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SOURCE APPORTIONMENT AND ECOLOGICAL RISK OF PAHS IN DANUBE RIVER SEDIMENTS (SERBIA)

Research paper

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Abstract: Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants widely distributed in aquatic environments, with sediments representing a major sink for their accumulation. In addition to concentration levels, the identification of pollution sources and assessment of toxic fractions are essential for understanding environmental risks. This study investigates the origin and ecological risk of PAHs in sediments of the Danube River (Serbia), based on a long-term monitoring dataset (2012–2024) previously reported in detail by Nenin et al. (2026). Source identification was performed using diagnostic ratios, particularly the low molecular weight to high molecular weight PAH ratio (LMW/HMW), while ecological relevance was evaluated through the proportion of carcinogenic PAHs (%7cPAH). Furthermore, sediment quality guidelines (SQGs), including the Threshold Effect Level (TEL) and Probable Effect Level (PEL), together with their quotient-based indices (TEL-Q and PEL-Q), were applied to assess the potential ecotoxicological risk of both individual and total PAH concentrations. The obtained LMW/HMW ratios were consistently below 1 across all sampling sites, indicating a dominant pyrogenic origin associated with combustion processes such as traffic emissions, industrial activities, and fossil fuel burning. The share of carcinogenic PAHs ranged up to 50%. According to the SQG-based assessment, ecological risk was generally classified as low (TEL level), with occasional exceedances corresponding to probable effect levels (PEL), particularly at selected locations.
Key words: PAHs, source apportionment, LMW/HMW ratio, carcinogenic PAHs, sediment quality guidelines, ecotoxicological risk, Danube River

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic pollutants primarily generated during the incomplete combustion of organic matter, although they may also originate from petroleum-related sources. Due to their hydrophobic nature, low water solubility, and strong affinity for organic matter, PAHs readily associate with suspended particles and accumulate in sediments, where they can persist over long periods and reflect both historical and ongoing contamination processes (Neff, 1979; Karickhoff et al., 1979). In aquatic systems, sediments act not only as sinks but also as potential secondary sources of PAHs under changing environmental conditions, such as resuspension events or variations in redox conditions. Consequently, sediment analysis provides valuable insight into long-term pollution dynamics and the overall environmental status of river systems. Beyond concentration levels, identifying the origin of PAHs is essential for understanding pollution sources and supporting effective environmental management. Based on their formation mechanisms, PAHs are generally classified as petrogenic and pyrogenic, while biogenic and diagenetic sources are considered less significant in contamination studies. Diagnostic molecular ratios are widely applied for source apportionment, although their interpretation should be treated with caution due to potential alterations during environmental processes (Yunker et al., 2002; Tobiszewski & Namieśnik, 2012). The environmental relevance of PAHs is further emphasized by their toxic, mutagenic, and carcinogenic properties. High molecular weight PAHs are recognized as carcinogenic, and their relative contribution to total PAH concentrations is commonly used as an indicator of ecological risk (Boström et al., 2002; Nenin et al., 2026). However, concentration-based indicators alone may not fully reflect the potential biological effects of contaminants in sediments. Therefore, the application of sediment quality guidelines (SQGs), such as the Threshold Effect Level (TEL) and Probable Effect Level (PEL), provides an additional framework for evaluating the likelihood of adverse effects on benthic organisms.

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This study is based on a long-term monitoring dataset previously analyzed in detail by Nenin et al. (2026). The present work focuses on (i) source identification using diagnostic ratios, (ii) assessment of carcinogenic PAH fractions, and (iii) evaluation of ecological risk using a SQG-based approach (TEL/PEL and their quotient-based indices) in sediments of the Danube River (Serbia).

MATERIAL AND METHODS

Study area and sampling

The study was conducted along the Serbian sector of the Danube River. Seven sampling locations (S1–S7), including Smederevo (S1), Ram (S2), Veliko Gradište (S3), Donji Milanovac (S4), Tekija (S5), Kladovo (S6), and Kusjak (S7), were distributed along a longitudinal gradient between rkm 1112 and rkm 864. These sites represent different environmental settings along the river course. Surface sediment samples were collected within a long-term monitoring program (2012–2024), as described in detail in Nenin et al. (2026). The dataset was used for further analysis of PAH origin and ecological relevance through the application of diagnostic ratios and risk indicators.

