboratory. Reference material was prepared by decontaminating 20 g of natural sediment through Soxhlet extraction for 8 h, using 180 mL of DCM: MeOH (2:1 v/v). Then, 3.0 g of decontaminated sediment was transferred to an extraction tube with dichloromethane and spiked with 3.33 µg g^{-1} of AH, 32 ng g^{-1} of PAH, and 15 µg g^{-1} of sterols standards. Surrogate standards at 5 µg mL^{-1} n-C20D and n-C24D, 102.4 ng mL^{-1} p-terphenyl-D14, and 15 µg mL^{-1} androstanol were also added, followed by manual shaking. Analysis of spiked reference material was carried out in five replicates, and the precision was evaluated from relative standard deviation values obtained through recovery experiments.

Sediment sampling

The study area is presented in Figure 1. Samples included three rivers and two reservoirs belonging to the Iguaçu River basin. The sampling sites were selected to include densely urbanized regions under intense industrial activity and environmental protection areas. This strategy was adopted to permit the evaluation of the effects of human occupation and its activities along the Iguaçu Basin.

Surface sediment samples were collected with a polyvinyl chloride sampler (50 mm diameter × 25 cm length). Samples were transferred and stored in previously combusted (450 °C) glass jars sealed with aluminum foil-lined lids and kept frozen (-30 °C) until drying in the laboratory. Thereafter, they were dried (40 °C) until constant weight was attained. Dried samples free of leaves and other impurities were ground in a porcelain mortar and, without sieving, stored in previously cleaned glass vials until analysis. The determination of AH, PAH, and sterols was performed in triplicate according to the modified method.



Iraí Reservoir	25°23'05.0"S 49°05'01.7"W	S1
Passaúna Reservoir	25°30'42.8"S 49°22'06.6"W	S2
Iguaçu River	25°32'12.8"S 49°13'24.6"W	S3
Barigui River	25°33'22.6"S 49°20'32.6"W	S4
Timbu River	25°22'15.9"S 49°05'08.4"W	S5

Figure 1. Main rivers and reservoirs of the Iguaçu River Basin in the MRC. The marks (▲) indicate the approximate locations of sediment sampling in the Barigui River, Iguaçu River, Timbu River, Iraí Reservoir, and Passaúna Reservoir.

RESULTS AND DISCUSSION

Clean-up and fractionation

According to the literature, the clean-up step is essential for complex matrices such as aquatic sediments because it reduces the interferences, then increases the signal/noise ratio, provides greater analytical reliability, and minimizes maintenance of chromatographic system.[24–26] Based on this, the clean-up step was evaluated using different amounts of alumina (1.0 and 2.0 g), activated silica (2.0 g), and activated/deactivated silica (2.0 g), according to Table I.

The optimized conditions for AH, PAH, and sterols fractionation were obtained through Experiment 4 of Table I, that is, 2.0 g of deactivated SiO_2 and 1.0 g of Al_2O_3. In this experiment, when the first aliquot of solvent was eluted through the column, corresponding to approximately 5.5 mL of hexane, the AH was separated. In the second fraction, PAH obtained after elution was 10 mL of DCM:HX (4:1 v/v), and the third fraction contained 12 mL of Et.Ac.:MeOH (3:1 v/v), the most polar compounds (sterols).[27]

Under these conditions, the obtained recoveries of AH ranged from 85% to 104%. The relative standard deviation (RSD) was up to 9.6%. PAH recoveries ranged from 65% to 112%, RSD was up to 21.2%, sterols recoveries were between 74% and 89%, and maximum RSD was up to 9.2%. These values of precision and accuracy were considered suitable for these three classes of compounds, and the conditions of Experiment 4 were selected to continue the next steps of the work.[28]

Method performance

The performance of the proposed method was evaluated according to some parameters, such as correlation coefficient, limits of detection (LOD) and quantification (LOQ), recovery, and relative standard deviation (RSD). The analytical curves showed satisfactory linearity since the regression coefficients varied from 0.9924 to 0.9998 for AH, 0.9861 to 0.9973 for PAH, and 0.9765 to 0.9957 for sterols and were considered satisfactory.[29,30]

LOD values ranged from 0.021 to 0.069 µg g^{-1} for AH, 0.027 to 0.168 ng g^{-1} for PAH, and 0.039 to 0.159 µg g^{-1} for sterols. LOQ values were considered as the lowest concentration levels of the analytical curve (0.100 µg g^{-1} for aliphatic, 1.633 ng g^{-1} for 16 PAH, and 0.080 µg g^{-1} for all sterols, except for campesterol, which was 0.133 µg g^{-1}).[31] Therefore, the values of LOD and LOQ demonstrated the high sensitivity of the optimized method. The average recovery ranges for experiments of accuracy and precision were 67% to 88% for AH, 44% to 105% for PAH, and 40% to 76% for sterols.[29,32,33]

Surrogate internal standards recoveries ranged satisfactorily from 82% and 83% to n-C20D and n-C24D, respectively, 85% for p-terphenyl-D14, and 83% for androstanol (Table S7). Some PAHs, like naphthalene, acenaphthylene, and acenaphthene, presented recoveries below 70%. It can be attributed to the loss by volatilization and co-elution in the fraction of aliphatic hydrocarbons, as previously mentioned. RSD of AH, PAH, and sterols ranged from 1% to 19%, these values are regarded as satisfactory since in trace analysis and complex matrices such as sediments, values of up to 20% were acceptable.

Table II summarizes the steps optimized in this work and compares them to a method described in the literature. Comparing our modified method to the US EPA 8270 method, there is a significant decrease in the amounts of reagent. Another key issue is also present, and this method is a substantial reduction in sample preparation and instrumental analysis elapsed time.

Thus, it is possible to conclude that the method proposed in this work presents satisfactory results when compared to the consolidated method. In addition, the results were obtained through less expensive and polluting processes and caused less harm to the health of the analysts.

In this sense, Da Silva et al.[34] presented very approximate recovery values; however, the number of reagents and their toxicity were greater when compared to this work. For example, the extraction was carried out with 200 mL of organochlorine solvent with the assistance of an ultrasound bath, and the mass of sorbent was 10 g. Likewise, Kawakami et al.[7] developed a method for the determination of sterols that was proposed using Soxhlet extraction followed by a clean-up step.

Table II. Summary of extraction and clean-up steps for the methods optimized, standard according to US EPA 8270, and performance from the recovery (%)

Variables	Proposed method	US EPA 8270 [a]
Clean-up column	7 mm i.d. × 30 cm	13 mm i.d. × 30 cm
Silica	2 g	8 g
Alumina	1 g	1 g
F1 Solvent	5.5 mL of Hexane	40 mL of Hexane
F2 Solvent	10 mL of HX/DCM (4:1)	75 mL of HX/DCM (1:1)
F3 Solvent	12 mL of Et.Ac./MeOH (3:1)	---
Equipment	Ultrasound	Soxhlet
Solvent [b]	21 mL DCM/MeOH (2:1)	200 mL of DCM
HA Recovery (%)	67 to 88%	45 to 110%
PAH Recovery (%)	44 to 105%	60 to 105%
Esterols Recovery (%)	40 to 76%	---
Elapsed time (h)[c]	1:30	5:00

[a] Optimization based on US EPA standard method; [b] Total volume of solvent in the extraction step, [c] Total time of analysis, except chromatographic determination.

Distribution of AH, PAH, and sterols in sediments of rivers in the MRC

The modified method was then applied to sediment samples obtained from aquatic bodies in the MRC: Iraí and Passaúna reservoirs and the Iguaçu, Barigui, and Timbu rivers. Table III shows the concentrations of AH, PAH, and sterols obtained from these analyses.

The total AH concentrations ranged from 1.15 µg g^{-1} to 509.69 µg $g^{-1,}$ and the highest concentration obtained was from the Timbu River sample. Regarding the total levels of PAH, the sediment collected in predominantly urban and industrial areas, represented by the Iguaçu and Barigui rivers, showed lower concentrations compared to the sample from the Timbu River, located in an environmental protection area.

According to the literature, it is possible to distinguish the degree of contamination in impacted hydrographic environments based on the correlation between the total concentrations of PAH present in its sediments. In this classification, values of concentrations greater than 500 ng g^{-1} are called "highly contaminated", between 250 to 500 ng g^{-1} are "moderately contaminated," and below 250 ng g^{-1} are "slightly contaminated", and these criteria are used in several studies involving environmental assessment.[35–39]

Table III. Determination of AH, PAH, and sterols in sediment samples obtained from the Iraí and Passaúna reservoirs and the Iguaçu, Barigui, and Timbu rivers (n=3)

Parameter	Iraí Reservoir	Passaúna Reservoir	Iguaçu River	Barigui River	Timbu River
AH (µg g^{-1})					
∑alkanes (C_{16} - C_{36}/UCM)	3.05	1.18	1.15	4.18	509.69
UCM	-	-	-	-	488.26
REC (%) C_{20}d	69	84	82	86	118
REC (%) C_{24}d	65	85	65	78	84
PAH (ng g^{-1})					
Nap	17.20	16.30	24.56	9.11	17.93
Ace	9.14	8.63	8.99	9.06	< 1.63
Acy	6.20	4.99	5.53	5.32	13.50
Fl	9.97	7.93	9.28	8.44	25.50
Phen	12.20	8.26	13.06	8.21	37.40
Ant	9.92	9.19	12.80	9.56	30.70
Flu	10.10	8.96	16.90	10.70	65.10
Pyr	7.67	6.46	16.20	8.91	56.40
BaA	< 1.63	< 1.63	2.38	2.51	5.62
Chry	5.89	5.13	11.80	7.93	20.50
BbF	3.59	3.30	10.20	12.40	39.70
BbK	7.79	7.62	12.40	9.94	26.60
BaP	5.79	6.64	16.10	6.84	34.90
IP	4.15	3.90	10.90	5.63	23.60

(continued on next page)

Table III. Determination of AH, PAH, and sterols in sediment samples obtained from the Iraí and Passaúna reservoirs and the Iguaçu, Barigui, and Timbu rivers (n=3) (continued)

Parameter	**Iraí Reservoir**	**Passaúna Reservoir**	**Iguaçu River**	**Barigui River**	**Timbu River**
DahA	6.29	< 1.63	8.68	5.70	18.30
BghI	< 1.63	< 1.63	10.70	8.84	24.90
∑PAH	116	99	190	129	440
REC (%) p-terphenyl-D_{14}	103	87	88	119	63
Sterols (μg g^{-1})					
Cop	< 0.08	< 0.08	0.75	0.15	410
E-cop	< 0.08	< 0.08	0.35	< 0.08	24.6
Coprostanone	< 0.08	< 0.08	0.27	< 0.08	173
Cholesterol	0.44	0.08	0.22	0.08	11.2
Cholestanol	0.48	0.10	0.47	< 0.08	36.1
Stigmasterol	3.06	0.37	0.28	0.14	7.67
Stigmastanol	2.11	0.37	0.60	0.68	13.8
β-sitosterol	3.33	0.36	0.28	0.22	7.15
Campesterol	10.3	1.34	0.52	0.46	64.4
∑sterols	19.8	2.62	3.73	1.73	749
REC (%) Androstanol	112	87	102	87	125

AH: Aliphatic Hydrocarbons; PAH: Polycyclic Aromatic Hydrocarbons; UCM: Unresolved complex mixture; REC: Surrogate standard recovery; *Ratio is calculated from the area values of each compound.

