DOI:10.5937/IIZS26386P

SPATIAL AND SEASONAL DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS AND TOTAL PETROLEUM HYDROCARBONS IN DANUBE RIVER SEDIMENTS (SERBIA)

Research paper

Marija Perović[1*], Tanja Nenin[2], Tatjana Mitrović[3]
[1,2] Jaroslav Černi Water Institute, Belgrade, Serbia
[3]Institute of Physics Belgrade, Serbia

Abstract: Polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPH) are persistent organic pollutants widely distributed in various environmental compartments, including air, water, soil, and sediments, where they tend to accumulate due to their hydrophobic nature. This study investigates the spatial and seasonal distribution of PAHs in sediments along the Serbian sector of the Danube River based on a long-term monitoring dataset (2012–2024). Surface sediment samples were collected at seven locations during spring and autumn sampling campaigns. The total concentration of 16 priority PAHs (Σ16PAHs) was analyzed to evaluate spatial variability and seasonal differences. The results showed that PAHs were present at all sampling sites, with noticeable spatial variability reflecting differences in anthropogenic pressures and local environmental conditions. Seasonal analysis revealed higher average Σ16PAHs concentrations during the autumn period (426.3 µg/kg) compared to spring (335.9 µg/kg), indicating the influence of runoff, atmospheric deposition, and hydrological conditions on PAH accumulation. Overall, contamination levels were classified as low to moderate, suggesting that although PAHs are persistently present, pollution does not reach levels typical of heavily impacted river systems. TPH were detected in more narrow range 114 mg/kg to 235 mg/kg in both season campaign. The findings highlight the importance of long-term and seasonal monitoring for reliable assessment of sediment quality in large river basins.
Key words: Polycyclic aromatic hydrocarbons (PAHs), Danube River, sediments, spatial distribution, seasonal variability, environmental monitoring

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of ubiquitous organic pollutants composed of two or more fused aromatic rings, primarily generated during incomplete combustion of organic matter. Due to their persistence, hydrophobicity, and semi-volatile nature, PAHs are widely distributed across environmental compartments, including air, water, soil, and sediments (Neff, 1979; Yunker et al., 2002). Total petroleum hydrocarbons (TPH), representing a broad group of aliphatic and aromatic hydrocarbons derived mainly from crude oil and petroleum products, are also commonly detected in aquatic environments. TPH originate predominantly from oil spills, fuel leakage, industrial discharges, and urban runoff, and are frequently associated with transport and storage of petroleum-derived products. PAHs originate from both natural and anthropogenic sources. Natural inputs include forest fires, volcanic activity, and diagenetic formation of PAHs in soils and sediments, as well as transformation of natural organic matter, while anthropogenic sources are predominantly associated with fossil fuel combustion, industrial processes, vehicle emissions, domestic heating, and waste incineration (Mastral & Callén, 2000; Ravindra et al., 2008). In contrast, TPH are primarily linked to petrogenic inputs, reflecting direct contamination by petroleum and its derivatives, although some overlap exists between PAH and TPH sources. Due to their low solubility and strong affinity for organic matter, both PAHs and TPH readily adsorb onto suspended particles and accumulate in river sediments. As a result, sediments act as long-term sinks of contamination, reflecting both historical inputs and ongoing pollution processes (Karickhoff et al., 1979; Baumard et al., 1998). These characteristics make sediments a suitable matrix for assessing the distribution and variability of hydrocarbon pollution in aquatic systems. The Danube River, as one of the most important European river systems, is exposed to diverse anthropogenic pressures along its course, including urban, industrial, and transport-

[1]Corresponding author, marija.perovic@jcerni.rs, ORCID: 0000-0003-2045-001X

related activities. These influences make it a relevant system for investigating the distribution of hydrocarbons in sediments.
This study is based on a long-term monitoring dataset previously analyzed in a more comprehensive study (Nenin et al., 2026), while the present work focuses on: (a) spatial variability of PAHs along the Serbian sector of the Danube, (b) seasonal differences between sampling campaigns, and (c) complementary assessment of TPH concentrations as an indicator of petrogenic contamination.