Data analysis

To determine the origin of PAHs, diagnostic molecular ratios were applied to the long-term monitoring dataset previously described in Nenin et al. (2026). Source identification was performed using the ratio between low molecular weight (LMW) and high molecular weight (HMW) PAHs, expressed as:

$$\frac{\mathrm{LMW}}{\mathrm{HMW}} \tag{1}$$

where LMW represents the sum of low molecular weight PAHs (2–3 rings), typically including compounds such as naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene, while HMW represents high molecular weight PAHs (4–6 rings), including fluoranthene, pyrene, benzo[a]pyrene, and related compounds. Values lower than 1 indicate a dominant pyrogenic origin, while values above 1 suggest petrogenic sources.

The ecological relevance of PAHs was evaluated using the proportion of carcinogenic compounds, calculated as:

$$\%7cPAH = \frac{\Sigma 7cPAH}{\Sigma 16PAH} \times 100 \tag{2}$$

where Σ7cPAH represents the sum of carcinogenic PAHs, including benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd] pyrene, and dibenzo[a,h]anthracene, while Σ16PAH represents the total concentration of priority PAHs.

The potential ecotoxicological risk of PAHs in sediments was assessed using SQGs, including the TEL and the PEL (Chen et al., 2015). For each individual PAH compound, the ratio between the measured concentration (Ci) and the corresponding guideline value (TELi or PELi) was calculated as TEL-Q and PEL-Q, respectively:

$$TEL\text{-}Q_i = \frac{C_i}{TEL_i} \tag{3}$$

$$PEL\text{-}Q_i = \frac{C_i}{PEL_i} \quad (4)$$

In order to evaluate the combined effect of PAH mixtures, mean quotient values (Mean TEL-Q and Mean PEL-Q) were calculated as:

$$SOG\ (TEL\ or\ PEL) = \frac{1}{n}\sum_{i=1}^{n}\frac{C_i}{PEL(or\ TEL)_i} \quad (5)$$

where C_i is the measured concentration of individual PAHs (μg/kg, dw), TEL_i and PEL_i are the corresponding guideline values, and n represents the number of detected compounds (Pichler et al., 2021). The obtained values were interpreted according to established SQG classification criteria, where lower values indicate a low probability of adverse effects, while higher values correspond to an increased likelihood of ecological risk.

TELi and PELi values were adopted from Pichler et al. (2021, Table 1). The classification criteria for SQG-TEL and SQG-PEL values, as well as the corresponding abbreviations, are presented in Table 2. Mean SQG-TEL and SQG-PEL values for Σ16PAHs were calculated according to Eq. (5). Average concentrations of individual PAHs were derived from the supplementary dataset reported by Nenin et al. (2026).

RESULTS AND DISCUSSION

Source identification

Site-averaged LMW/HMW ratios calculated over the entire monitoring period ranged from approximately 0.17 to 0.22, consistently indicating a dominant pyrogenic origin of PAHs and suggesting that combustion processes represent the primary source of contamination. (Figure 1). These sources are typically associated with traffic emissions, industrial activities, fossil fuel combustion, and atmospheric deposition of combustion-derived particles. The dominance of high molecular weight PAHs further supports the conclusion that pyrogenic inputs prevail over petrogenic sources. Similar patterns have been widely reported in large river systems, where combustion-related emissions are recognized as the dominant contributors to sediment contamination (Yunker et al., 2002).