Thus, the Timbu River sample is classified as moderately contaminated and the samples from the Iguaçu and Barigui Rivers and reservoirs samples as low level of contamination. Meniconi et al.[40] detected 532 ng g^{-1} and 70 ng g^{-1} (Σ16 PAH) in sediment samples collected in 2000 from the Barigui and Iguaçu rivers, respectively, after the rupture of the pipeline of a Petrobras oil refinery that caused the spill of 4000 m^3 of crude oil into the bed of the Barigui River. Leite et al.[41] showed that sediments from the rivers Iguaçu and Barigui collected in 2005 in the same local in this study were classified as highly contaminated, with total PAH concentrations of 1713 ng g^{-1} and 1206 ng g^{-1}, respectively.

The Timbu River and Iraí Reservoir samples were classified as slightly contaminated, with a total concentration of PAH 222 ng g^{-1} and 131 ng g^{-1}, respectively. Regarding the presence of sterols, the largest concentrations were found in the Timbu River and Irai Reservoir.

Positive detection of coprostanol is widely used as evidence of sewage contamination in aquatic environments.[42–44] Other sterols were found in a broad range of concentrations, with the highest levels in the Timbu River.

Composition of organic matter sources and source quantified

The composition of the total concentrations of each group of quantified compounds in Timbu, Barigui, and Iguaçu Rivers and Passaúna and Iraí Reservoirs is shown in Figure 2. For all samples, except the

Barigui River, the quantified compounds were mainly composed of sterols. The Barigui River sample was characterized by the predominance of AH, while the PAH, molecular markers of anthropogenic source, had the lowest contributions. Organic matter can have various sources, and when derived from the anthropogenic origin is directly related to the types of activities in that area.[42,45,46] Of the samples from the Barigui River and reservoirs, more than 95% of the compounds quantified were of natural input. For the samples from the Iguaçu and Timbu rivers, 53% and 88% of the markers quantified, respectively, are of anthropogenic origin, as presented in Figure 3.

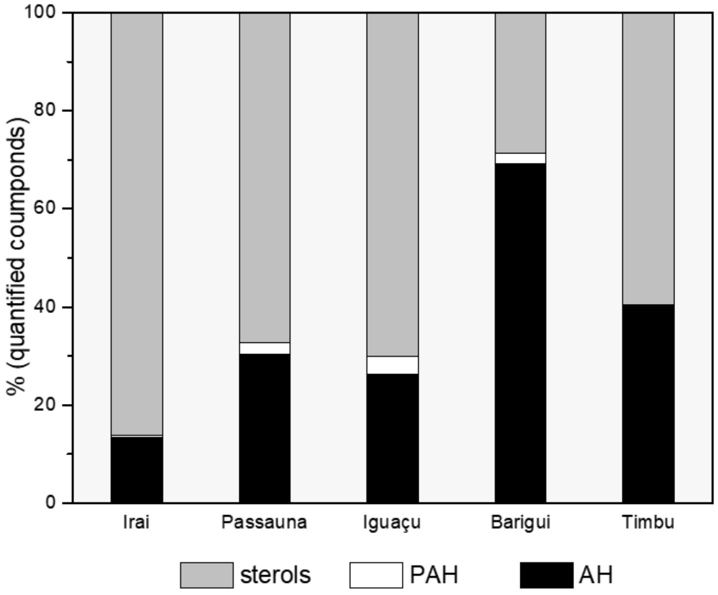


Figure 2. Composition of organic matter quantified. Sterols: Cop, e-cop, coprostanone, cholesterol, cholestanol, stigmasterol, stigmastanol and campesterol; PAH: ∑16 PAH; AH: C16 to C36, pristane, phytane and UCM.

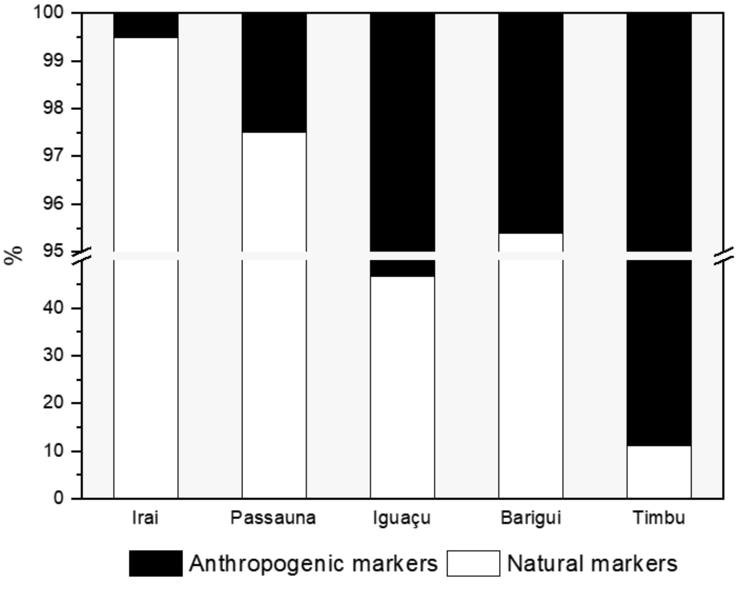


Figure 3. Comparison of quantitative molecular markers of natural and anthropogenic origin.

The sampling encompasses areas with different types of anthropogenic activities. The reservoirs are characterized by the presence of rural areas and proximity to industrialized regions. Barigui River is present in a densely urbanized area, and Timbu River in a region with high demographic expansion exhibits low levels of sanitation, finally the sample from the Iguaçu River is in an industrial site.[45,47,48]

The compounds quantified were classified according to their possible sources. The calculated (Table IV) by carbon preference index, CPI according to Equation 2.

$$\text{CPI}=\frac{1}{2}\times\left[\left(\frac{C_{23}+C_{25}+C_{27}+C_{29}+C_{31}}{C_{22}+C_{24}+C_{26}+C_{28}+C_{30}+}\right)+\left(\frac{C_{23}+C_{25}+C_{27}+C_{29}+C_{31}}{C_{24}+C_{26}+C_{28}+C_{30}+C_{32}+}\right)\right] \qquad \text{(Equation 2)}$$

The distinction between PAH from petrogenic and pyrogenic sources can be made by the presence of a higher concentration of PAH of low molecular weight (2 – 3 rings) and alkylated PAH, which suggest petrogenic sources since PAH of high molecular weight (4 – 6 rings) are indicated pyrogenic sources.[49] Another very effective way to identify the possible sources of these compounds, in sediment, is the calculation of the ratio of isomers of molecular weight 202 (Flu, Pyr), 228 (BaA, Chry), and 276 (IP, BghiP), that, due to thermodynamic stability and to a greater abundance of these compounds.[4]

Table IV. Reasons and specific limits for distinguishing the origin of the AH, PAH, and sterols

AH and PAH			
	Petrogenic	**Pyrogenic**	**Natural**
CPI [a]	< or ≈ 1	–	> 1
Ant/(Ant+Fen) [b]	< 1	> 1: coal and diesel oil combustion	
Flu/(Flu+Pyr) [b]	< 0.4	> 0.5: biomass combustion < 0.5 e > 0.4: fossil fuels	
BaA/(BaA+Cris) [b]	< 0.2 0.2 to 0.35	0.2 to 0.35: fossil fuels > 0.35: biomass combustion	
IP/(IP+BghiP) [b]	< 0.2	0.2 to 0.5: fossil fuels > 0.50: biomass combustion	
Sterols			
		Domestic sewage	
% (cop + e-cop)/ ∑sterols [c]		> 50 %: highly contaminated	
e-cop/cop [d]		< 0.2: effluent not treated; > 0.8: treated effluent	
cop/cholesterol [c]		> 1.0: contaminated; < 1.0 natural	
cop / (cop + cholestanol) [e]		> 0.7 contaminated; < 0.3: not contaminated	

AH: Aliphatic Hydrocarbons; PAH: Polycyclic Aromatic Hydrocarbons; CPI: Carbon Preference Index; [a] Aboul-Kassim;[50] [b] Yunker;[4] [c] Venkatesan;[3] [d] Mudge;[51] [e] Grimalt[52].