MATERIAL AND METHODS

Study area

The study was conducted along the Serbian section of the Danube River, one of the most important transboundary river systems in Europe. Seven sampling locations (S1–S7), including Smederevo (S1), Ram (S2), Veliko Gradište (S3), Donji Milanovac (S4), Tekija (S5), Kladovo (S6), and Kusjak (S7), were selected along a longitudinal gradient between rkm 1112 and rkm 864, covering areas characterized by different environmental conditions and potential anthropogenic influences, including navigation and hydromorphological modifications. A long-term monitoring program was implemented over the period 2012–2024, during so-called spring (April–July) and autumn sampling campaigns (September–November), as described in detail in Nenin et al. (2026). This design enabled the assessment of both spatial variability and seasonal differences in hydrocarbon contamination in river sediments, with particular focus on polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPH).

Sampling and sample handling

Sediment samples were collected using a Van Veen grab sampler in accordance with ISO 5667–12:2017, targeting recently deposited surface material. After collection, samples were placed in pre-cleaned glass containers, transported to the laboratory under cooled conditions (≤4 °C), and analyzed within 30 days to minimize potential changes in composition.

Sample preparation and analysis

In the laboratory, sediment samples were air-dried at room temperature, homogenized, and sieved to obtain a representative fraction for analysis. Simultaneous extraction of PAHs and TPH (C10–C40) was performed using accelerated solvent extraction (ASE) in accordance with U.S. EPA Method 3545, an organic solvent mixture suitable for hydrophobic compounds, followed by concentration and purification of extracts. Quantitative determination of 16 priority PAHs (Σ16PAHs) and TPH (C10-C40) was carried out using gas chromatography coupled with mass spectrometry (GC–MS), in accordance with standard analytical procedures for semi-volatile organic compounds in environmental samples following analytical procedures described in Nenin et al. (2026).

Quality assurance and quality control

Quality assurance and quality control (QA/QC) procedures included the use of certified reference materials, participation in proficiency testing schemes, calibration with external standards, procedural blanks, and replicate analyses. Method performance was evaluated in terms of accuracy, precision, and recovery rates, ensuring the reliability of the analytical results.

Data analysis

PAH concentrations were expressed as Σ16PAHs and TPH in range C10 – C40 and analysed to assess spatial and seasonal variability. Seasonal mean values were calculated as the

average of site-specific concentrations for spring and autumn sampling campaigns. Descriptive statistical analysis was applied to summarize PAH and TPH concentrations, including calculation of minimum, maximum, and mean values. Sampling sites represent a range of environmental conditions along the river course, enabling the assessment of spatial variability in relation to potential anthropogenic influences.

RESULTS AND DISCUSSION

Spatial distribution of PAHs

PAHs were detected at all investigated sampling sites along the Serbian sector of the Danube River, confirming their widespread occurrence in sediments of large river systems influenced by anthropogenic activities. The mean concentrations of Σ16PAHs showed clear spatial variability among the sampling locations during both the spring and autumn campaigns (Figures 1 and 2). During the spring campaign, elevated concentrations were observed at downstream locations, particularly at S5 and S7, while lower values were recorded at S2 and S4. In contrast, during the autumn campaign, the highest concentrations were detected at S1 and S2, followed by S5, whereas lower levels were observed at S4. These differences indicate a seasonal shift in the spatial distribution of PAHs, likely influenced by variations in hydrological conditions, sediment transport, and local anthropogenic inputs. Despite the observed variability between sites and seasons, the overall contamination levels can be classified as low to moderate, which is consistent with findings reported for other European river systems. This suggests that, although PAHs are persistently present, contamination does not reach levels characteristic of heavily polluted environments.