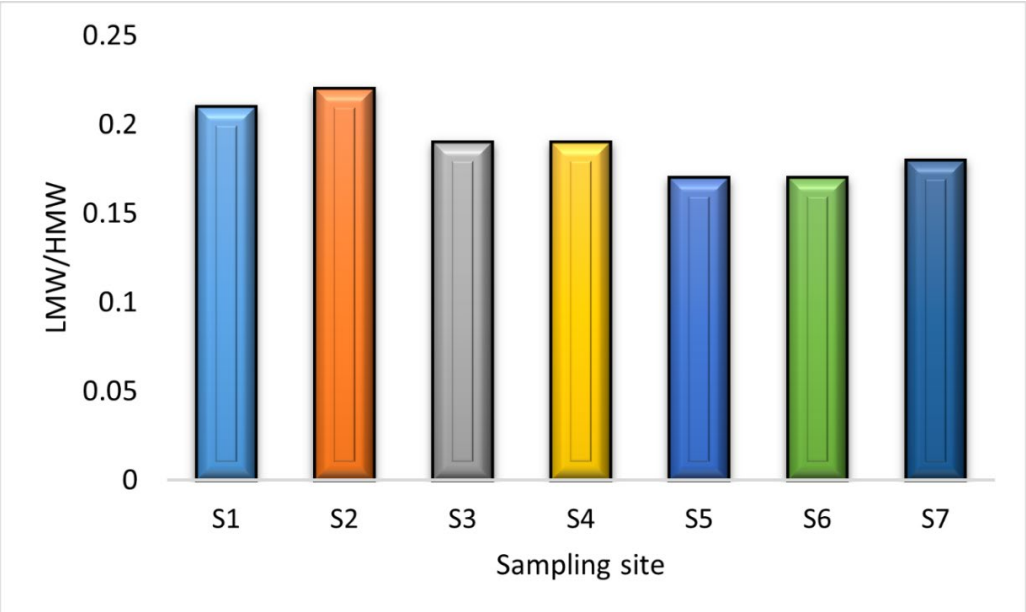


Fig. 1. *Averaged spatial variation of LMW/HMW ratios at sampling sites S1–S7*

Carcinogenic PAH fraction and ecological relevance

The proportion of carcinogenic PAHs (%7cPAH) ranged from 40% to 50%, indicating a notable contribution of toxic compounds (Figure 2). This relatively high share reflects the predominance of high molecular weight PAHs, which are typically associated with pyrogenic sources and are known for their carcinogenic properties (Boström et al., 2002). Although the overall PAH concentrations correspond to low to moderate contamination levels, the elevated proportion of carcinogenic compounds suggests that potential ecological risks should not be overlooked. This finding highlights the importance of complementing concentration-based assessments with compositional indicators that better reflect the toxicological relevance of sediment contamination. A summary of source indicators and carcinogenic PAH contributions is presented in Table 1.

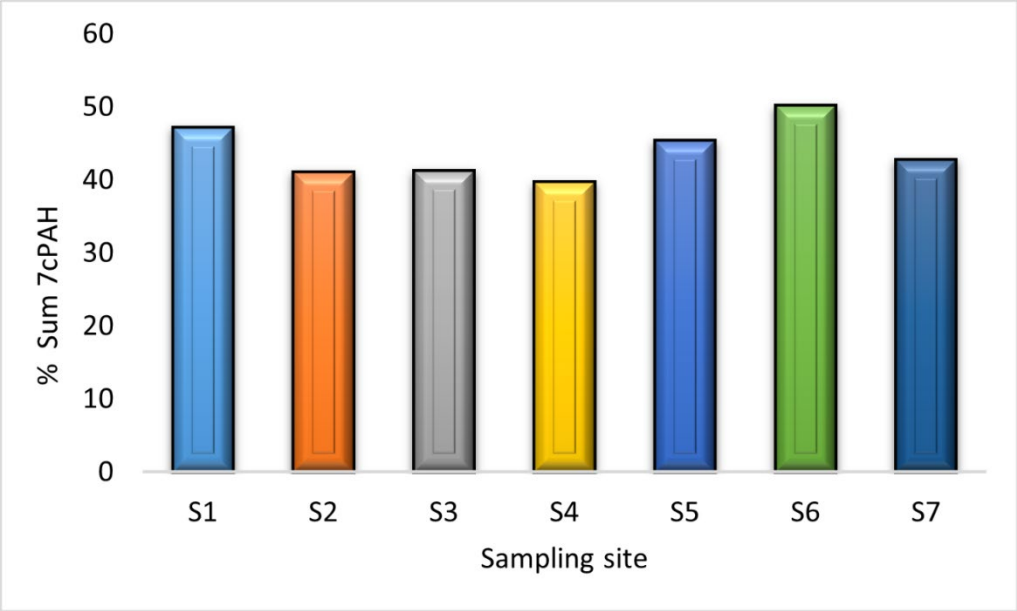


Fig. 2. *Average distribution of carcinogenic PAH fraction (%7cPAH) at sampling sites S1–S7*