According to the data shown in Table III and the data presented in Figure 4, it is noted that combustion was the predominant source of the isomeric pairs of PAH in the sediment analyzed. However, the combustion source cannot be made clear since there are discrepancies among the ratios used to determine them (Figure 3). Nevertheless, it is possible to assume that vegetation burning in the surrounding areas of the water reservoirs was the major source of these compounds related to the combustion of biomass.[53,54]

AH of biogenic origin is characterized by a predominance of compounds with odd carbon numbers. Small molecular chains, from 15 to 23 carbon atoms, indicate the presence of aquatic organisms, while the predominance of long molecular chains, between 23 and 33 carbons, suggests the presence of higher plants.[55]

For the samples of Iraí Reservoir and Barigui River, there is a predominance of AH containing an odd number of the linear carbon chain, especially those of higher molecular weight (n-C25, n-C27, and n-C29). The presence of n-C27 and n-C29 is typical of lacustrine sediments where higher plants are predominant, whereas the presence of n-C25 alkane is related to the proliferation of floating macrophytes.[55–57]

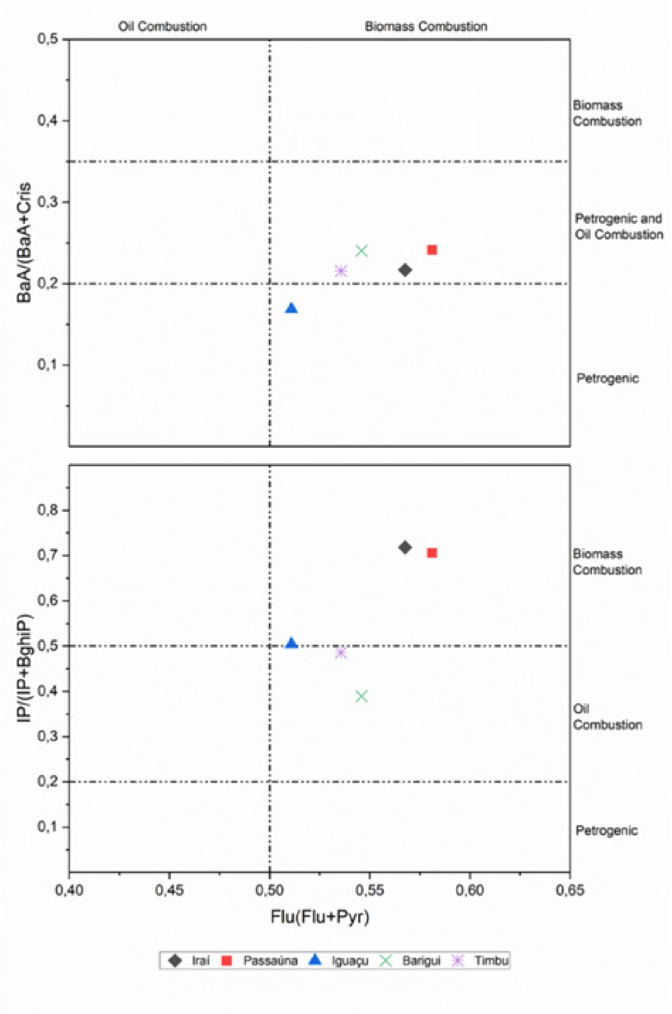


Figure 4. Representation of two-dimensional calculated ratios to identify specific sources of the isomeric pairs of PAHs (202, 228, and 276).

Due to the morphometric characteristics of the Iraí Reservoir, the proliferation of macrophytes plants is abundant, which justifies the presence of n-alkane n-C25 in the sample. The presence of AH of biogenic sources in the Barigui River and the reservoir samples can be confirmed by the CPI>1. CPI values for samples from the Iguaçu and Timbu Rivers (Table V) suggest the petrogenic input of AH (CPI<1).

The chromatographic profile of the Timbu River sample is characteristic of a UCM (Unresolved Complex Mixture) with a concentration of 488 μg g^{-1}. UCM is characterized by a broad hump in the baseline of the chromatogram resulting from the analysis of sediment contaminated with biodegraded petroleum, unburned petroleum, lubricants, and asphalts from urban runoff.[57,58] The Timbu River, despite being present in the environmental protection area of Iraí, cuts across one of the busiest highways for motor vehicles in the MRC.

Table V. Values of AH calculated for specific reasons and sterols

Parameter	Irai Reservoir	Passaúna Reservoir	Iguaçu River	Barigui River	Timbu River
AH					
CPI	2.67	3.46	0.91	3.59	1,19
Sterols					
% (cop + e-cop) / ∑sterols	0.31[a]	1.32[a]	30.44	9.06[a]	75.62
e-cop / cop	0.42[a]	0.37[a]	0.46	0.10[a]	0.06
cop/cholesterol	0.10[a]	0.28[a]	3.39	2.00	36.64
cop / (cholesterol + cholestanol)	0.05[a]	0.12[a]	1.00	1.14	8.68
cop / (cop + cholestanol)	0.08[a]	0.16[a]	0.59	0.73	0.92

AH: Aliphatic hydrocarbons; CPI: Carbon Preference Index; [a] Ratio calculated from the area values of each compound.

The chromatographic profile of the Timbu River sample is characteristic of a UCM (Unresolved Complex Mixture) with a concentration of 488 μg g^{-1}. UCM is characterized by a broad hump in the baseline of the chromatogram resulting from the analysis of sediment contaminated with biodegraded petroleum, unburned petroleum, lubricants, and asphalts from urban runoff.[57,58] The Timbu River, despite being present in the environmental protection area of Iraí, cuts across one of the busiest highways for motor vehicles in the MRC.

Thus, the presence of AH petrogenic sources in this river's sediments can be caused by the leaching of oil vehicles that travel on this road or asphalts from runoff. In general, we can say that the contribution of AH by petrogenic origin occurred in areas near roads with intense traffic of vehicles (Timbu River) and highly urbanized areas (Iguaçu River), thus giving a large anthropogenic input into these environments.

In contrast, the sediment from the Barigui River, despite being collected near a significant highway vehicle traffic in a highly industrialized and urbanized area, showed no indications of AH derived from petroleum and derivatives. Due to the specificity and high half-life of fecal sterols (coprostanol, epicoprostanol, and coprostanone), these compounds have been widely mentioned in studies involving fecal contamination and effluents.[3,59,60]

Coprostanol concentration > 0.1 μg g^{-1}, may be indicative of sewage contamination,[52] however, this parameter cannot be conclusive since this compound can be produced in situ anoxic conditions.[61] Thus, to confirm the sediment examined received input from domestic sewage is necessary to consider the concentrations of other sterols and the main relationships between them. The ratios used in this study and the results obtained are listed in Table III and Table IV, respectively.

The ratios obtained for the Timbu River indicate strong contamination by sewage. The discharge of sewage in nature in the vicinity of the Timbu River is a reality and accounts for more than 700 illegal connections to sewers along the bed of the river.[60] The value obtained from the E-COP/COP ratio (0.06) allows estimates of the degree of effluent treatment plant disposed of in an area. This value demonstrated that there is a predominance of coprostanol relative to epicoprostanol, noting the contribution of untreated sewage. Note also that for this sample, there is a relative abundance of coprostanone (173 μg g^{-1}). According to Grimalt et al.,[52] coprostanone is an estanone produced in smaller quantities than coprostanol in the biotransformation of cholesterol, and its presence is associated with fecal contamination, thus proving contamination by sewage at this site.

Regarding the Iguaçu River, it was found by the percentage ratio cop + e-cop/∑sterols that the value obtained for the sampled sediment (30%) is slightly below the threshold to be considered highly polluted. The value of E-COP/COP for this sediment was 0.46 within the maximum and minimum levels used in predicting the presence or absence of treated effluent. However, it can be said that this river receives the discharge of treated effluent since the collection point is located downstream of the WWTP-Belem. It was found for the sample Barigui River, which is an industrialized and urbanized region, which although not heavily polluted (COP + E-COP/∑sterols = 9%), there is no influence of wastewater treated on-site sampled (e-cop/cop = 0.10).

This result corroborates the study by Froehner and Martins,[62] which evaluated the presence of fecal sterols in 6 different regions of the river Barigui and found that all sampling sites were contaminated by sewage, especially in regions of greater human interference. The values of individual concentrations of fecal sterols obtained for the sources were below LOD, showing that there is little or no evidence that these samples are contaminated by sewage. The sterol that occurred at higher concentrations for these samples was campesterol, which is associated with sources of natural organic material of terrestrial or aquatic origin and, specifically, in this case, can result from the contribution of these algae present in the water reservoir.

From the evaluation of individual markers, it was possible to make an approximation of the relative contributions of anthropogenic markers quantified in this study (Figure 5). For reservoir samples, where no suppression demographic, combustion was the predominant source of molecular markers quantified, with no contribution of markers of the fecal source. However, for the samples of the Iguaçu, Barigui, and Timbu rivers, located in urbanized and industrialized areas, contributions of molecular markers from combustion and sewage were approximately the same proportion.

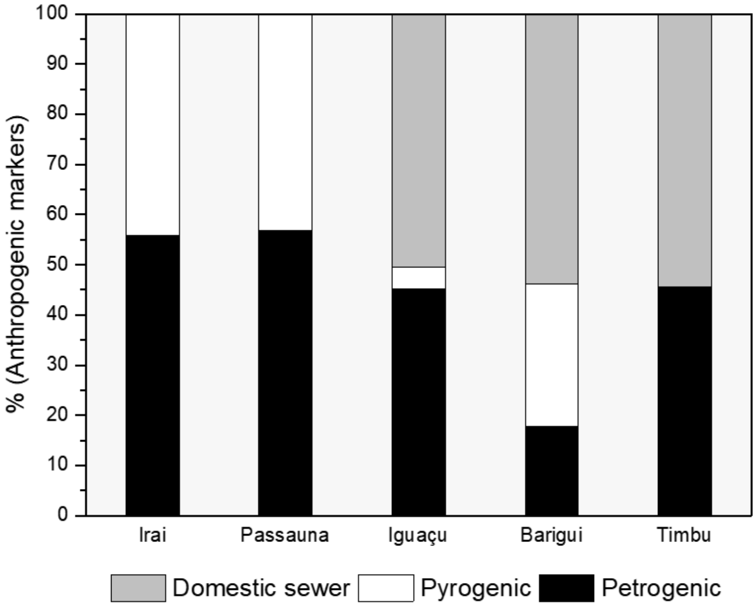


Figure 5. Distribution of quantitative molecular markers of anthropogenic origin for the samples analyzed.

Comparative analysis with previous studies

PAH concentrations in sediment samples from rivers and reservoirs in Curitiba, Brazil, were evaluated against previously published data (Table S4). The total PAH concentrations (ΣPAHs) ranged from 97.3 to 440.65 μg kg⁻¹, which are relatively low compared to many other global regions. For example, the Yinma River Basin in China[63] reported concentrations between 1000 and 5750 μg kg⁻¹, while the Niger Delta in Nigeria[64] had even higher levels, ranging from 1620 to 19800 μg kg⁻¹. In southeastern Poland,[65] ΣPAHs reached as high as 33900 μg kg⁻¹. In contrast, the Poxim River in Brazil showed much lower concentrations, between 2.2 and 28.4 μg kg⁻¹.[66]

The PAH profile in Curitiba indicates a dominant contribution from pyrogenic sources, particularly biomass burning. This contrasts with numerous other areas where sources are typically mixed. For instance, petroleum-related pollution is significant in the Yinma River (China), Salt River (Taiwan), and Niger Delta (Nigeria), often accompanied by pyrogenic contributions from vehicle emissions and coal burning. This variation in source distribution may be indicative of different levels of industrialization and land-use practices. Regarding ecological and human health risks, the concentrations observed in Curitiba are likely to pose a lesser concern compared to heavily impacted environments such as the Salt River and the Tigris River.[67,68] In these regions, high molecular weight polycyclic aromatic hydrocarbons (PAHs) are prevalent and associated with increased carcinogenic risks. Studies in these areas frequently report moderate to high ecological threats, including significant adverse effects on aquatic biota.

