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ORIGINAL PAPER

# Spatiotemporal variability of heavy metals and metalloid contamination in Danube River sediments (Serbia) based on 23-year integrated monitoring

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**Abstract** Contamination of aquatic ecosystems by potentially toxic elements, including heavy metals and metalloid (HMs), is a persistent environmental concern due to their toxicity, persistence, and bioaccumulation. Regulated rivers with large dam systems are particularly vulnerable because altered hydrodynamics and sediment retention promote pollutant accumulation. Here, we present a first 23-year integrated dataset (2001–2023) assessment of HMs in surface sediments of the Serbian Danube River based on 620 samples collected at ten profiles from Novi Sad to Kusjak. Concentrations of Fe, Pb, Zn, Cu, Ni, Cr, As and Cd were determined, and contamination was evaluated using the geoaccumulation index (*Igeo*), enrichment factor (*EF*), pollution load index (*PLI*), SQGs and toxic risk index (*TRI*). To move beyond routine monitoring, site-specific background values for each element were derived statistically, variability was quantified by coefficients of variation (*CV*), and multivariate analysis (PCA) was applied to identify geochemical patterns and distinct element behavior. Most HMs showed low to moderate levels, with localized hotspots. *Igeo* and *EF* indicated As and Cd as the most critical elements, ranging from unpolluted to locally heavily polluted conditions, whereas Cu, Zn, and Cr generally indicated moderate contamination. *PLI* and *TRI* exhibited the highest values in downstream Iron Gate Reservoir profiles highlighting dam-driven sediment trapping. Upstream profiles showed improving temporal trends, likely associated with reduced local anthropogenic inputs, whereas downstream reservoir profiles remained stable or slightly deteriorated due to dam-induced sediment trapping and long-term accumulation of contaminants.

**Keywords** Danube River · Sediment quality · Heavy metals

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## Introduction

The Danube River, the second-longest river in Europe, represents one of the most important transboundary freshwater systems, draining a catchment of approximately 817,000 km$^2$ across nineteen countries and discharging into the Black Sea. While the river flows through ten countries, the full basin, including its tributaries, covers nine more. Four capital cities are directly located on the Danube River (Vienna, Bratislava, Budapest and Belgrade). The Serbian sector of the Danube receives inputs from major tributaries, including the Tisa, Sava, and Velika Morava rivers, whose catchments contain numerous

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urban, industrial, and mining centers, contributing to complex pollutant inputs (Culicov et al., 2022). Extensive hydromorphological modifications during the twentieth century, particularly the construction of the Iron Gate I and II dams, have profoundly altered sediment transport dynamics. These reservoirs retain approximately 50% of the sediment load, significantly modifying sedimentation patterns and promoting accumulation of sediment-associated contaminants (Mîndrescu et al., 2022; Vuković et al., 2014). Dams have disrupted the natural balance, influencing both the backwater zone of the reservoir and the areas downstream, with variations in the reservoir's length, backwater extent, and volume depending on the operations of the dams (Vuković et al., 2014).

Sediments play a critical role in contaminant cycling, functioning both as sinks and secondary sources of pollutants. HMs (Pb, Ni, Zn, Cu, Cd, Cr and As) are of particular concern due to their persistence, toxicity, and capacity for long-term accumulation in sediments. Once deposited, these contaminants may remain stored for extended periods but can also be remobilized under changing hydrological or environmental conditions, posing risks to aquatic ecosystems and human health (Eggleton & Thomas, 2004; Latosińska et al., 2025; Li et al., 2014; Liu et al., 2019; Milačič et al., 2017; Sun et al., 2016; Wen et al., 2025). Their presence in the Danube River has been recognized for decades and incorporated into international monitoring programs under the Bucharest Declaration, highlighting their significance as priority contaminants in this transboundary river system (Liska, 2015; Literathy & Laszlo, 1995).

Anthropogenic sources, including industrial discharge, untreated municipal wastewater, mining, and agricultural runoff, represent major contributors to HMs contamination in river systems (Simionov et al., 2021). In Serbia, anthropogenic pressures on the Danube are particularly significant due to limited wastewater treatment infrastructure. Currently, only approximately 8.1% of wastewater undergoes treatment prior to discharge, increasing the vulnerability of river sediments to contamination and facilitating downstream transport of pollutants toward the Danube Delta and the Black Sea (Gvozdić et al., 2023). Despite the recognized importance of sediment quality for aquatic ecosystem health, sediment monitoring has been less systematically implemented than water quality within Serbia's national programs, highlighting the need for comprehensive sediment assessments (Tomić et al., 2025).

Previous investigations have documented HMs contamination in Danube sediments and tributaries (Calmuc et al., 2021; Crnković et al., 2008; Milenković et al., 2005; Pavlović et al., 2016; Vuković et al., 2014). However, most studies have focused on short-term monitoring or localized assessments. Long-term datasets capable of identifying temporal trends, spatial variability, and underlying contamination sources remain limited, particularly for the Serbian sector of the Danube. Such long-term assessments are essential for understanding the extent of anthropogenic impacts, identifying contamination hotspots, and supporting effective environmental management.

Therefore, the present study provides a comprehensive long-term assessment of HMs concentrations in surface sediments of the Serbian sector of the Danube River over a 23-year period (2001–2023), based on a large dataset comprising approximately 620 sediment samples. The objectives were to (a) establish specific geochemical background concentrations for each HM, (b) assess sediment contamination levels (c) evaluate spatial and temporal trends in HMs concentrations, and (d) identify potential contamination sources using multivariate statistical analysis. This study provides the first long-term reconstruction of HMs contamination trends in Danube River sediments in Serbia and contributes critical scientific evidence for sediment quality assessment and sustainable river basin management in large transboundary river systems.

## Materials and methods

### Study area

This study was conducted along the Serbian sector of the Danube River (right riverbank), encompassing an approximately 400 km reach monitored over a 23-year period (2001–2023). Ten monitoring profiles were selected to represent key hydrological, geomorphological, and anthropogenic conditions along the river stream covering almost the whole river course through Serbia. The investigated profiles included Novi Sad (NS), Stari Banovci (SB), Ritopek (RT), Smederevo (SM), Ram (RM), Veliko Gradište (VG),

Donji Milanovac (DM), Tekija (TK), Kladovo (KL), and Kusjak (KS) (Fig. 1).

The NS and SB profiles are located within the Pannonian Plain reach of the Danube River, which is characterized by typical lowland river conditions and is only intermittently affected by the backwater influence of the Iron Gate I Reservoir during low-flow periods. Other monitoring profiles are located within hydrologically altered sections of the river influenced by the Iron Gate hydropower system, where the river is confined within a gorge and functions as a reservoir system, resulting in substantial alterations to its natural hydromorphological and hydrodynamic regime (Crnković et al., 2016).