Spatial distribution of TPH

TPH were detected at all sampling sites, indicating their continuous presence in Danube River sediments throughout the monitoring period (Table 1). Compared to PAHs, TPH concentrations exhibited a narrower range of variability (114–235 mg/kg), suggesting more stable input conditions and less pronounced spatial differentiation (Table 2). In the spring campaign, slightly elevated TPH concentrations were observed at S3 and S7, while lower values were recorded at S2 and S4. This pattern is generally consistent with the distribution of PAHs at downstream locations, indicating potential accumulation processes associated with sediment transport and deposition zones. During the autumn campaign, TPH concentrations increased at most sites, particularly at S1, S3, and S6, which may be related to enhanced surface runoff and remobilization of petroleum-derived contaminants. Despite these seasonal changes, spatial differences remained less pronounced compared to PAHs, suggesting that TPH inputs are more uniform and likely associated with diffuse sources such as navigation activities, fuel handling, and urban runoff along the river corridor. The classification of TPH concentrations indicates that most samples fall within the 100–500 mg/kg range, while lower concentrations (<100 mg/kg) were primarily observed at S2 and S4. Concentrations above 500 mg/kg were rare, confirming that petroleum hydrocarbon contamination is present but does not reach levels characteristic of heavily polluted environments. Overall, the relatively moderate and spatially uniform distribution of TPH, compared to the more variable PAH patterns, suggests different dominant input mechanisms, with TPH primarily reflecting petrogenic sources and PAHs being more strongly influenced by pyrogenic inputs and localized anthropogenic pressures.

Table 1. *Seasonal variation of average Σ16PAHs and TPH concentrations in sediment samples along the Danube River (Serbia)*

Location	Ave - spring Σ16PAH (μ/kg)	Ave - autumn Σ16PAH (μg/kg)	Ave - spring TPH (C10-C40) (mg/kg)	Ave - autumn TPH (C10-C40) (mg/kg)
S1	320.66	560.81	148.83	200.25
S2	203.22	508.57	115.48	114.26
S3	324.45	367.71	211.11	235.22
S4	216.35	268.75	133.39	156.98
S5	466.87	507.37	137.42	144.62
S6	386.03	407.84	132.52	186.25
S7	434.31	363.03	154.26	159.55
Ave	335.98	426.30	147.57	171.02

Table 2. *Distribution (%) of TPH concentration classes (<100, 100–500, >500 mg/kg) across sampling sites during spring and autumn campaigns*

Location	% spring < 100	% spring 100-500	% autumns < 100	% autumn 100-500	% autumn > 500
S1	45	55	40	50	10
S2	55	45	70	30	0
S3	27	73	20	70	10
S4	64	36	40	60	0
S5	55	45	30	70	0
S6	27	73	70	20	10
S7	27	73	30	70	0
MIN	27	36	20	20	0
MAX	64	73	70	70	10

Seasonal variation

Seasonal differences in PAH concentrations were observed between the spring and autumn sampling campaigns (Figures 1 and 2; Table 1). Mean Σ16PAHs concentrations were 336.0 μg/kg in spring and 426.3 μg/kg in autumn, indicating overall higher levels during the autumn period. This pattern is particularly evident at upstream locations (S1 and S2), where a pronounced increase in concentrations was recorded in autumn compared to spring. In contrast, downstream site S7 exhibited comparable or slightly lower values in autumn, indicating spatial variability in seasonal trends.

The observed increase in autumn concentrations may be associated with enhanced surface runoff, increased atmospheric deposition, and intensified anthropogenic activities such as domestic heating during colder months. In addition, hydrological conditions likely influence the accumulation of hydrophobic compounds, as lower flow regimes and sediment deposition processes can promote the retention of PAHs. These findings highlight the importance of seasonal monitoring, as single sampling campaigns may not adequately capture the spatial and temporal variability of sediment-associated contaminants.

In contrast to PAHs, TPH concentrations exhibited less pronounced seasonal variability (Figure 3; Table 1). Mean TPH concentrations were 147.6 mg/kg in spring and 171.0 mg/kg in autumn, indicating a moderate increase during the autumn period, but without a clear and consistent seasonal pattern across all sampling sites. Slight increases were observed at several locations (e.g., S1, S3, and S6), while others showed relatively stable values between campaigns.

The weaker seasonal signal observed for TPH suggests more continuous and diffuse inputs, likely related to navigation activities, fuel handling, and urban runoff along the river corridor.