In the present study, coprostanol concentrations ranged from 0.75 to 410 µg g^{-1}. These values suggest moderate to high levels of fecal contamination, particularly in densely populated areas and regions with direct untreated sewage discharge. In comparison to other studies (Table S5), the levels in Curitiba ranged across a wide international spectrum, indicating different levels of urbanization, sanitation facilities, and anthropogenic influence. The Ipojuca River in Brazil showed a significantly elevated coprostanol concentration of 557.3 µg g^{-1}, attributed to intense human activity and the proximity of urban settlements to the riverbanks.[69] In South Korea, the Geumho River exhibited a wide range of coprostanol concentrations (9 to 1282 µg g^{-1}), and these elevated levels were associated with extensive urbanization and industrialization in the area.[70] These findings highlight the significant impact of land-use patterns on sewage contamination levels. In contrast, the Guamá River in Brazil had a coprostanol concentration of 292.52 µg g^{-1} linked to insufficient sewage treatment infrastructures and intense port operations.[71] The Kibera River in Kenya[72] showed considerable levels of contamination, ranging from 55 to 298 µg g^{-1}, a result of the continuous discharge of untreated domestic wastewater, echoing the circumstances in Curitiba where direct sewage inputs are a major concern. On the other hand, rivers in areas with more advanced wastewater management systems exhibited considerably substantially reduced concentration levels. For instance, the Thames River in England presented coprostanol levels ranging from 0.0091 to 0.42 µg g^{-1}.[73] Historical sediment core analyses revealed a significant decrease in coprostanol levels over time, correlating with the increasing use and effectiveness of sewage treatment systems. The results of this study highlight the urgent need for investments in basic sanitation infrastructure in urban centers to reduce environmental and public health risks associated with untreated sewage discharge.

Aliphatic hydrocarbon (AH) concentrations ranging from 0.75 to 410 µg g^{-1} and these values suggest moderate contamination, primarily driven by the discharge of untreated sewage and the influence of a densely populated urban area. In comparison to other aquatic systems throughout the world (Table S6), AH levels in Curitiba varied widely, indicating variances in land use, pollution sources, and environmental management techniques. Whereas the Tehran River in Iran[74] had values ranging from 2.94 to 114.7 µg g^{-1} in a densely populated region. However, in this situation, the hydrocarbon input was primarily petrogenic, as opposed to the Curitiba region, which is likely influenced by both anthropogenic and biogenic sources. Al Wajh Lagoon in Saudi Arabia, located near the Red Sea and vulnerable to hydrocarbon contamination from neighboring oil-related operations, showed a similar petrogenic effect (64-302.6 µg g^{-1}).[75] The concentration range in Brazil's rural aquatic system, the Mangueira Lagoon, was larger and wider (5.0–652.7 µg g^{-1}), with hydrocarbons mostly coming from petrogenic and biogenic sources.[76] This implies that natural and diffuse anthropogenic influences might cause significant AH levels to be present even in regions with lower metropolitan densities. Lower concentrations were recorded in the Lafayette River (USA), with values ranging from 4.94 to 40.83 µg g^{-1}, where the sources were attributed to atmospheric deposition and automotive activity.[77] This scenario reflects a more diffuse contamination profile typical of urban areas with relatively controlled direct discharge. The Norilsk–Pyasino water system in Russia[78] had the highest AH values among the examined studies, with concentrations ranging from 15 to 1914 µg g^{-1}, resulting from a large-scale diesel fuel spill. In contrast to the ongoing urban and domestic inputs seen in Curitiba, this is an acute contamination episode. In summary, the AH concentrations in Curitiba are moderate when viewed in the global context, with values exceeding those of more regulated urban areas (e.g., Lafayette River) but significantly lower than those impacted by major industrial or accidental events (e.g., Norilsk–Pyasino). The sources in Curitiba appear to be primarily related to untreated domestic sewage and urban runoff, reinforcing the need for improved wastewater infrastructure to mitigate hydrocarbon inputs into aquatic systems.

CONCLUSIONS

This work has resulted in a significant decrease in the number of reagents and the total analysis time compared to the official methodology described in the literature. Some figures of merit of the method demonstrated that the accuracy and precision obtained are suitable for the determination of the compounds in sediments; results were obtained with high-reliability analysis.

The use of geochemical markers for preliminary assessment of sources of organic matter and contamination in the sediments showed that the sediment with a higher input of organic matter of anthropogenic origin corresponds to the sample the Timbu River, this river despite being in an area of environmental protection. The presence of coprostanol as an indicator of fecal contamination showed that the pollution of the Iguaçu and Barigui rivers is heavily influenced by urban and industrial activities, respectively, and was a significant contribution to domestic sewage. Overall, the results obtained regarding the origin of the PAH demonstrate that combustion was the predominant source of this class of compounds evaluated for sediment.

Conflicts of interest

The authors confirm that there are no known conflicts of interest associated with this publication.

Acknowledgements

The authors would like to thank the “Ministério da Ciência, Tecnologia Inovações e Comunicações” (MCTIC), the “Financiadora de Estudos e Projetos” (FINEP), CTHIDRO 01/2013, the “Instituto Nacional de Ciências e Tecnologias Analíticas Avançadas” (INCTAA, 465768/2014-8), and PETROBRAS for the financial support. This study was also financed in part by the “Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil” (CAPES) – Finance Code 001. M.T. Grassi is also thankful to the “Conselho Nacional de Desenvolvimento Científico e Tecnológico” (CNPq), grant number 308055/2017-9.

REFERENCES

(1) Isobe, K. O.; Tarao, M.; Zakaria, M. P.; Chiem, N. H.; Minh, L. Y.; Takada, H. Quantitative Application of Fecal Sterols Using Gas Chromatography - Mass Spectrometry to Investigate Fecal Pollution in Tropical Waters: Western Malaysia and Mekong Delta, Vietnam. *Environ. Sci. Technol.* **2002**, *36* (21), 4497–4507. https://doi.org/10.1021/es020556h

(2) Kwan, C. S.; Takada, H.; Boonyatumanond, R.; Kato, Y.; Mizukawa, K.; Ito, M.; Dung, L. Q.; Zakaria, M. P.; Santiago, E. C. Historical Occurrences of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls in Manila Bay, Philippines, and in the Upper Gulf of Thailand. *Sci. Total Environ.* **2014**, *470–471*, 427–437. https://doi.org/10.1016/j.scitotenv.2013.09.076

(3) Venkatesan, M. I.; Kaplan, I. R. Sedimentary Coprostanol as an Index of Sewage Addition in Santa Monica Basin, Southern California. *Environ. Sci. Technol.* **1990**, *24* (2), 208–214. https://doi.org/10.1021/es00072a009

(4) Yunker, M. B.; Macdonald, R. W.; Vingarzan, R.; Mitchell, R. H.; Goyette, D.; Sylvestre, S. PAHs in the Fraser River Basin: A Critical Appraisal of PAH Ratios as Indicators of PAH Source and Composition. *Org. Geochem.* **2002**, *33* (4), 489–515. https://doi.org/10.1016/S0146-6380(02)00002-5

(5) Saito, Y.; Ueta, I. Miniaturization for the Development of High Performance Separation Systems. *Chromatography* **2017**, *38* (3), 85–94. https://doi.org/10.15583/jpchrom.2017.019

(6) Kim, N. Y.; Loganathan, B. G.; Kim, G. B. Determination and Comparison of Freely Dissolved PAHs Using Different Types of Passive Samplers in Freshwater. *Sci. Total Environ.* **2023**. https://doi.org/10.1016/j.scitotenv.2023.164802

(7) Kawakami, S. K.; Montone, R. C. An Efficient Ethanol-Based Analytical Protocol to Quantify Faecal Steroids in Marine Sediments. *J. Braz. Chem. Soc.* **2002**, *13* (2), 226–232. https://doi.org/10.1590/S0103-50532002000200014

(8) Pouch, A.; Zaborska, A.; Mazurkiewicz, M.; Winogradow, A.; Pazdro, K. PCBs, HCB and PAHs in the Seawater of Arctic Fjords – Distribution, Sources and Risk Assessment. *Mar. Pollut. Bull.* **2021**, *164*. https://doi.org/10.1016/j.marpolbul.2021.111980

(9) Fontana, A. R.; Lana, N. B.; Martinez, L. D.; Altamirano, J. C. Ultrasound-Assisted Leaching-Dispersive Solid-Phase Extraction Followed by Liquid-Liquid Microextraction for the Determination of Polybrominated Diphenyl Ethers in Sediment Samples by Gas Chromatography-Tandem Mass Spectrometry. *Talanta* **2010**, *82* (1), 359–366. https://doi.org/10.1016/j.talanta.2010.04.050

(10) Zhao, L.; Zhao, Z.; Zhang, J.; Zhang, P. Seasonal Variation, Spatial Distribution, and Sources of PAHs in Surface Seawater from Zhanjiang Bay Influenced by Land-Based Inputs. *Mar. Environ. Res.* **2023**, *188*. https://doi.org/10.1016/j.marenvres.2023.106028

(11) United States Environmental Protection Agency (US EPA). *Method 3540C: Soxhlet Extraction, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 1996*. Available at: https://www.epa.gov/sites/default/files/2015-12/documents/3540c.pdf (accessed 03/2024).

(12) United States Environmental Protection Agency (US EPA). *Method 3610B: Alumina Cleanup, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 1996.* Available at: https://www.epa.gov/sites/default/files/2015-12/documents/3610b.pdf (accessed 03/2024).

(13) United States Environmental Protection Agency (US EPA). *Method 3630C: Silica Gel Cleanup, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 1996*. Available at: https://www.epa.gov/sites/default/files/2015-12/documents/3630c.pdf (accessed 03/2024).