Specifically, the profiles at RM, VG, DM, and TK are situated within the Iron Gate I Reservoir, while the downstream profiles at KL and KS are located within the Iron Gate II Reservoir. The Iron Gate I Reservoir represents the largest artificial impoundment on the Danube River and plays a critical role in modifying sediment transport dynamics, retaining more than 50% of the suspended sediment load and associated organic matter, with an average sedimentation rate of approximately 1.9 cm $y^{-1}$ (Seremet et al., 2025). This substantial sediment retention enhances the accumulation of sediment-associated contaminants and influences their spatial distribution along the river.

Sampling frequency varied among monitoring profiles depending on the monitoring program phase. Profiles, extending from Smederevo to Kusjak, were monitored quarterly, encompassing all four seasons (spring, summer, autumn, and winter). In selected monitoring cycles beginning in 2012, the monitoring program was expanded to include upstream profiles at Novi Sad, Stari Banovci, and Ritopek, with sampling conducted biannually during spring and autumn campaigns. These sampling periods were selected to capture seasonal hydrological variability, including high-flow conditions

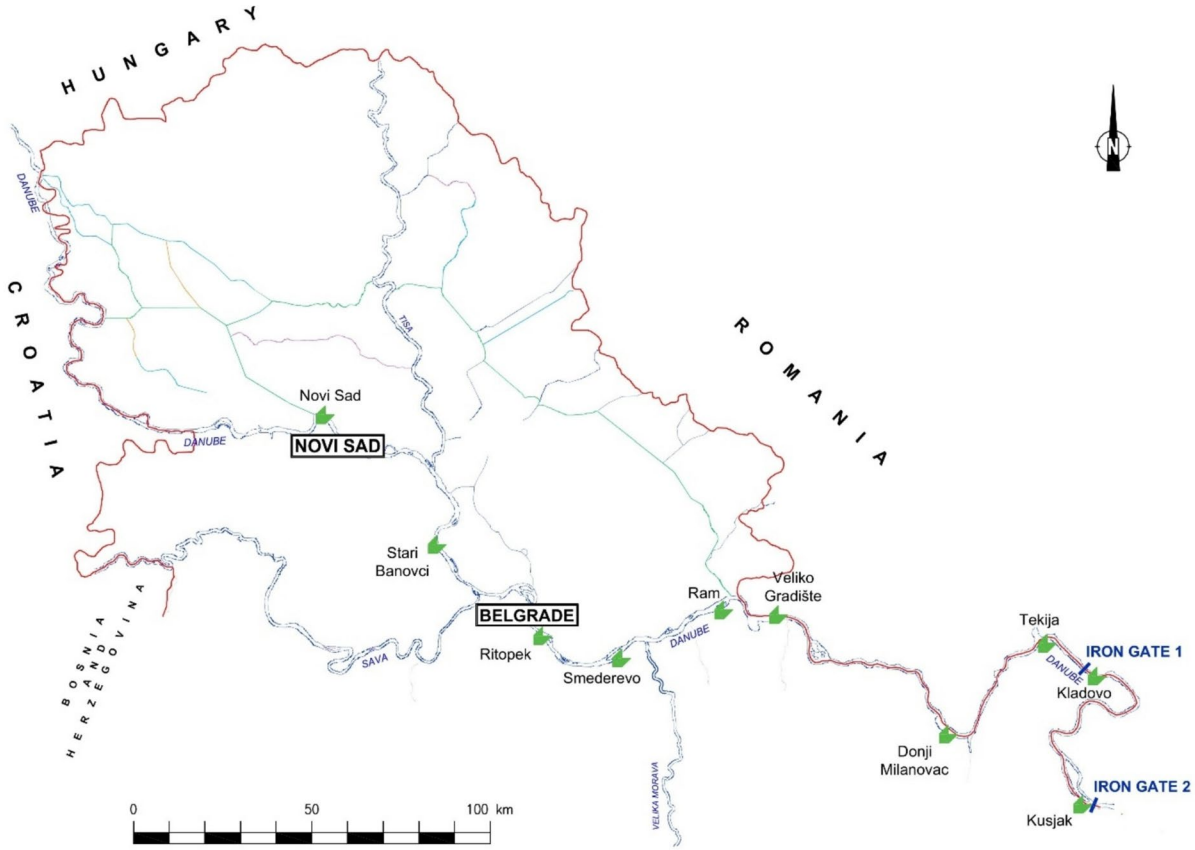



**Fig. 1** Danube River sediment sampling profiles

during spring, characterized by flow velocities ranging from 0.9 to 1.6 m $s^{-1}$, and low-flow conditions during autumn, with velocities typically below 0.22 m $s^{-1}$ (Vuković et al., 2014).

## Sample preparation

Upon collection, surface sediment samples have been air-dried and subsequently oven-dried at 105 °C for 48h to determine moisture content and ensure complete removal of residual water. The dried samples have been homogenized to a fine powder, sieved to obtain the < 63 µm fraction and subjected further to acid digestion procedure to determine the total concentrations of HMs (Milenković et al., 2005; Woitke et al., 2003). For acid digestion (2001—2011), approximately 1 g of homogenized sediment samples have been weighed into a 100 mL glass digestion vessel. The samples have been initially treated with 5 mL of concentrated $HNO_3$ and heated gently until partial evaporation reduced the volume and initiated matrix decomposition. After cooling, 5 mL of trace-metal grade $HClO_4$ has been added, and the mixtures have been heated gradually to approximately 180–200 °C until dense white fumes appeared, indicating the completion of digestion and removal of residual organic matter. The digested solutions have been cooled and subsequently filtered and diluted with deionized water to a known final volume (50 mL). From 2012, conventional acid digestion was replaced with microwave-assisted acid digestion. Microwave digestion was performed in accordance with U.S. EPA Method 3051 (Soil), using a BERGHOF MWS-4 microwave pressure digestion system. Approximately 0.5 g of sediment samples have been digested with 9 mL of concentrated $HNO_3$ and 3 ml HCl in closed PTFE vessels. The microwave digestion program consisted of a gradual temperature increase to 180 °C followed by a holding period of 10 min at this temperature. After digestion, the vessels have been cooled to room temperature, and the resulting solutions have been filtered and diluted to a known volume with deionized water prior to instrumental analysis. This method ensured rapid and controlled digestion of sediment matrices under elevated temperature and pressure conditions, enabling efficient extraction of sediment-bound metals for subsequent instrumental analysis.

## Chemical analysis

Prior to 2007, metal concentrations in the digested sediment samples have been determined using atomic absorption spectrometry (AAS). Flame atomic absorption spectrometry (FAAS), employing an air–acetylene flame, has been used for the determination of Ni, Cr, Fe, Zn, and Cu, while electrothermal atomic absorption spectrometry (ETAAS) with graphite furnace atomization has been applied for the quantification of Pb, Cd, and As. All measurements have been performed using a Perkin-Elmer 560 atomic absorption spectrophotometer equipped with an HGA 400 graphite furnace.