Table 1. *Source identification of PAHs based on diagnostic LMW/HMW ratios and carcinogenic fraction (%7cPAH) and the Mean SQG-TEL and SQG-PEL values in Danube River sediments (2012–2024)*

Site	LMW/HMW	Source type	%7cPAH max	%7cPAH Ave (2012-2024)
S1	0.214	Pyrogenic	62.65	47.15
S2	0.217	Pyrogenic	61.54	41.07
S3	0.191	Pyrogenic	54.23	41.26
S4	0.191	Pyrogenic	57.46	39.69
S5	0.168	Pyrogenic	59.53	45.35
S6	0.168	Pyrogenic	65.90	50.15
S7	0.180	Pyrogenic	54.39	42.75

Ecotoxicological risk assessment (SQG approach)

The ecological risk of PAHs in Danube River sediments was further evaluated using SQGs, based on TEL and PEL values. The obtained SQG indices (Mean TEL-Q and Mean PEL-Q) indicate that ecological risk is predominantly low, with localized moderate risk observed at

selected sites (S1, S2 and S7) across the investigated period (Table 2). Mean TEL-Q values ranged from 0.47 to 1.56, corresponding predominantly to low to moderate risk levels, while Mean PEL-Q values remained below 0.16, indicating that adverse biological effects are unlikely under most environmental conditions (Table 3). According to the classification criteria (Table 4), most locations fall within the low-risk category, suggesting that adverse biological effects are unlikely under typical environmental conditions. However, spatial variability was observed. Location S1 showed slightly elevated SQG-PEL values, indicating occasional effects, while locations S1, S2, and S7 exhibited moderate risk levels based on SQG-TEL values (Table 3 and Table 4). These variations may reflect localized anthropogenic influences, such as urban or industrial inputs. Despite the predominantly low risk classification, the combined interpretation of SQG indices and carcinogenic PAH fractions indicates that the ecological relevance of PAHs cannot be considered negligible. The coexistence of pyrogenic sources, elevated carcinogenic fractions, and moderate risk levels at selected sites suggest persistent anthropogenic pressure on the sediment quality.

***Table 2**. Ecotoxicological risk assessment of Σ16 PAHs in Danube River sediments based on the SQG approach, using seasonal average concentrations (spring and autumn) and guideline values (TELi and PELi) (Nenin et al., 2026; Pichler et al., 2021).*

Location	Ave - spring Σ16PAH (µg/kg)	Ave - autumn Σ16PAH (µg/kg)	TEL_i	PEL_i	SQG-TEL spring	SQG-PEL - spring	SQG-TEL autumn	SQG-PEL - autumn
S1	320.66	560.81	619	5672	0.52	0.06	0.91	0.10
S2	203.22	508.57	619	5672	0.33	0.04	0.82	0.09
S3	324.45	367.71	619	5672	0.52	0.06	0.59	0.06
S4	216.35	268.75	619	5672	0.35	0.04	0.43	0.05
S5	466.87	507.37	619	5672	0.75	0.08	0.82	0.09
S6	386.03	407.84	619	5672	0.62	0.07	0.66	0.07
S7	434.31	363.03	619	5672	0.70	0.08	0.59	0.06
Average	**335.98**	**426.30**	619	5672	**0.54**	**0.06**	**0.69**	**0.08**

TELi and PELi values correspond to sediment quality guideline values for priority PAHs.
na – not available; nd – below the limit of quantification (LoQ).