(14) Hara, E. L. Y.; da Silva, C. A.; Souza, R. S.; Saint Clair Colimo, A. G.; Grassi, M. T. Determination of Polybrominated Diphenyl Ethers in Riverine Sediments by Ultrasound-Assisted Microextraction (USAME), Reduced Scale Cleanup, and GC-MS. *Curr. Anal. Chem.* **2018**, *14* (6), 615–625. https://doi.org/10.2174/1573411014666171229161613

(15) Martín-Pozo, L.; de Alarcón-Gómez, B.; Rodríguez-Gómez, R.; García-Córcoles, M. T.; Çipa, M.; Zafra-Gómez, A. Analytical Methods for the Determination of Emerging Contaminants in Sewage Sludge Samples. A Review. *Talanta* **2019**, *192*, 508–533. https://doi.org/10.1016/j.talanta.2018.09.056

(16) Wacheski, T.; Hara, E.; Soares, B.; da Silva, B.; Abate, G.; Grassi, M. O-DGT Devices for the Determination of Emerging Contaminants in Aqueous Matrices. *J. Braz. Chem. Soc.* **2021**, *32* (1), 72–82. https://doi.org/10.21577/0103-5053.20200157

(17) Orecchio, S.; Amorello, D.; Indelicato, R.; Barreca, S.; Orecchio, S. A Short Review of Simple Analytical Methods for the Evaluation of PAHs and PAEs as Indoor Pollutants in House Dust Samples. *Atmosphere (Basel)* **2022**, *13* (11). https://doi.org/10.3390/atmos13111799

(18) United States Environmental Protection Agency (US EPA). *Method 3550C: Ultrasonic Extraction, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 2007*. Available at: https://www.epa.gov/sites/default/files/2015-12/documents/3550c.pdf (accessed 2025-04-05).

(19) Martinez, E.; Gros, M.; Lacorte, S.; Barceló, D. Simplified Procedures for the Analysis of Polycyclic Aromatic Hydrocarbons in Water, Sediments and Mussels. *J. Chromatogr. A* **2004**, *1047*, 181–188. https://doi.org/10.1016/j.chroma.2004.07.003

(20) Patire, V. F.; de Albergaria-Barbosa, A. C. R.; Barreto, I. S.; Taniguchi, S.; Fernandez, W. S.; Dias, J. F.; da Silva, D. A. M.; Bícego, M. C. Bioavailability of Polycyclic Aromatic Hydrocarbons in Santos Bay (Brazil) and its Adjacent Continental Shelf. *Ocean and Coastal Research* **2023**, *71* (2), e23024. https://doi.org/10.1590/2675-2824071.22047VFP

(21) Kawakami, S. K.; Mello, L.; Dergan, A. L.; Evangelista, C.; Aquino, R. F.; Mendes, R. A.; Carmo, A. M. C.; Amado, L. L. Sedimentary PAH and Oxidative Stress Biomarkers Responses on Namalycastis Abiuma (Polychaeta: Nereididae) from an Urbanized Amazon Estuary. *Reg. Stud. Mar. Sci.* **2023**, *57*. https://doi.org/10.1016/J.RSMA.2022.102757

(22) Mater, L.; Alexandre, M. R.; Hansel, F. A.; Madureira, L. A. S. Assessment of Lipid Compounds and Phosphorus in Mangrove Sediments of Santa Catarina Island, SC, Brazil. *J. Braz. Chem. Soc.* **2004**, *15* (5), 725–734. https://doi.org/10.1590/S0103-50532004000500019

(23) United States Environmental Protection Agency (US EPA). *Method 8270E (SW-846): Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC-MS)*. Available at: https://www.epa.gov/esam/epa-method-8270e-sw-846-semivolatile-organic-compounds-gas-chromatographymass-spectrometry-gc (accessed 2025-03-12).

(24) Cavalcante, R. M.; De Lima, D. M.; Correia, L. M.; Nascimento, R. F.; Silveira, E. R.; Freire, G. S. S.; Viana, R. B. Técnicas de Extrações e Procedimentos de Clean-up Para a Determinação de Hidrocarbonetos Policílicos Aromáticos (HPA) em Sedimentos da Costa do Ceará. *Quim. Nova* **2008**, *31* (6), 1371–1377. https://doi.org/10.1590/S0100-40422008000600019

(25) Leite, N. F.; Peralta-Zamora, P.; Grassi, M. T. Multifactorial Optimization Approach for the Determination of Polycyclic Aromatic Hydrocarbons in River Sediments by Gas Chromatography-Quadrupole Ion Trap Selected Ion Storage Mass Spectrometry. *J. Chromatogr. A* **2008**, *1192* (2), 273–281. https://doi.org/10.1016/j.chroma.2008.03.067

(26) Sánchez-Avila, J.; Fernandez-Sanjuan, M.; Vicente, J.; Lacorte, S. Development of a Multi-Residue Method for the Determination of Organic Micropollutants in Water, Sediment and Mussels Using Gas Chromatography-Tandem Mass Spectrometry. *J. Chromatogr. A* **2011**, *1218* (38), 6799–6811. https://doi.org/10.1016/j.chroma.2011.07.056

(27) Jimenez Martinez, A. E.; Galoski, C. E.; Cardoso Borillo, G.; Moreton Godoi, R. H.; Lopes Figueira, R. C.; Alves de Lima Ferreira, P.; Froehner, S. Forensic Assessment of Polycyclic Aromatic Hydrocarbons to Reconstruct Anthropogenic Activities in a Nearby Urban Reservoir. *J. South Am. Earth Sci.* **2022**, *120*. https://doi.org/10.1016/J.JSAMES.2022.104104

(28) Teixeira, M.; Cesar, R.; Abessa, D.; Siqueira, C.; Lourenço, R.; Vezzone, M.; Fernandes, Y.; Koifman, G.; Perina, F. C.; Meigikos dos Anjos, R.; Polivanov, H.; Castilhos, Z. Ecological Risk Assessment of Metal and Hydrocarbon Pollution in Sediments from an Urban Tropical Estuary: Tijuca Lagoon (Rio de Janeiro, Brazil). *Environ. Sci. Pollut. Res.* **2023**, *30* (1), 184–200. https://doi.org/10.1007/S11356-022-22214-6

(29) Association of Official Analytical Collaboration (AOAC) International. *Guidelines for Single Laboratory Validation of Chemical Methods for Dietary Supplements and Botanicals*. *AOAC International* **2002**, 1–38.

(30) Cai, Y.; Wang, Z.; Cui, L.; Wang, J.; Zuo, X.; Lei, Y.; Zhao, X.; Zhai, X.; Li, J.; Li, W. Distribution, Source Diagnostics, and Factors Influencing Polycyclic Aromatic Hydrocarbons in the Yellow River Delta Wetland. *Reg. Stud. Mar. Sci.* **2023**, *67*. https://doi.org/10.1016/J.RSMA.2023.103181

(31) Allouche, M.; Nasri, A.; Harrath, A. H.; Mansour, L.; Beyrem, H.; Boufahja, F. Migratory Behavior of Free-Living Marine Nematodes Surrounded by Sediments Experimentally Contaminated by Mixtures of Polycyclic Aromatic Hydrocarbons. *J. King Saud Univ., Sci.* **2020**, *32* (2), 1339-1345. https://doi.org/10.1016/j.jksus.2019.11.025

(32) Bottoli, C. B. G.; Collins, C. H.; Jardim, I. C. S. F.; Ribani, M. Validação em métodos cromatográficos e eletroforéticos. *Quim. Nova* **2004**, *27* (5), 771–780. https://doi.org/10.1590/S0100-40422004000500017

(33) Parra, Y. J.; Oloyede, O. O.; Pereira, G. M.; de Almeida Lima, P. H. A.; da Silva Caumo, S. E.; Morenikeji, O. A.; Vasconcellos, P. C. Polycyclic Aromatic Hydrocarbons in Soils and Sediments in Southwest Nigeria. *Environmental Pollution* **2020**, *259*. https://doi.org/10.1016/j.envpol.2019.113732

(34) Da Silva, T. F.; Azevedo, D. de A.; Neto, F. R. D. A. Distribution of Polycyclic Aromatic Hydrocarbons in Surface Sediments and Waters from Guanabara Bay, Rio de Janeiro, Brazil. *J. Braz. Chem. Soc.* **2007**, *18* (3), 628–637. https://doi.org/10.1590/s0103-50532007000300021

(35) Venturini, N.; Tommasi, L. R. Polycyclic Aromatic Hydrocarbons and Changes in the Trophic Structure of Polychaete Assemblages in Sediments of Todos os Santos Bay, Northeastern, Brazil. *Mar. Pollut. Bull.* **2004**, *48* (1–2), 97–107. https://doi.org/10.1016/S0025-326X(03)00331-X

(36) Benlahcen, K. T.; Chaoui, A.; Budzinski, H.; Bellocq, J.; Garrigues, P. Distribution and Sources of Polycyclic Aromatic Hydrocarbons in Some Mediterranean Coastal Sediments. *Mar. Pollut. Bull.* **1997**, *34* (5), 298–305. https://doi.org/10.1016/S0025-326X(96)00098-7

(37) Johnson, A. C.; Larsen, P. F.; Gadbois, D. F.; Humason, A. W. The Distribution of Polycyclic Aromatic Hydrocarbons in the Surficial Sediments of Penobscot Bay (Maine, USA) in Relation to Possible Sources and to Other Sites Worldwide. *Mar. Environ. Res.* **1985**, *15* (1), 1–16. https://doi.org/10.1016/0141-1136(85)90034-0

(38) Notar, M.; Leskovšek, H.; Faganeli, J. Composition, Distribution and Sources of Polycyclic Aromatic Hydrocarbons in Sediments of the Gulf of Trieste, Northern Adriatic Sea. *Mar. Pollut. Bull.* **2001**, *42* (1), 36–44. https://doi.org/10.1016/S0025-326X(00)00092-8

(39) Lin, X.; Lin, L.; Liao, Z.; Wu, P.; Yang, C. Occurrence and Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Marine Organisms from Shenzhen Coastal Waters and Human Health Risk Assessment. *Mar. Pollut. Bull.* **2023**, *195*. https://doi.org/10.1016/j.marpolbul.2023.115498

(40) Meniconi, M. D. F. G.; Gabardo, I. T.; Carneiro, M. E. R.; Barbanti, S. M.; da Silva, G. C.; Massone, C. G. Brazilian Oil Spills Chemical Characterization - Case Studies. *Environ. Forensics* **2002**, *3* (3–4), 303–321. https://doi.org/10.1006/enfo.2002.0101