Beginning in 2007, elemental analysis was transitioned to inductively coupled plasma optical emission spectrometry (ICP-OES). HMs concentrations have been determined using a Spectro Genesis ICP-OES instrument, in accordance with Standard Methods for the Examination of Water and Wastewater (method 3120B) and U.S. EPA Method 6010C (Inductively Coupled Plasma–Atomic Emission Spectrometry). To ensure data comparability sediment samples have been analyzed using both techniques during the method transition period, confirming the consistency and comparability of the analytical results, with differences generally within ± 5% and correlation coefficients exceeding 0.98 for the tested elements.

## Quality assurance and quality control

Quality assurance and quality control (QA/QC) procedures were implemented through the use of certified reference materials (CRM 277 Trace Metals in Estuarine Sediments, RM 3 Qualco Danube Sediment, CRM 320 Trace Elements in River Sediment), reference materials from proficiency testing schemes (RMPT), and procedural blanks (one per 20 samples). All blank concentrations have been consistently below the method quantification limits, confirming the absence of contamination.

Method reproducibility over the 23-year monitoring period has been validated through participation in international interlaboratory proficiency testing schemes (e.g., LGC Standards

Proficiency Testing, BIPEA 38a), with acceptable performance defined by z-scores within ± 2.

To evaluate potential contamination during sample handling and preparation, field and transport blanks have been systematically included and processed alongside samples. Analytical precision has been assessed by duplicate sample analysis, expressed as Relative Percent Difference (RPD), which ranged from 4.18% to 18.33%. Method accuracy has been confirmed through recovery of reference materials analyzed prior to each monitoring campaign under identical digestion and analytical conditions. Recoveries ranged from 90 to 110% indicating satisfactory accuracy.

Sampling uncertainty ($U_s$) has been quantified via duplicate sampling and incorporated into the expanded measurement uncertainty (2Uc). The combined expanded uncertainty ranged from 4.2% to 18.8%. Instrumental performance and calibration stability have been continuously verified by the analysis of certified calibration standards (CPA Chem) and control samples (blanks, CRMs and RMPT) throughout each analytical sequence. All reagents have been of analytical grade purity and deionized water was used consistently. Limit of detection was determined by analyzing at least six standards at concentrations within the lower range of the calibration curve, performed in duplicate series, followed by calculation of the within-series standard deviation. Limit of quantification was estimated as 10 times the standard deviation. Methodological consistency was maintained throughout the 23-year monitoring program. Although instrumental analysis transitioned, identical digestion protocols, calibration strategies, and QA/QC procedures were preserved to ensure data comparability.

**Table 1** Classification of sediment contamination based on *Igeo* and *EF*

| | *Igeo* |
|---|---|
| $(Igeo) \leq 0$ | Uncontaminated |
| $0 < (Igeo) \leq 1$ | Uncontaminated to moderately contaminated |
| $1 < (Igeo) \leq 2$ | Moderately contaminated |
| $2 < (Igeo) \leq 3$ | Moderately to heavily contaminated |
| $3 < (Igeo) \leq 4$ | Heavily contaminated |
| $4 < (Igeo) \leq 5$ | Heavily to extremely contaminated |
| | *EF* |
| $(EF) \leq 2$ | Depletion to minimum enrichment |
| $2 < (EF) \leq 5$ | Moderate enrichment |
| $5 < (EF) \leq 20$ | Significant enrichment |
| $20 < (EF) \leq 40$ | Very high enrichment |

## Data analyses

Quantification of HMs contamination in sediments requires comparison of measured concentrations with appropriate background values representing natural, uncontaminated conditions. This approach enables differentiation between natural geochemical variability and anthropogenic enrichment and provides a basis for evaluating contamination levels and ecological risk (Kabir et al., 2011).

To comprehensively assess sediment contamination, three widely applied indices were used: the geoaccumulation index (*Igeo*), enrichment factor (*EF*), and pollution load index (*PLI*). These indices provide complementary information on contamination intensity, anthropogenic influence, and overall pollution status (Calmuc et al., 2021; Ceccopieri et al., 2025; Savic et al., 2025; Tomlinson et al., 1980).

The geoaccumulation index (*Igeo*), originally proposed by Müller (1969), was used to evaluate metal accumulation relative to background concentrations. It was calculated as (Eq. 1) (Müller, 1969):

$$I_{geo} = \log_2 \left( \frac{C_i}{1.5 \times C_{bi}} \right) \quad (1)$$

where $C_i$ represents the measured metal concentration and $C_{bi}$ represents the background concentration. The classification of sediment contamination based on *Igeo* and *EF* values is presented in Table 1.

The *EF* values (Buat-Menard & Chesselet, 1979) were calculated to evaluate anthropogenic enrichment of trace metals relative to natural background levels. Fe was used as a normalizing reference element, as normalization of HMs concentrations is a recommended approach to mitigate variability arising from sediment grain size and the diluting effects of organic matter (Matys Grygar & Popelka, 2016) (Eq. 2):

$$EF = \frac{\left(C_i / C_{Fe}\right)}{\left(C_{bi} / C_{bFe}\right)} \quad (2)$$

The *PLI* (Tomlinson et al., 1980) was used to evaluate overall sediment contamination (Eqs. 3 and 4):

$$PLI = \left( \prod_{i=1}^{n} CF_i \right)^{1/n} \tag{3}$$

$$CF_i = \frac{C_i}{C_{bi}} \tag{4}$$

And $n$ represents the number of analyzed elements. *PLI* values greater than 1 indicate contamination, whereas values below 1 indicate unpolluted conditions (Goswami et al., 2021).

In all these equations, distinguishing between anthropogenic and natural (geochemical, background concentration) contributions to their concentrations in sediments presents a significant challenge. This difficulty arises from the characteristic spatial variability of metal distributions as natural components in sediments and the influence of fluvial processes on sediment dynamics. Background geochemical concentrations can also be extensive in areas where the parent rocks contain basin specific pollutants such as HMs (Pavlović et al., 2016). Furthermore, to avoid potential overestimation of metal concentrations in unpolluted sediments, it is essential to select an appropriate reference concentration for comparison since average crustal values may be not appropriate because the studied area is very heterogeneous due to the heterogeneity of rock types present along its course (Comero et al., 2014). This underscores the necessity of accounting for regional characteristics to prevent misinterpretation of anthropogenic influences, thereby emphasizing the value of a site-specific approach when sediment quality guidelines are inappropriate or inadequate (Yottiam et al., 2025). Consequently, the classification of contamination levels at a given sampling site is highly dependent on the background concentration selected for each metal under investigation (Bábek et al., 2015; Matys Grygar & Popelka, 2016; Reis et al., 2025; Sakan et al., 2010).

In literature different approaches were used for determination the background levels. In order to reconstruct the geological background of HMs accumulation, as well as to evaluate the potential sources of metals distinguishing natural from anthropogenic inputs radiometric dating, together with geochemical analyses of major elements (Al, Fe, Ca, and S) and trace metals (Cu, Zn, Pb, Ni, Cr, Cd), was conducted on the upper 4 m of a 9 m sediment core (Mîndrescu et al., 2022). Ceccopieri et al. assumed that deepest seven layers of the sediment core (50–95 cm depth) reflect pre-industrial conditions before the 1900s and used average concentrations from them as background values for all calculations (Ceccopieri et al., 2025). The application of a multivariate statistical technique positive matrix factorization (PMF), was also used to determine the natural vs anthropogenic origin of HMs and other possible sources affecting the sediments of the Danube and its tributaries by Comero et al. (Comero et al., 2014; Wei et al., 2025).