Unlike PAHs, which are strongly influenced by seasonal combustion-related emissions and atmospheric deposition, TPH appears to reflect more stable petrogenic sources, resulting in lower temporal variability.

Temporal variability

The long-term monitoring dataset (2012–2024), previously reported in Nenin et al. (2026), confirms the persistent presence of PAHs in Danube River sediments. Due to their hydrophobic nature and strong affinity for particulate matter, PAHs tend to accumulate and remain in sediments over extended periods, reflecting both historical contamination and continuous anthropogenic inputs. Despite this persistence, no pronounced long-term increasing or decreasing trend was observed, suggesting relatively stable contamination levels throughout the monitoring period. In addition to PAHs, total petroleum hydrocarbons (TPH) were evaluated to provide complementary insight into hydrocarbon contamination. TPH concentrations also indicate a continuous presence in sediments, with relatively limited temporal variability compared to PAHs. This behavior suggests stable and diffuse petrogenic inputs over time, likely associated with navigation, fuel-related activities, and urban influences along the river.
Summary statistics of Σ16PAHs and TPH concentrations, based on site-averaged values, are presented in Table 3. The obtained results indicate moderate variability within each season, with slightly higher mean concentrations observed during the autumn period for both PAHs and TPH. However, the absence of strong temporal trends highlights the importance of long-term monitoring for reliable assessment of sediment quality and contaminant persistence in large river systems.

Table 3. *Summary statistics of Σ16PAHs and TPH (C10-C40) in Danube River sediments in μg/kg and mg/kg respectively*

Season	Parameter	Units	Min	Max	Mean
Spring	Σ16PAH	(μg/kg)	203.22	466.87	~336
Autumn	Σ16PAH	(μg/kg)	268.22	560.81	~426
Spring	TPH	(mg/kg)	115.48	211.11	~148
Autumn	TPH	(mg/kg)	114.26	235.22	~171

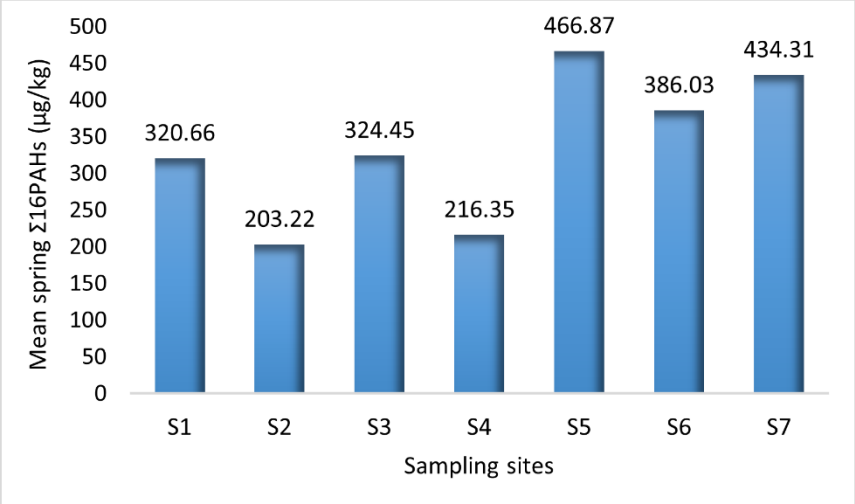


Fig. 1. *Mean Σ16PAHs concentrations along the Danube River during the spring campaign*