(41) Leite, N. F.; Peralta-Zamora, P.; Grassi, M. T. Distribution and Origin of Polycyclic Aromatic Hydrocarbons in Surface Sediments from an Urban River Basin at the Metropolitan Region of Curitiba, Brazil. *Journal of Environmental Sciences* **2011**, *23* (6), 904–911. https://doi.org/10.1016/S1001-0742(10)60496-2

(42) Jeanneau, L.; Faure, P.; Montarges-Pelletier, E. Quantitative Multimolecular Marker Approach to Investigate the Spatial Variability of the Transfer of Pollution from the Fensch River to the Moselle River (France). *Sci. Total Environ.* **2008**, *389* (2–3), 503–513. https://doi.org/10.1016/j.scitotenv.2007.09.023

(43) Martins, C. C.; Braun, J. A. F.; Seyffert, B. H.; Machado, E. C.; Fillmann, G. Anthropogenic Organic Matter Inputs Indicated by Sedimentary Fecal Steroids in a Large South American Tropical Estuary (Paranaguá Estuarine System, Brazil). *Mar. Pollut. Bull.* **2010**, *60* (11), 2137–2143. https://doi.org/10.1016/j.marpolbul.2010.07.027

(44) Gurgatz, B. M.; Garcia, M. R.; Cabral, A. C.; de Souza, A. C.; Nagai, R. H.; Figueira, R. C. L.; de Mahiques, M. M.; Martins, C. C. Polycyclic Aromatic Hydrocarbons in a Natural Heritage Estuary Influenced by Anthropogenic Activities in the South Atlantic: Integrating Multiple Source Apportionment Approaches. *Mar. Pollut. Bull.* **2023**, *188*, 114678. https://doi.org/10.1016/j.marpolbul.2023.114678

(45) Rodrigues, C. C. S.; Messias, M. S.; Morales, J. H. A.; Damasceno, F. C.; Corrêa, J. A. M. Insights about Levels and Sources of Organic Pollution in an Urbanized Amazon Estuary (Belém, PA, Northern Brazil). *Environ. Monit. Assess.* **2023**, *195* (6), 1–15. https://doi.org/10.1007/S10661-023-11271-0

(46) Li, J.; Chang, R.; Ban, X.; Yuan, G. L.; Du, X.; Yin, G.; Lin, T. Aged Polycyclic Aromatic Hydrocarbons as Stratigraphic Marker in the Anthropocene: Evidence from Tibetan Lake Sediments. *Water Res.* **2023**, *245*. https://doi.org/10.1016/j.watres.2023.120652

(47) Billah, M.; Bhuiyan, K. A.; Al Amran, I. U.; Cabral, A. C.; Garcia, M. R. D. Polycyclic Aromatic Hydrocarbons (PAHs) Pollution in Mangrove Ecosystems: Global Synthesis and Future Research Directions. *Rev. Environ. Sci. Bio/Technol.* **2022**, *21* (3), 747–770. https://doi.org/10.1007/S11157-022-09625-0

(48) Gripp, L.; Carreira, R. S.; Moreira, D.; Scofield, A. L.; Massone, C. G. Method Development and Application to Sediments for Multi-Residue Analysis of Organic Contaminants Using Gas Chromatography-Tandem Mass Spectrometry. *Anal. Bioanal. Chem.* **2022**, *414* (19), 5845–5855. https://doi.org/10.1007/S00216-022-04148-7

(49) Yonis, S.; Kahkashan, S.; Adelman, D.; Lohmann, R. Transects of Polycyclic Aromatic Hydrocarbons and Organochlorine Pesticides in an Urban Estuary Using Passive Samplers. *Mar. Pollut. Bull.* **2023**, *197*. https://doi.org/10.1016/j.marpolbul.2023.115768

(50) Aboul-Kassim, T. A. T.; Simoneit, B. R. T. Lipid Geochemistry of Surficial Sediments from the Coastal Environment of Egypt I. Aliphatic Hydrocarbons-Characterization and Sources. *Mar. Chem.* **1996**, *54* (1–2), 135–158. https://doi.org/10.1016/0304-4203(95)00098-4

(51) Mudge, S. M.; Norris, C. E. Lipid Biomarkers in the Conwy Estuary (North Wales, U.K.): A Comparison between Fatty Alcohols and Sterols. *Mar. Chem.* **1997**, *57* (1–2), 61–84. https://doi.org/10.1016/S0304-4203(97)00010-8

(52) Grimalt, J. O.; Fernández, P.; Bayona, J. M.; Albaigés, J. Assessment of Fecal Sterols and Ketones as Indicators of Urban Sewage Inputs to Coastal Waters. *Environ. Sci. Technol.* **1990**, *24* (3), 357–363. https://doi.org/10.1021/es00073a011

(53) Lu, J.; Li, M.; Tan, J.; He, M.; Wu, H.; Kang, Y.; Hu, Z.; Zhang, J.; Guo, Z. Distribution, Sources, Ecological Risk and Microbial Response of Polycyclic Aromatic Hydrocarbons in Qingdao Bays, China. *Environmental Pollution* **2023**, *338*, 122687. https://doi.org/10.1016/J.ENVPOL.2023.122687

(54) Bartley, M. C.; Tremblay, T.; De Silva, A. O.; Kamula, C. M.; Ciastek, S.; Kuzyk, Z. Z. A. Sedimentary Records of Contaminant Inputs in Frobisher Bay, Nunavut. *Environ. Sci. Ecotechnology* **2024**, *18*. https://doi.org/10.1016/J.ESE.2023.100313

(55) Meyers, P. A.; Ishiwatari, R. Lacustrine Organic Geochemistry-an Overview of Indicators of Organic Matter Sources and Diagenesis in Lake Sediments. *Org. Geochem.* **1993**, *20* (7), 867–900. https://doi.org/10.1016/0146-6380(93)90100-P

(56) Meyers, P. A. Applications of Organic Geochemistry to Paleolimnological Reconstructions: A Summary of Examples from the Laurentian Great Lakes. *Org. Geochem.* **2003**, *34* (2), 261–289. https://doi.org/10.1016/S0146-6380(02)00168-7

(57) Volkman, J. K.; Barrett, S. M.; Blackburn, S. I.; Mansour, M. P.; Sikes, E. L.; Gelin, F. Microalgal Biomarkers: A Review of Recent Research Developments. *Org. Geochem.* **1998**, *29* (5), 1163–1179. https://doi.org/10.1016/S0146-6380(98)00062-X

(58) Gogou, A.; Bouloubassi, I.; Stephanou, E. G. Marine Organic Geochemistry of the Eastern Mediterranean: 1. Aliphatic and Polyaromatic Hydrocarbons in Cretan Sea Surficial Sediments. *Mar. Chem.* **2000**, *68* (4), 265–282. https://doi.org/10.1016/S0304-4203(99)00082-1

(59) Froehner, S.; Martins, R. F.; Errera, M. R. Assessment of Fecal Sterols in Barigui River Sediments in Curitiba, Brazil. *Environ. Monit. Assess.* **2009**, *157* (1–4), 591–600. https://doi.org/10.1007/s10661-008-0559-0

(60) Carneiro, C.; Kelderman, P.; Irvine, K. Assessment of Phosphorus Sediment–Water Exchange through Water and Mass Budget in Passaúna Reservoir (Paraná State, Brazil). *Environ. Earth Sci.* **2016**, *75* (7), article number 564. https://doi.org/10.1007/s12665-016-5349-3

(61) Venkatesan, M. I.; Santiago, C. A. Sterols in Ocean Sediments: Novel Tracers to Examine Habitats of Cetaceans, Pinnipeds, Penguins and Humans. *Mar. Biol.* **1989**, *102* (4), 431–437. https://doi.org/10.1007/BF00438343

(62) Froehner, S.; Martins, R. F. Avaliação Da Composição Química de Sedimentos Do Rio Barigüi Na Região Metropolitana de Curitiba. *Quim. Nova* **2008**, *31* (8), 2020–2026. https://doi.org/10.1590/S0100-40422008000800020

(63) Sun, C.; Zhang, J.; Ma, Q.; Chen, Y.; Ju, H. Polycyclic Aromatic Hydrocarbons (PAHs) in Water and Sediment from a River Basin: Sediment–Water Partitioning, Source Identification and Environmental Health Risk Assessment. *Environ. Geochem. Health* **2017**, *39* (1), 63–74. https://doi.org/10.1007/s10653-016-9807-3

(64) Iwegbue, C. M. A.; Irerhievwie, G. O.; Tesi, G. O.; Olisah, C.; Nwajei, G. E.; Martincigh, B. S. Polycyclic Aromatic Hydrocarbons (PAHs) in Surficial Sediments from Selected Rivers in the Western Niger Delta of Nigeria: Spatial Distribution, Sources, and Ecological and Human Health Risks. *Mar. Pollut. Bull.* **2021**, *167*. https://doi.org/10.1016/j.marpolbul.2021.112351

(65) Baran, A.; Tarnawski, M.; Urbański, K.; Klimkowicz-Pawlas, A.; Spałek, I. Concentration, Sources and Risk Assessment of PAHs in Bottom Sediments. *Environ. Sci. Pollut. Res.* **2017**, *24* (29), 23180–23195. https://doi.org/10.1007/s11356-017-9944-y

(66) Souza, M. R. R.; Santos, E.; Suzarte, J. S.; Carmo, L. O.; Frena, M.; Damasceno, F. C.; Alexandre, M. R. Concentration, Distribution and Source Apportionment of Polycyclic Aromatic Hydrocarbons (PAH) in Poxim River Sediments, Brazil. *Mar. Pollut. Bull.* **2018**, *127*, 478–483. https://doi.org/10.1016/j.marpolbul.2017.12.045

(67) Chen, C.-F.; Ju, Y.-R.; Su, Y.-C.; Lim, Y. C.; Kao, C.-M.; Chen, C.-W.; Dong, C.-D. Distribution, Sources, and Behavior of PAHs in Estuarine Water Systems Exemplified by Salt River, Taiwan. *Mar. Pollut. Bull.* **2020**, *154*. https://doi.org/10.1016/j.marpolbul.2020.111029

(68) Grmasha, R. A.; Stenger-Kovács, C.; Bedewy, B. A. H.; Al-sareji, O. J.; Al-Juboori, R. A.; Meiczinger, M.; Hashim, K. S. Ecological and Human Health Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAH) in Tigris River near the Oil Refineries in Iraq. *Environ. Res.* **2023**, *227*. https://doi.org/10.1016/j.envres.2023.115791