Box and whisker plots are widely accepted as effective statistical instruments for delineating geochemical background levels in environmental geochemistry, assuming that outliers and extreme observations represent no more than approximately 15% of the dataset. The geochemical background is typically defined by the interval encompassed by the lower and upper whiskers of Tukey's box and whisker plot (i.e. threshold limits), whereas the median is interpreted as the representative geochemical baseline (Bábek et al., 2015; Castro et al., 2013). For this study the same principle was used and the background values were calculated from the statistical characteristics of each trace HMs distribution and median values were adopted.

The coefficient of variation (*CV*) was calculated to evaluate spatial variability and heterogeneity of metal concentrations (Eq. 5):

$$CV = \frac{\sigma}{\mu} \times 100 \tag{5}$$

where $\sigma$ is standard deviation and $\mu$ is mean concentration. *CV* values < 20% indicate low variability, 20–50% moderate variability, and > 50% high variability, typically reflecting anthropogenic influence (Anaman et al., 2022; Lv et al., 2013).

Principal component analysis (PCA) was applied to identify potential sources and controlling factors influencing HMs distribution. PCA reduces dataset dimensionality while preserving variance and enables identification of element associations and

common sources. Prior to analysis, data suitability was evaluated using the Kaiser–Meyer–Olkin (KMO) test. Components with eigenvalues > 1 were retained, and varimax rotation was applied to improve interpretability (Anaman et al., 2022). All statistical and multivariate analyses, as well as graphical representations, were performed using XLSTAT (Excel data analysis add-in) software. Descriptive statistics, including the mean, median, geomean, first and third quartiles and coefficient of variations were calculated.

Sediment toxicity and the associated ecological risk were evaluated using two complementary approaches. Sediment Quality Guidelines (SQGs) were applied to assess sediment toxicity, as the potential impact of contaminated sediments on aquatic organisms. The measured concentrations of HMs in the studied sediments were compared with the Threshold Effect Concentration (*TEC*) and Probable Effect Concentration (*PEC*) values reported previously (MacDonald et al., 2000). *TEC* represents the consensus-based concentration below which adverse effects on sediment-dwelling organisms are unlikely, whereas *PEC* denotes the consensus-based concentration above which adverse biological effects are expected to occur (Dorleon et al., 2025; Ju et al., 2022; MacDonald et al., 2000).

The ecological risks posed by HMs to aquatic life were assessed using the Toxic Risk Index (*TRI*) (Duman et al., 2022; Radomirović et al., 2023). This approach also depends on *TEC* and *PEC* concentrations (MacDonald et al., 2000). The *TRI* values of specific HMs in sediments were calculated according to Eq. (6), while the combined index of multiple HMs was obtained using the formula in Eq. (7).

$$TRI_i = \sqrt{\frac{(Ci/TEC)^2 + (Ci/PEC)^2}{2}} \quad (6)$$

$$TRI = \sum_{i=1}^{n} TRI_i \quad (7)$$

$TRI_i$ represents the toxic risk index for an individual HM, $C_i$ the concentration of that HM, and $n$ the total number of HMs considered. *TRI* reflects the overall toxic risk associated with a single sample (Radomirović et al., 2023).

## Results and discussion

### The distribution of HMs concentrations in Danube sediment

All HMs concentrations showed substantial spatial and temporal variability. Descriptive statistical parameters (Table 2), including minimum, maximum, median, geometric mean, quartiles, and coefficient of variation (*CV*), were used to evaluate contamination patterns. Based on median concentrations, the elements followed the order: Fe > Zn > Ni > Cr > Pb > Cu > As > Cd, reflecting the dominance of lithogenic element and the comparatively lower abundance of anthropogenic trace metals. Iron exhibited the highest concentrations (3.44–70.42 g/kg), which is consistent with its role as a major constituent of sediment mineral matrices (Milenković et al., 2005; Woitke et al., 2003).

Among the analyzed trace HMs, zinc exhibited the broadest concentration range (32.29–844.39 mg/kg),

**Table 2** Descriptive statistics of HMs concentrations in Danube River surface sediment samples from 2001 to 2023

| | Min | Max | Median[c)] | Average | Geomean | Q1[a)] | Q3[a)] | CV[b)] |
|---|---|---|---|---|---|---|---|---|
| g/kg dry weight | | | | | | | | % |
| Fe | 3.44 | 70.42 | 34.44 | 33.90 | 31.97 | 26.47 | 41.30 | 30.39 |
| mg/kg dry weight | | | | | | | | % |
| Pb | 8.52 | 160.84 | 65.86 | 67.41 | 59.82 | 45.54 | 91.71 | 43.15 |
| Zn | 32.29 | 844.39 | 270.11 | 280.01 | 255.27 | 207.06 | 343.53 | 40.19 |
| Cu | 0.91 | 309.60 | 60.93 | 63.15 | 54.93 | 43.28 | 79.27 | 38.64 |
| Cr | 10.08 | 239.45 | 78.95 | 81.02 | 75.35 | 65.00 | 95.54 | 34.98 |
| Ni | 8.27 | 221.54 | 80.48 | 83.41 | 75.87 | 62.15 | 103.02 | 39.62 |
| Cd | < 1 | 11.45 | 1.27 | 1.55 | 1.04 | 0.55 | 2.04 | 87.31 |
| As | < 1 | 131.39 | 12.70 | 14.29 | 12.08 | 9.81 | 17.31 | 65.24 |

a) First and third quartiles

b) Coefficient of Variations

c) Concentrations used as background values

followed by copper (0.91–309.6 mg/kg). Nickel and chromium showed comparable concentration intervals (Ni: 8.27–221.54 mg/kg; Cr: 10.08–239.45 mg/kg), with maximum values recorded at Ram and Smederevo, indicating site-specific enrichment. Lead concentrations demonstrated substantial variability, ranging from 8.52 to 160.84 mg/kg. Arsenic levels varied from below the limit of quantification (< 1 mg/kg) to 131.4 mg/kg, with the highest concentrations observed at Smederevo. Cadmium displayed a maximum concentration of 11.45 mg/kg at the Kladovo profile. The occurrence of several elevated cadmium concentrations during the 2009–2010 period suggests a short-term contamination episode, likely linked to localized anthropogenic inputs.

Overall, most elements were characterized by relatively stable median concentrations accompanied by isolated extreme values, pointing to localized contamination hotspots. The pronounced disparity between median and maximum concentrations further indicates episodic contamination events rather than persistent, large-scale pollution.