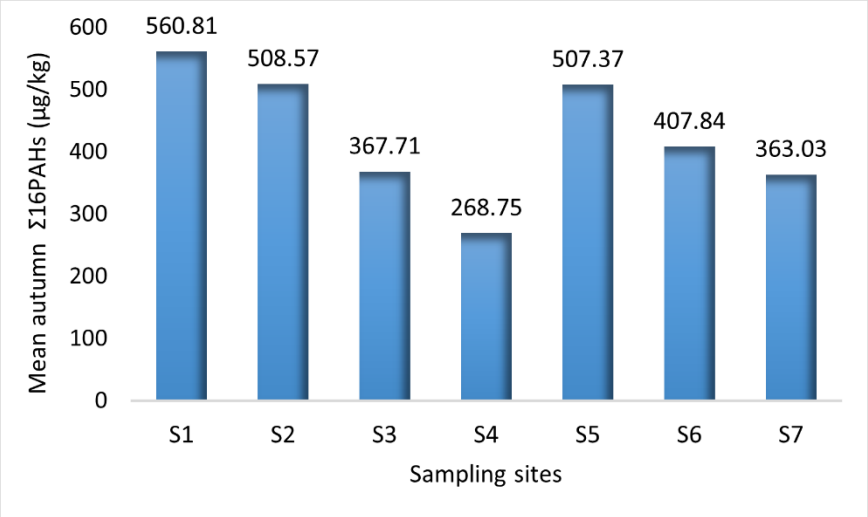


Fig. 2. *Mean Σ16PAHs concentrations along the Danube River during the autumn campaign*

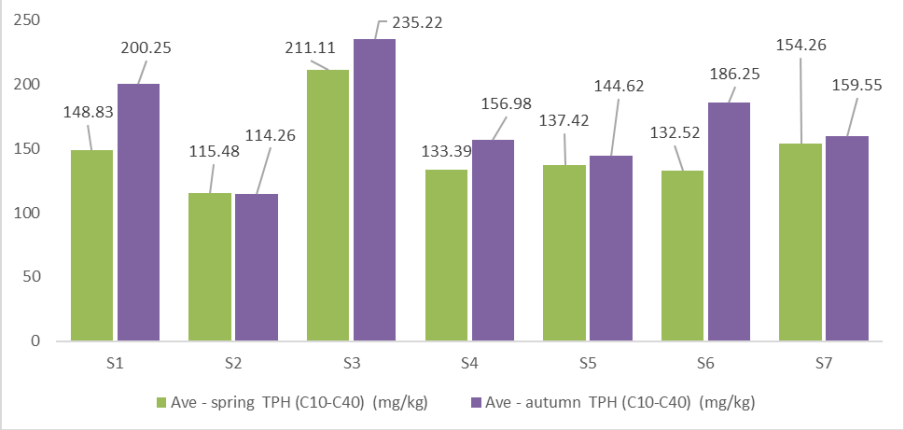


Fig. 3. *Seasonal variation of TPH (C10-C40) concentrations along the Danube River during the spring and autumn campaign*

Environmental implications

The results confirm that river sediments act as long-term sinks for hydrophobic organic pollutants such as PAHs and TPH. Due to their persistence and strong affinity for particulate matter, these compounds accumulate in sediments and may contribute to chronic exposure of benthic organisms, even at moderate concentrations. Such conditions can influence sediment quality and pose potential ecological risks over extended time scales. From a management perspective, the findings emphasize the importance of continuous monitoring programs, particularly in large transboundary river systems such as the Danube. Long-term datasets provide valuable insight into pollution dynamics, allowing for the identification of spatial patterns, temporal stability, and potential sources of contamination, while also supporting the evaluation of environmental policies and sediment management strategies. The observed spatial variability reflects differences in local environmental conditions and varying anthropogenic pressures along the river course. Variations in PAH concentrations along the longitudinal gradient suggest the influence of site-specific factors, including hydrological conditions, sediment characteristics, and localized emission sources related to urban, industrial, and transport activities. TPH concentrations were detected within a relatively narrow range (114–235 mg/kg) across both sampling campaigns, indicating moderate but consistent levels of petroleum hydrocarbons in sediments. According to Vane et al. (2018), concentrations below 100 mg/kg are typically associated with natural organic inputs (e.g., plant waxes and algal material), while values between 100 and 500 mg/kg suggest low to moderate anthropogenic petroleum influence. In this study, the dominance of the 100–500 mg/kg range

across most locations, particularly during the autumn campaign, indicates the prevalence of diffuse petrogenic inputs along the river system. In contrast, concentrations exceeding 500 mg/kg were rare and limited to isolated occurrences at specific sites (S1, S3, and S6), suggesting occasional episodic pollution events rather than persistent high-level contamination. Overall, the combined assessment of PAHs and TPH highlights the coexistence of pyrogenic and petrogenic inputs in Danube River sediments. While PAHs exhibit greater spatial and seasonal variability linked to combustion-related activities, TPH reflects more stable and diffuse sources associated with petroleum-derived contamination. This integrated approach provides a more comprehensive understanding of hydrocarbon pollution and supports informed environmental management in large river systems.