(69) de Oliveira, A. F.; Gomes, B.; França, R.; Moraes, A.; Bataglion, G.; Santos, J. Assessment of Urban Contamination by Sewage in Sediments from Ipojuca River in Caruaru City, Pernambuco, Brazil. *J. Braz. Chem. Soc.* **2022**, *33* (2), 163–172. https://doi.org/10.21577/0103-5053.20210133

(70) Lee, D. H.; Kim, S. H.; Won, E. J.; Kim, M. S.; Hur, J.; Shin, K. H. Integrated Approach for Quantitative Estimation of Particulate Organic Carbon Sources in a Complex River System. *Water Res.* **2021**, *199*. https://doi.org/10.1016/J.WATRES.2021.117194

(71) Rodrigues, C. C. S.; Messias, M. S.; Morales, J. H. A.; Damasceno, F. C.; Corrêa, J. A. M. Insights about Levels and Sources of Organic Pollution in an Urbanized Amazon Estuary (Belém, PA, Northern Brazil). *Environ. Monit. Assess.* **2023**, *195* (6), article number 731. https://doi.org/10.1007/s10661-023-11271-0

(72) Vane, C. H.; Kim, A. W.; dos Santos, R. A. L.; Gill, J. C.; Moss-Hayes, V.; Mulu, J. K.; Mackie, J. R.; Ferreira, A. M.; Chenery, S. R.; Olaka, L. A. Impact of Organic Pollutants from Urban Slum Informal Settlements on Sustainable Development Goals and River Sediment Quality, Nairobi, Kenya, Africa. *Appl. Geochem.* **2022**, *146*. https://doi.org/10.1016/J.APGEOCHEM.2022.105468

(73) Vane, C. H.; Kim, A. W.; dos Santos, R. A. L.; Moss-Hayes, V. Contrasting Sewage, Emerging and Persistent Organic Pollutants in Sediment Cores from the River Thames Estuary, London, England, UK. *Mar. Pollut. Bull.* **2022**, *175*. https://doi.org/10.1016/J.MARPOLBUL.2022.113340

(74) Moghaddam, A. H.; Hashemi, S. H.; Ghadiri, A. Aliphatic Hydrocarbons in Urban Runoff Sediments: A Case Study from the Megacity of Tehran, Iran. *J. Environ. Health Sci. Eng.* **2021**, *19* (1), 205–216. https://doi.org/10.1007/s40201-020-00596-4

(75) Al-Otaibi, M. T.; Rushdi, A. I.; Rasul, N.; Bazeyad, A.; Al-Mutlaq, K. F.; Aloud, S. S.; Alharbi, H. A. Occurrence, Distribution, and Sources of Aliphatic and Cyclic Hydrocarbons in Sediments from Two Different Lagoons along the Red Sea Coast of Saudi Arabia. *Water (Switzerland)* **2024**, *16* (1). https://doi.org/10.3390/w16010187

(76) Sanches Filho, P. J.; Andrade, G. O.; Moreira, K.; Rockenbach, C. K. Determination of Aliphatic Hydrocarbons in Surface Sediments of Mangueira Lagoon (RS—Brazil). *Environ. Earth Sci.* **2021**, *80* (21), article number 728. https://doi.org/10.1007/s12665-021-10010-3

(77) Maynard, N.; Harvey, H. R. Distribution and Source Assignments of Polycyclic Aromatic and Aliphatic Hydrocarbons in Sediments and Biota of the Lafayette River, VA. *Environ. Sci. Pollut. Res.* **2023**, *30* (16), 47527–47543. https://doi.org/10.1007/s11356-023-25563-y

(78) Nemirovskaya, I. A.; Glyaznetsova, Yu. S. The Effect of Accidental Spill of Diesel Fuel in Noril'sk on Hydrocarbon Concentrations and Composition in Bottom Sediments. *Water Resour.* **2022**, *49* (6), 1027–1039. https://doi.org/10.1134/S0097807822060100

SUPPLEMENTARY MATERIAL

Table S1. Analytical curves, linear range, correlation coefficient, and detection and quantification limits for PAHs determination

Compound	Concentration range (ng mL^{-1})	R	LOD (ng g^{-1})	LOQ (ng g^{-1})
Nap	4.9 a 490	0.9946	0.087	1.633
Ace	4.9 a 490	0.9883	0.078	1.633
Acy	4.9 a 490	0.9967	0.093	1.633
Flu	4.9 a 490	0.9920	0.111	1.633
Phen	4.9 a 490	0.9937	0.123	1.633
Ant	4.9 a 490	0.9888	0.150	1.633
Flua	4.9 a 490	0.9909	0.168	1.633
Pyr	4.9 a 490	0.9970	0.105	1.633
BaA	4.9 a 490	0.9973	0.066	1.633
Chry	4.9 a 490	0.9965	0.027	1.633
BbF	4.9 a 490	0.9967	0.027	1.633
BbK	4.9 a 490	0.9861	0.078	1.633
BaP	4.9 a 490	0.9933	0.123	1.633
IP	4.9 a 490	0.9967	0.144	1.633
DahA	4.9 a 490	0.9970	0.129	1.633
BghI	4.9 a 490	0.9941	0.111	1.633

Table S2. Analytical curves, linear range, correlation coefficient, and detection and quantification limits for determination of sterols

Compound	Concentration range (ng mL^{-1})	R	LOD (µg g^{-1})	LOQ (µg g^{-1})
Cop	0.24 a 15	0.9957	0.051	0.080
E-cop	0.24 a 15	0.9924	0.051	0.080
Coprostanone	0.24 a 15	0.9950	0.042	0.080
Cholesterol	0.24 a 15	0.9916	0.039	0.080
Cholestanol	0.24 a 15	0.9892	0.060	0.080
Stigmasterol	0.24 a 15	0.9960	0.051	0.080
Stigmastanol	0.24 a 15	0.9916	0.051	0.080
β-sitosterol	0.24 a 15	0.9952	0.051	0.080
Campesterol	0.40 a 20	0.9765	0.051	0.080

Table S3. Analytical curves, linear range, correlation coefficient, and detection and quantification limits for aliphatic hydrocarbon determination

Compound	Concentration range (μg mL^{-1})	R	LOD (μg g^{-1})	LOQ (μg g^{-1})
Hexadecane (C16)	0.3 a 25	0.9993	0.069	0.100
Heptadecane (C17)	0.3 a 25	0.9985	0.045	0.100
Pristane	0.3 a 25	0.9992	0.048	0.100
Octadecane (C18)	0.3 a 25	0.9985	0.048	0.100
Phytane	0.3 a 25	0.9997	0.036	0.100
Nonadecane (C19)	0.3 a 25	0.9992	0.036	0.100
Eicosane (C20)	0.3 a 25	0.9995	0.021	0.100
Heneicosane (C21)	0.3 a 25	0.9924	0.027	0.100
Docosane (C22)	0.3 a 25	0.9950	0.024	0.100
Tricosane (C23)	0.3 a 25	0.9995	0.024	0.100
Tetracosane (C24)	0.3 a 25	0.9998	0.024	0.100
Pentacosane (C25)	0.3 a 25	0.9998	0.021	0.100
Hexacosane (C26)	0.3 a 25	0.9997	0.024	0.100
Heptacosane (C27)	0.3 a 25	0.9996	0.024	0.100
Octacosane (C28)	0.3 a 25	0.9997	0.027	0.100
Nonacosane (C29)	0.3 a 25	0.9996	0.027	0.100
Triacontane (C30)	0.3 a 25	0.9995	0.042	0.100
n-Hentriacontane (C31)	0.3 a 25	0.9993	0.024	0.100
Dotriacontane (C32)	0.3 a 25	0.9992	0.027	0.100
Titriacontane (C33)	0.3 a 25	0.9992	0.063	0.100
Tetratriacontane (C34)	0.3 a 25	0.9994	0.024	0.100
Pentatriacontane (C35)	0.3 a 25	0.9991	0.078	0.100
Hexatriacontane (C36)	0.3 a 25	0.9995	0.027	0.100

Table S4. Polycyclic aromatic hydrocarbon (PAH) levels in sediment from rivers and reservoirs found in this study and globally

Study Area	Range ΣPAHs (μg kg^{-1})	Characteristics	Reference*
Rivers and Reservoirs Curitiba, Brazil	97.3 – 440.65	PAH revealed the combustion of biomass as the primary source	This work

(continued on next page)

Table S4. Polycyclic aromatic hydrocarbon (PAH) levels in sediment from rivers and reservoirs found in this study and globally (continued)

Study Area	Range ΣPAHs (µg kg^{-1})	Characteristics	Reference*
Yinma River Basin, China	1000 – 5750	Predominantly light PAHs (2-3 rings), naphthalene: 825.06 µg kg^{-1}. Mixed sources: petroleum and combustion	Sun et al., 2017[1]
Poxim River, Brazil	2.2 – 28.4	Predominantly pyrogenic sources, anthropogenic influence	Souza et al., 2018[2]
Brisbane River, Australia	148 – 3079	Pyrogenic sources (vehicular emissions), low ecological risk, some degree of cancer risks for children	Duodu et al., 2017[3]
South-Eastern Poland Reservoirs	150 – 33900	Both pyrolytic and petrogenic sources, varying ecological risks: moderate and substantial effects on biological communities	Baran et al., 2017[4]
Salt River, Taiwan	343 – 29400	Coal and petroleum combustion, moderate to high ecological risks	Chen et al., 2020[5]
Ovia River, Nigeria	5.25 – 573.33	Predominantly 2-3 ring PAHs, exceeding safe drinking water guidelines	Tongo et al., 2017[6]
Niger Delta, Nigeria	1620 – 19800	High molecular weight PAHs, high ecological and human health risks	Iwegbue et al., 2021[7]
Nenjiang and Second Songhua Rivers, China	76.5 – 9447	Biomass combustion and vehicle emissions are significant sources with negligible ecological risks.	Yang et al., 2023[8]
Tigris River, Iraq	5619.2 – 12795.0	High molecular weight PAHs prevalent; pyrogenic sources; high cancer risk.	Grmasha et al., 2023[9]

*Supplementary Material Reference

Table S5. Coprostanol in sediment from rivers and reservoirs found in this study and globally