The coefficient of variation (*CV*) was used to assess the degree of spatial variability and heterogeneity in HMs concentrations within Danube River sediments. Elevated *CV* values generally indicate greater spatial variability and may reflect heterogeneous inputs, including localized anthropogenic contamination. The obtained *CV* values show that Fe, Pb, Zn, Cu, Cr, and Ni exhibited *CV*s below 50%, indicating low to moderate variability and suggesting predominantly natural control or relatively uniform distribution along the investigated river reach. These elements are commonly associated with geochemical sources and sediment mineral composition, which tend to exhibit more stable spatial patterns. Relatively high nickel background levels, suggesting a predominantly geochemical origin associated with regional geological formations was already confirmed (Sakan et al., 2010; Vignati et al., 2013). In contrast, Cd and As exhibited considerably higher *CV* values of 87.3% and 65.24%, respectively, indicating high spatial variability. Such elevated variability indicates localized enrichment and heterogeneous distribution patterns, likely reflecting stronger anthropogenic influence.

The calculated *Igeo* values (Fig. 2) indicate that cadmium and arsenic exhibit the highest degree of contamination among the investigated elements, with values ranging from uncontaminated conditions ($Igeo \leq 0$) to moderately contaminated ($Igeo > 1$), and locally moderately to heavily contaminated conditions ($Igeo > 2$). These elevated *Igeo* values reflects enhanced anthropogenic loading, which are commonly associated with agricultural practices, industrial emissions, and wastewater inputs. This observation indicates progressive accumulation in sediments and highlights their potential ecological significance, as higher

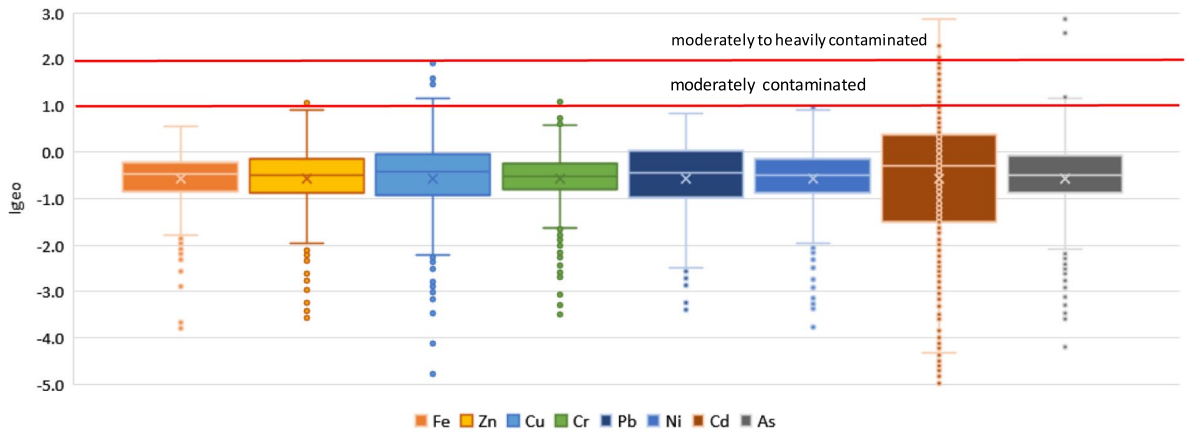



**Fig. 2** The Geoaccumulation Index (*Igeo*) of HMs concentrations in Danube River Sediments (Serbia) from Novi Sad to Kusjak, 2011–2023

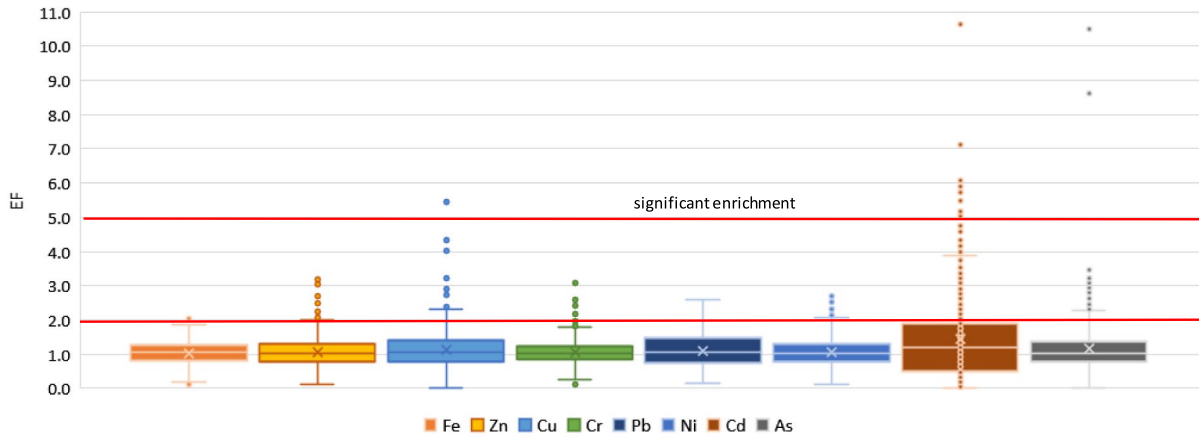



**Fig. 3** The Enrichment Factor (*EF*) of HMs concentrations in Danube River Sediments (Serbia) from Novi Sad to Kusjak, 2011–2023

sediment concentrations may serve as a long-term source of contamination to aquatic ecosystems. In contrast, copper, zinc and chromium generally fall within the uncontaminated to moderately contaminated classes, indicating limited anthropogenic influence. Lead, nickel, and iron consistently exhibited *Igeo* values corresponding to uncontaminated conditions, suggesting that their concentrations are primarily controlled by natural geochemical background rather than anthropogenic inputs.

The *EF* values (Fig. 3) corroborate the *Igeo* results and provide further insight into anthropogenic contributions. Cadmium, arsenic, and copper exhibit the highest *EF* values, indicating significant enrichment relative to background levels and confirming their strong anthropogenic influence. In contrast, zinc, chromium, lead, and nickel show predominantly moderate enrichment, reflecting a combination of geochemical and anthropogenic sources. Iron displays *EF* values close to unity, indicating minimal enrichment and confirming its geochemical behavior and suitability as a reference element. *CV*, *Igeo* and *EF* values observed for Cd and As are mutually consistent, confirming their greater sensitivity to anthropogenic inputs compared to other investigated elements.

## Spatial distribution of HMs in the Danube river sediment

Boxplot analysis (Fig. 4) further revealed substantial spatial variability. A clear spatial trend was observed along the river stream, with increasing HMs concentrations toward the downstream Iron Gate Reservoir system. Despite significant urban pressure, the Novi Sad profile exhibited relatively low contamination levels, whereas downstream profiles, particularly Ritopek, Veliko Gradište, Tekija, and Kladovo, showed elevated HMs concentrations. This pattern reflects the combined influence of hydrological modifications due to the dam's constructions, geochemical background, tributary inputs and urban discharges. These findings are consistent with previous studies demonstrating increased HMs accumulation within the Iron Gate Reservoir and downstream sections of the Danube River (Woitke et al., 2003), as well as the significant influence of tributaries and anthropogenic activities on sediment quality (Comero et al., 2014; Simionov et al., 2021).