CONCLUSION

The results of this study confirm the widespread presence of PAHs in sediments along the Serbian sector of the Danube River, with clear spatial and seasonal variability. Differences among sampling locations reflect the influence of local anthropogenic pressures, hydrological conditions, and sediment dynamics. Higher Σ16PAHs concentrations observed during the autumn period indicate the role of enhanced runoff, atmospheric deposition, and accumulation processes under seasonal hydrological regimes. Despite this variability, overall contamination levels remain within the low to moderate range, suggesting that PAH pollution, although persistent, does not reach levels characteristic of heavily impacted river systems. TPH concentrations exhibited a relatively narrow range, indicating stable and generally low to moderate petroleum hydrocarbon input. The predominance of the 100–500 mg/kg fraction across most locations' points to diffuse petrogenic sources, while the limited occurrence of higher concentrations suggests occasional episodic inputs rather than widespread contamination. The combined assessment of PAHs and TPH provides a more comprehensive understanding of hydrocarbon contamination in river sediments, highlighting the coexistence of pyrogenic and petrogenic influences. These findings emphasize the importance of long-term and seasonal monitoring for reliable sediment quality assessment and provide a sound basis for future environmental management of large river systems such as the Danube.

REFERENCES

Baumard, P., Budzinski, H., Garrigues, P., Dizer, H., & Hansen, P. D. (1998). Polycyclic aromatic hydrocarbons in recent sediments and mussels (Mytilus edulis) from the Western Baltic Sea: Occurrence, bioavailability and seasonal variations. Marine Environmental Research, 47(1), 17–47. https://doi.org/10.1016/S0141-1136(98)00008-7

Karickhoff, S. W., Brown, D. S., & Scott, T. A. (1979). Sorption of hydrophobic pollutants on natural sediments. Water Research, 13(3), 241–248. https://doi.org/10.1016/0043-1354(79)90201-X

Mastral, A. M., & Callén, M. S. (2000). A review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation. Environmental Science & Technology, 34(15), 3051–3057. https://doi.org/10.1021/es001028d

Neff, J. M. (1979). Polycyclic aromatic hydrocarbons in the aquatic environment: Sources, fates and biological effects. Applied Science Publishers.

Nenin, T., Perović, M., Vuković, N., & Mitrović, T. (2026). Assessment of polycyclic aromatic hydrocarbons pollution in Danube River sediments across Serbia: Sources and ecological risk. Environmental Geochemistry and Health, 48, 56. https://doi.org/10.1007/s10653-025-02921-y

Pichler, N., de Souza, F. M., Ferreira dos Santos, V., & Martins, C. C. (2021). Polycyclic aromatic hydrocarbons (PAHs) in sediments of the Amazon coast: Evidence for localized sources in contrast to massive regional biomass burning. Environmental Pollution, 268 (Pt B), 115958. https://doi.org/10.1016/j.envpol.2020.115958.

Ravindra, K., Sokhi, R., & Van Grieken, R. (2008). Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atmospheric Environment, 42(13), 2895–2921. https://doi.org/10.1016/j.atmosenv.2007.12.010

Vane, C. H., Lopes dos Santos, R. A., Kim, A. W., Moss-Hayes, V., Fordyce, F. M. & Bearcock, J. M. (2018). Persistent organic pollutants (PAH, PCB, TPH) in freshwater, urban tributary and estuarine surface sediments of the River Clyde, Scotland, UK. Earth and Environmental Science Transactions of the Royal Society of Edinburgh, 108(2–3), 299–313. https://doi.org/10.1017/S1755691018000294

Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., & Sylvestre, S. (2002). PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry, 33(4), 489–515. https://doi.org/10.1016/S0146-6380(02)00002-5