Study Area	Coprostanol (µg g^{-1})	Characteristics	Reference*
Rivers and Reservoirs Curitiba, Brazil	0.75 – 410	Densely populated areas and discharge of untreated sewage directly into the river.	This work
Ipojuca River, Brazil	557.3	Contamination is due to intense anthropogenic activities close to the river.	Oliveira et al., 2022[10,11]
Kibera River, Kenya	55 – 298	Discharge of untreated sewage directly into the river.	Vane et al., 2022[11]
Thames River, England	0.0091 – 0.42	Decrease in COP concentration in sediment core over time due to the evolution of sewage treatment.	Vane et al., 2022[12]
Geumbo River, S. Korea	9 – 1282	High levels of urbanization and industrialization near the Geumho River and land-use types involving human activities	Lee et al., 2021[13]
Guamá River, Brazil	292.52	Region with low sewage treatment, densely populated, and intense port activity	Rodrigues et al., 2023[14]

*Supplementary Material Reference

Table S6. Aliphatic hydrocarbons in sediment from rivers and reservoirs found in this study and globally

Study Area	AH (µg g^{-1})	Characteristics	Reference*
Rivers and Reservoirs Curitiba, Brazil	0,75 – 410	Densely populated areas and discharge of untreated sewage directly into the river.	This work
Tehran river, Iran	2.94 - 114.7	Densely populated area with predominance of petrogenic origin of AH	Hasani et al., 2021[15]
Mangueira Lagoon, Brazil	5.0 - 652.7	Relevant lagoon located in a rural area slightly by petrogenic and biogenic AH	Sanches et al., 2021[16]
Al Wajh Lagoon, Saudi Arabia	64 - 302.6	Lagoon, located close to Red Sea, influenced by petrogenic activities	Al Otaibi et al., 2024[17]
Lafayette River, USA	4.94 - 40.83	Possible sources such as automotive and atmospheric transport of coal dust contribute to the AH into urban area	Maynard et al., 2023[18]
Norilsk-Pyasino water system, Russia	15 -1914	Accidental spill of Diesel fuel	Nemirovskaya et al., 2022[19]

*Supplementary Material Reference

Table S7. Recovery rates of AH, PAH, and sterols (%)

AH	
C16	82
C17	92
Pristane	88
C18	98
Phytane	97
C19	102
C20	102
C21	103
C22	104
C23	104
C24	104
C25	102
C26	104
C27	107
C28	107
C29	104
C30	105
C31	104
C32	105
C33	103
C34	102
C35	103
C36	99

PAH	
Nap	63
Acy	72
Ace	70
Flu	88
Phe	103
Ant	92
Flt	98
Pyr	109
BaA	99
Chr	108
BbF	54
BkF	114
BaP	113
IcdP	110
DahA	112
BghiP	119

Sterols	
Coprostanol	93
E-cop	82
Coprostanone	60
Cholesterol	87
Cholestanol	88
Stigmasterol	88
β-sitosterol	89
Stigmastanol	89

SUPPLEMENTARY MATERIAL REFERENCES

(1) Sun, C.; Zhang, J.; Ma, Q.; Chen, Y.; Ju, H. Polycyclic Aromatic Hydrocarbons (PAHs) in Water and Sediment from a River Basin: Sediment–Water Partitioning, Source Identification and Environmental Health Risk Assessment. *Environ. Geochem. Health* **2017**, *39* (1), 63–74. https://doi.org/10.1007/s10653-016-9807-3

(2) Souza, M. R. R.; Santos, E.; Suzarte, J. S.; Carmo, L. O.; Frena, M.; Damasceno, F. C.; Alexandre, M. R. Concentration, Distribution and Source Apportionment of Polycyclic Aromatic Hydrocarbons (PAH) in Poxim River Sediments, Brazil. *Mar. Pollut. Bull.* **2018**, *127*, 478–483. https://doi.org/10.1016/J.MARPOLBUL.2017.12.045

(3) Duodu, G. O.; Ogogo, K. N.; Mummullage, S.; Harden, F.; Goonetilleke, A.; Ayoko, G. A. Source Apportionment and Risk Assessment of PAHs in Brisbane River Sediment, Australia. *Ecol. Indic.* **2017**, *73*, 784–799. https://doi.org/10.1016/J.ECOLIND.2016.10.038

(4) Baran, A.; Tarnawski, M.; Urbański, K.; Klimkowicz-Pawlas, A.; Spałek, I. Concentration, Sources and Risk Assessment of PAHs in Bottom Sediments. *Environ. Sci. Pollut. Res.* **2017**, *24* (29), 23180–23195. https://doi.org/10.1007/S11356-017-9944-Y

(5) Chen, C. F.; Ju, Y. R.; Su, Y. C.; Lim, Y. C.; Kao, C. M.; Chen, C. W.; Dong, C. Distribution, Sources, and Behavior of PAHs in Estuarine Water Systems Exemplified by Salt River, Taiwan. *Mar. Pollut. Bull.* **2020**, *154*. https://doi.org/10.1016/J.MARPOLBUL.2020.111029

(6) Tongo, I.; Ezemonye, L.; Akpeh, K. Levels, Distribution and Characterization of Polycyclic Aromatic Hydrocarbons (PAHs) in Ovia River, Southern Nigeria. *J. Environ. Chem. Eng.* **2017**, *5* (1), 504–512. https://doi.org/10.1016/J.JECE.2016.12.035

(7) Iwegbue, C. M. A.; Irerhievwie, G. O.; Tesi, G. O.; Olisah, C.; Nwajei, G. E.; Martincigh, B. S. Polycyclic Aromatic Hydrocarbons (PAHs) in Surficial Sediments from Selected Rivers in the Western Niger Delta of Nigeria: Spatial Distribution, Sources, and Ecological and Human Health Risks. *Mar. Pollut. Bull.* **2021**, *167*. https://doi.org/10.1016/J.MARPOLBUL.2021.112351

(8) Yang, Y.; Zhao, Z.; Chang, Y.; Wang, H.; Wang, H.; Dong, W.; Yan, G. PAHs and PAEs in the Surface Sediments from Nenjiang River and the Second Songhua River, China: Distribution, Composition and Risk Assessment. *Process Saf. Environ. Prot.* **2023**, *178*, 765–775. https://doi.org/10.1016/J.PSEP.2023.08.037

(9) Grmasha, R. A.; Stenger-Kovács, C.; Bedewy, B. A. H.; Al-sareji, O. J.; Al- Juboori, R. A.; Meiczinger, M.; Hashim, K. S. Ecological and Human Health Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAH) in Tigris River near the Oil Refineries in Iraq. *Environ. Res.* **2023**, *227*. https://doi.org/10.1016/J.ENVRES.2023.115791

(10) de Oliveira, A. F.; Gomes, B.; França, R.; Moraes, A.; Bataglion, G.; Santos, J. Assessment of Urban Contamination by Sewage in Sediments from Ipojuca River in Caruaru City, Pernambuco, Brazil. *J. Braz. Chem. Soc.* **2022**, *33* (2), 163–172. https://doi.org/10.21577/0103-5053.20210133

(11) Vane, C. H.; Kim, A. W.; dos Santos, R. A. L.; Gill, J. C.; Moss-Hayes, V.; Mulu, J. K.; Mackie, J. R.; Ferreira, A. M.; Chenery, S. R.; Olaka, L. A. Impact of Organic Pollutants from Urban Slum Informal Settlements on Sustainable Development Goals and River Sediment Quality, Nairobi, Kenya, Africa. *Appl. Geochem.* **2022**, *146*. https://doi.org/10.1016/J.APGEOCHEM.2022.105468

(12) Vane, C. H.; Kim, A. W.; dos Santos, R. A. L.; Moss-Hayes, V. Contrasting Sewage, Emerging and Persistent Organic Pollutants in Sediment Cores from the River Thames Estuary, London, England, UK. *Mar. Pollut. Bull.* **2022**, *175*. https://doi.org/10.1016/J.MARPOLBUL.2022.113340

(13) Lee, D. H.; Kim, S. H.; Won, E. J.; Kim, M. S.; Hur, J.; Shin, K. H. Integrated Approach for Quantitative Estimation of Particulate Organic Carbon Sources in a Complex River System. *Water Res.* **2021**, *199*. https://doi.org/10.1016/J.WATRES.2021.117194

(14) Rodrigues, C. C. S.; Messias, M. S.; Morales, J. H. A.; Damasceno, F. C.; Corrêa, J. A. M. Insights about Levels and Sources of Organic Pollution in an Urbanized Amazon Estuary (Belém, PA, Northern Brazil). *Environ. Monit. Assess.* **2023**, *195* (6), 1–15. https://doi.org/10.1007/s10661-023-11271-0

(15) Moghaddam, A. H.; Hashemi, S. H.; Ghadiri, A. Aliphatic Hydrocarbons in Urban Runoff Sediments: A Case Study from the Megacity of Tehran, Iran. *J. Environ. Health Sci. Eng.* **2021**, *19* (1), 205–216. https://doi.org/10.1007/s40201-020-00596-4

(16) Sanches Filho, P. J.; Andrade, G. O.; Moreira, K.; Rockenbach, C. K. Determination of Aliphatic Hydrocarbons in Surface Sediments of Mangueira Lagoon (RS, Brazil). *Environ. Earth Sci.* **2021**, *80* (21), article number 728. https://doi.org/10.1007/s12665-021-10010-3

(17) Al-Otaibi, M. T.; Rushdi, A. I.; Rasul, N.; Bazeyad, A.; Al-Mutlaq, K. F.; Aloud, S. S.; Alharbi, H. A. Occurrence, Distribution, and Sources of Aliphatic and Cyclic Hydrocarbons in Sediments from Two Different Lagoons along the Red Sea Coast of Saudi Arabia. *Water (Switzerland)* **2024**, *16* (1), 187. https://doi.org/10.3390/w16010187

(18) Maynard, N.; Harvey, H. R. Distribution and Source Assignments of Polycyclic Aromatic and Aliphatic Hydrocarbons in Sediments and Biota of the Lafayette River, VA. *Environ. Sci. Pollut. Res.* **2023**, *30* (16), 47527–47543. http://dx.doi.org/10.1007/s11356-023-25563-y

(19) Nemirovskaya, I. A.; Glyaznetsova, Y. S. The Effect of Accidental Spill of Diesel Fuel in Noril'sk on Hydrocarbon Concentrations and Composition in Bottom Sediments. *Water Resour.* **2022**, *49* (6), 1027–1039. http://dx.doi.org/10.1134/S0097807822060100