The Iron Gate dam system plays a critical role in controlling sediment dynamics and contaminant accumulation. Reduced flow velocity and enhanced sedimentation promote the deposition of fine particles and associated contaminants, transforming the reservoir into a long-term sink for HMs (Crnković et al., 2016; Mîndrescu et al., 2022; Oaie et al., 2005). These findings confirm that dam-induced hydrological modifications

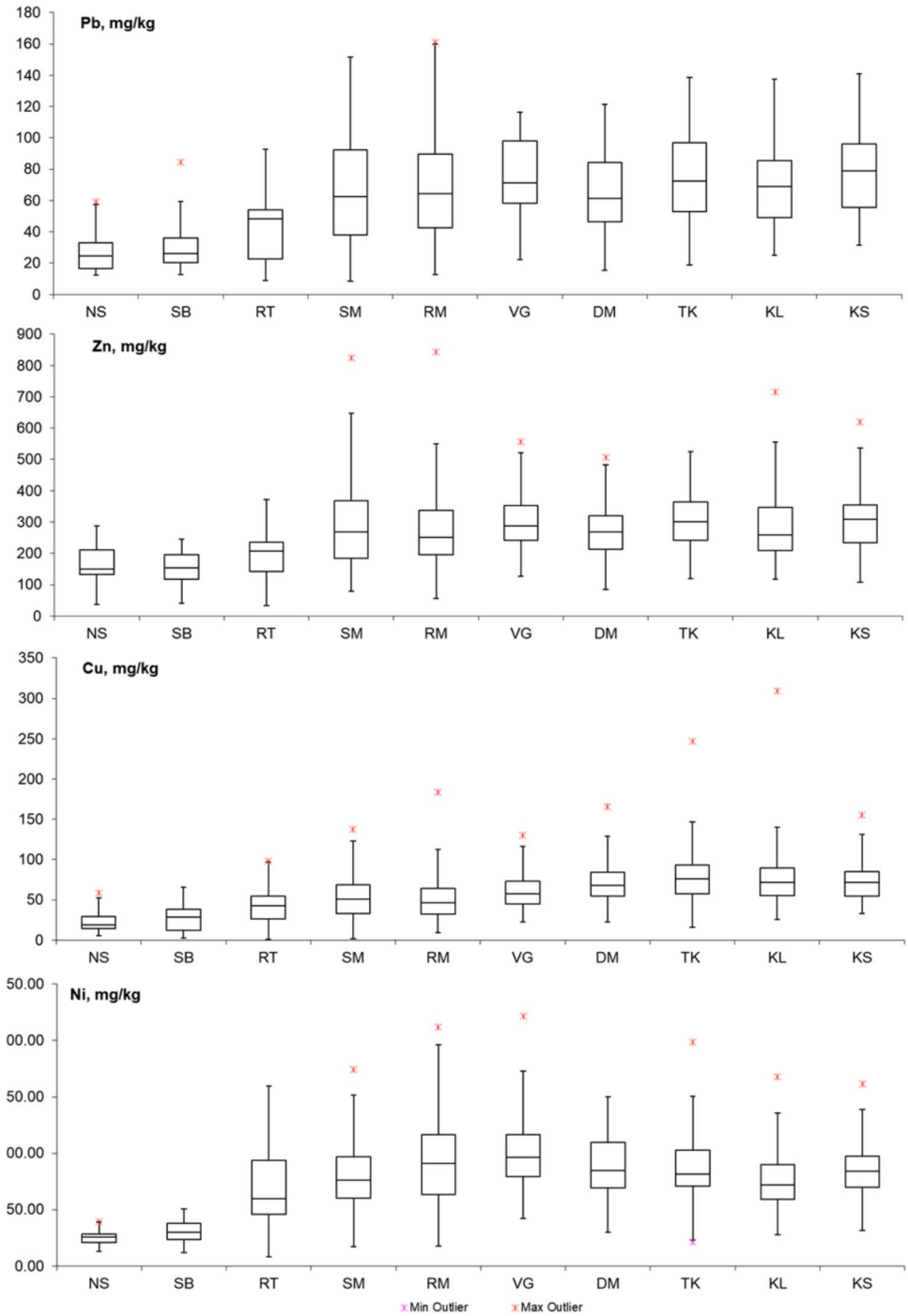



**Fig. 4** **a** Boxplots showing the spatial variation of the measured Pb, Zn, Cu, Ni concentrations in sediments: median, 1st and 3rd quartiles, whiskers and outliers (lowest and highest values). **b** Boxplots showing the spatial variation of the measured Cr, Cd, As concentrations in sediments: median, 1st and 3rd quartiles, whiskers and outliers (lowest and highest values)

significantly influence contaminant accumulation patterns. Similar spatial patterns were reported by Vuković et al. (2014) and Milenković et al. (2005) confirming the role of reservoir sedimentation as a major controlling factor in HMs accumulation (Milenković et al., 2005; Vuković et al., 2014).

Figure 4 also illustrates the pronounced influence of nickel, lead, cadmium, and arsenic on the sediment quality of the Danube River. Among the analyzed elements, nickel exhibits the most substantial spatial variability, as reflected by the difference in median concentrations between the Stari Banovci profile (29.86 mg/kg) and the Ritopek profile (59.89 mg/kg), amounting to approximately 30 mg/kg. A similar pattern is observed for chromium, with median concentrations of 35.17 mg/kg at Stari Banovci and 57.92 mg/kg at Ritopek, corresponding to a difference of about 20 mg/kg. These findings indicate a