***Table 3**. SQG-based ecotoxicological risk assessment of individual PAHs in Danube River sediments using average concentrations (2012–2024) and TELi/PELi guideline values (Nenin et al., 2026; Pichler et al., 2021)*

TEL_i	PEL_i	PAH (average values)	S1	S2	S3	S4	S5	S6	S7
34.6	391	Naphthalene	30.87	26.69	15.90	16.63	23.73	27.70	29.64
6.7	88.9	Acenaphthylene	nd	51.91	15.38	nd	nd	nd	10.00
5.9	128	Acenaphthene	nd	nd	nd	nd	nd	nd	23.46
21.2	144	Fluorene	17.37	67.32	16.43	12.18	18.74	16.54	19.76
86.7	544	Phenanthrene	67.42	44.64	63.20	37.88	58.30	43.77	49.14
46.9	245	Anthracene	24.39	23.22	14.34	15.94	17.83	16.32	17.16
113	1494	Fluoranthene	104.21	92.36	114.64	78.12	127.52	100.46	107.70
153	1398	Pyrene	85.89	65.97	94.02	61.69	96.70	86.32	83.31
74.8	693	Benz[a]anthracene	55.85	49.85	42.82	37.12	54.54	54.13	43.60
108	846	Chrysene	66.86	53.58	54.13	44.74	64.11	59.42	57.55
na	na	Benzo sum[b/k] fluoranthene	104.08	154.37	63.84	45.72	102.30	86.68	82.66

89	763	Benzo[a]pyrene	49.41	46.18	41.28	37.98	63.18	48.06	49.17
na	na	Indeno[1,2,3-cd] pyrene	51.61	78.44	49.26	na	na	37.75	57.24
6.22	135	Dibenzo[a,h]anthracene	33.90	nd	nd	nd	nd	nd	nd
na	na	Benzo[g,h,i] perylene	49.80	90.36	na	na	na	28.72	na
		SQG- TEL Σ16PAH*	1.19 MR	1.56 MR	0.77 Low	0.47 Low	0.71 Low	0.63 Low	1.03 MR
		SQG- PEL Σ16PAH*	0.10 OE	0.16 OE	0.08 Rare	0.06 Rare	0.08 Rare	0.07 Rare	0.09 Rare

TELi and PELi represent sediment quality guideline values for individual PAHs. SQG-TEL and SQG-PEL values for Σ16PAHs were calculated according to Eq. (5).
na – not available; nd – below the limit of quantification (LoQ). MR – moderate risk; Low – low risk; OE – occasional effects; Rare – rare effects

Table 4. *SQG-criteria for evaluating the potential eco-toxicological risks of the total PAH levels in the Danube River Sediment*

SQG-Q -TEL		**SQG-Q -PEL**	
< 0.1	No adverse effects expected	< 0.1	Rare effects- Rare
0.1 - 1.0	Low Risk - Low	0.1 - 0.5	Occasional effects- OE
1.0- 2.3	Moderate risk - MR	> 0.5	Frequent effects-Freq.E
> 2.3	High probability of toxicity -HR		

Integrated interpretation

The combined application of source identification (LMW/HMW), compositional indicators (%7cPAH), and SQG-based risk assessment provides a comprehensive understanding of PAH contamination in the Danube River sediments. While diagnostic ratios clearly indicate a dominant pyrogenic origin, and SQG values suggest generally low ecological risk, the relatively high contribution of carcinogenic PAHs highlights the importance of considering qualitative aspects of contamination. This integrated approach enables a more nuanced interpretation of sediment quality, bridging the gap between concentration-based assessments and ecotoxicological relevance, and represents a valuable tool for environmental monitoring in large river systems.

CONCLUSION

The results indicate that PAHs in Danube River sediments are predominantly of pyrogenic origin, as confirmed by consistently low LMW/HMW ratios across all sampling sites, reflecting the dominant influence of combustion-related sources such as traffic, industrial activities, and fossil fuel use. The relatively high proportion of carcinogenic PAHs (40–50%) highlights the prevalence of high molecular weight compounds and emphasizes the toxicological relevance of sediment contamination. Although total PAH concentrations correspond to low to moderate contamination levels, the application of sediment quality guidelines (SQGs) indicates that the overall ecological risk is generally low, with only occasional exceedances at the PEL level and moderate risk observed at selected locations. The combined use of source indicators, compositional metrics, and SQG-based indices demonstrates that concentration-based assessments alone may underestimate the environmental significance of PAHs. This integrated approach provides a more comprehensive evaluation of sediment quality and represents a robust framework for long-term monitoring and risk assessment in large river systems such as the Danube.

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