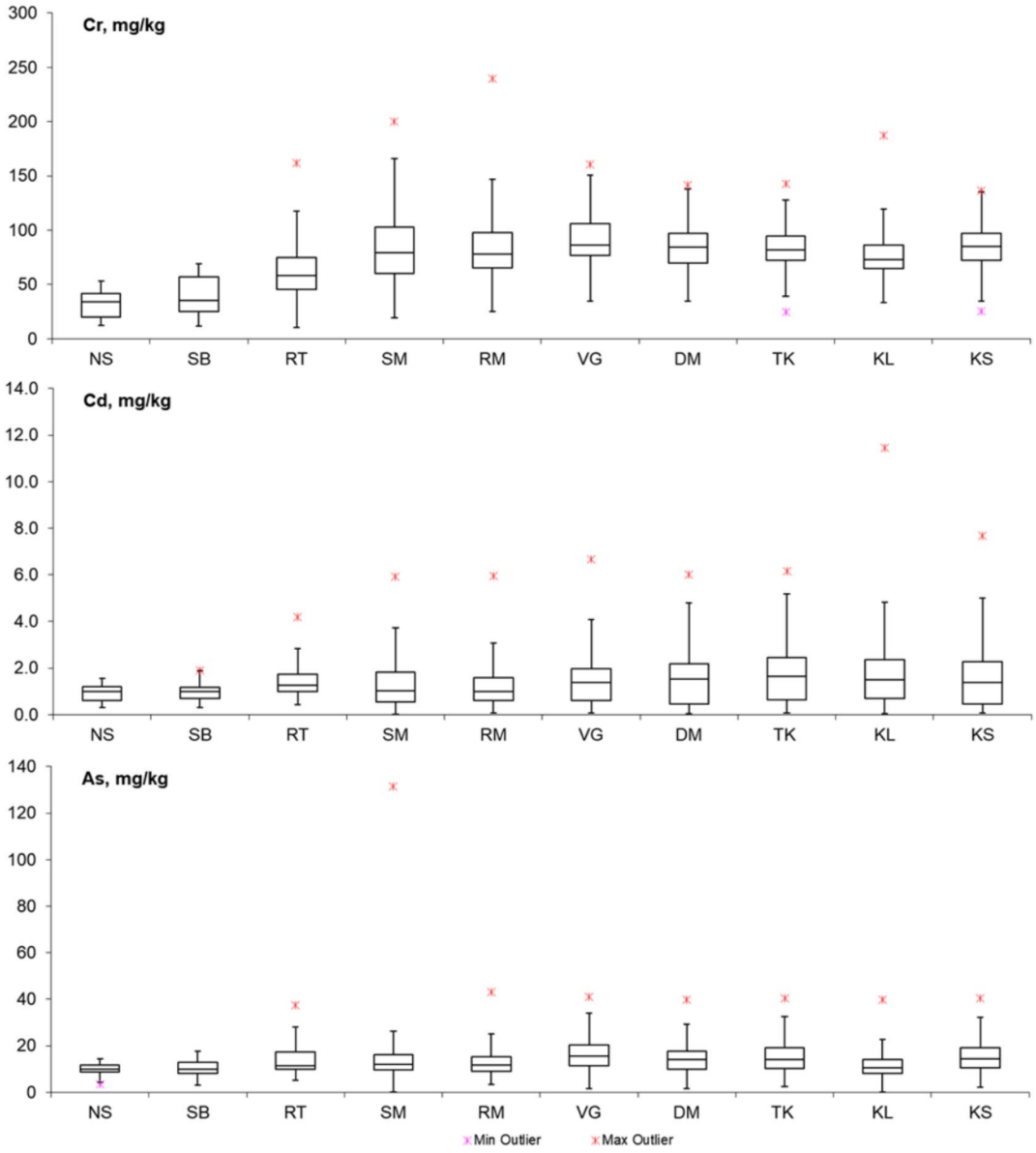



**Fig. 4** (continued)

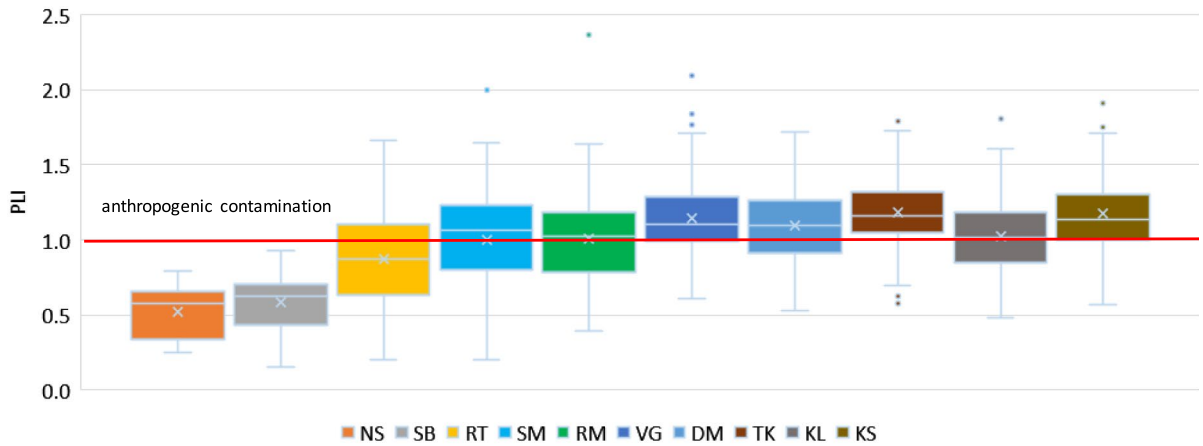



**Fig. 5** The Pollution Load Index (*PLI*) values of HMs concentrations in Danube River Sediments (Serbia) from Novi Sad to Kusjak, 2011–2023

marked spatial gradient in HMs concentrations and clearly demonstrate the significant influence of the Sava River on the sediment quality of the Danube.

The *PLI* was calculated to evaluate the overall contamination status and spatial variability among the investigated profiles (Fig. 5). These values support previous conclusions showing the increasing trend of the HMs content due to the Iron Gate I dam and obvious influence of the Sava River. The obtained *PLI* values ranged from 0.16 to 2.37, indicating considerable spatial heterogeneity in sediment contamination. The highest *PLI* value was recorded at the Ram profile in September 2011, indicating localized anthropogenic contamination probably caused by the Kostolac thermal power plant. This observation is consistent with previous study reporting elevated HMs concentrations in the same zone for Pb, Cd, Cu, Zn, and As (Crnković et al., 2016).

Overall, downstream profiles, particularly Veliko Gradište, Tekija, and Kusjak, exhibited the highest median and upper quartile *PLI* values, with first-quartile values already exceeding the threshold of $PLI = 1$. These profiles are located within the Iron Gate Reservoir system, where reduced flow velocity promotes the accumulation of fine sediments and associated contaminants.

Temporal distributions of HMs in Danube sediment

Temporal trends of *PLI* values (Fig. 6 and Table 3) reveal distinct longitudinal differences. Upstream profiles (Stari Banovci, Ritopek, Smederevo, and Ram) show a gradual decline in *PLI* values over time, indicating an overall improvement in sediment quality, likely reflecting reductions in industrial emissions and improved application of environmental regulations. The Novi Sad profile does not follow the same improving trend, likely reflecting ongoing anthropogenic pressures associated with urban discharge and untreated wastewater inputs. In contrast, downstream reservoir profiles exhibit stable or slightly increasing *PLI* values, suggesting long-term retention and accumulation of historically deposited contaminants. The descriptive statistics of the *PLI* values from 2001—2023 (Table 3) show moderate temporal variability over the period 2001–2023, ranging from 0.81 to 1.40. In the early period (2001–2007), the values fluctuated slightly around ~ 1.0. A temporary decline was observed in 2008 (0.89), followed by a recovery and a pronounced increase, reaching a peak in 2011 (1.40), the highest *PLI* value. After 2012, the values exhibited a general decreasing trend with some oscillations. In the most recent period (2018–2023), the values remained relatively stable but gradually declined to the minimum value of 0.81 in 2023. Overall, the long term *PLI* analysis was characterized by

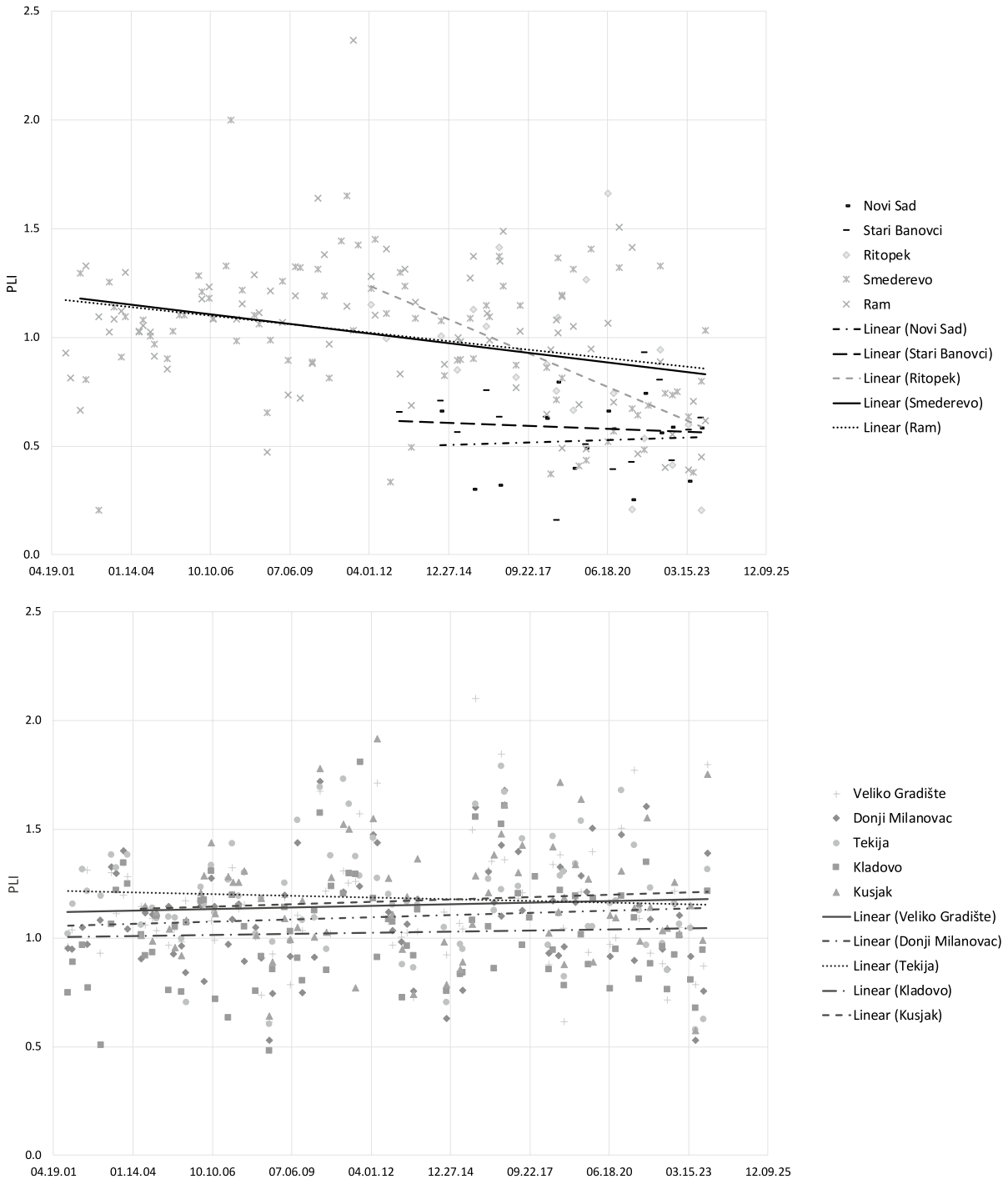



**Fig. 6** Long-term trends of the *PLI* values for the Danube River sediment profiles from Veliko Gradište to Kusjak, 2001–2023

an initial increasing trend, a peak around 2009–2012, and a subsequent decreasing trend.

As already confirmed, the Iron Gate Reservoir functions as a major sediment sink, with particularly high sedimentation rates observed near Donji

**Table 3** Desriptive statistics of the *PLI* Danube River sediment values from 2001–2023

| | Mean | Median | Range | Minimum | Maximum | Q1 | Q3 |
|---|---|---|---|---|---|---|---|
| 2001 | 0.94 | 0.95 | 0.41 | 0.75 | 1.16 | 1.03 | 1.97 |
| 2002 | 0.94 | 1.01 | 1.12 | 0.20 | 1.33 | 0.69 | 1.27 |
| 2003 | 1.21 | 1.25 | 0.49 | 0.91 | 1.40 | 1.10 | 1.32 |
| 2004 | 1.05 | 1.06 | 0.29 | 0.90 | 1.20 | 1.01 | 1.11 |
| 2005 | 0.98 | 1.00 | 0.47 | 0.70 | 1.17 | 0.91 | 1.09 |
| 2006 | 1.16 | 1.17 | 0.72 | 0.72 | 1.44 | 1.11 | 1.23 |
| 2007 | 1.19 | 1.19 | 1.37 | 0.63 | 2.00 | 1.08 | 1.29 |
| 2008 | 0.89 | 0.92 | 0.82 | 0.47 | 1.29 | 0.67 | 1.06 |
| 2009 | 1.07 | 1.07 | 0.82 | 0.72 | 1.54 | 0.91 | 1.19 |
| 2010 | 1.22 | 1.16 | 0.97 | 0.81 | 1.78 | 0.96 | 1.43 |
| 2011 | 1.40 | 1.31 | 1.60 | 0.77 | 2.37 | 1.24 | 1.57 |
| 2012 | 1.22 | 1.18 | 1.58 | 0.33 | 1.91 | 1.08 | 1.44 |
| 2013 | 0.98 | 0.99 | 0.87 | 0.49 | 1.36 | 0.75 | 1.16 |
| 2014 | 0.86 | 0.82 | 0.49 | 0.63 | 1.12 | 0.71 | 1.00 |
| 2015 | 1.07 | 0.99 | 1.80 | 0.30 | 2.10 | 0.83 | 1.28 |
| 2016 | 1.23 | 1.25 | 1.52 | 0.32 | 1.84 | 1.08 | 1.44 |
| 2017 | 1.12 | 1.14 | 0.74 | 0.71 | 1.45 | 1.01 | 1.25 |
| 2018 | 0.96 | 0.93 | 1.56 | 0.16 | 1.72 | 0.79 | 1.23 |
| 2019 | 1.04 | 1.16 | 1.24 | 0.40 | 1.64 | 0.78 | 1.30 |
| 2020 | 1.02 | 1.03 | 1.29 | 0.39 | 1.68 | 0.69 | 1.31 |
| 2021 | 0.96 | 0.96 | 1.56 | 0.21 | 1.77 | 0.67 | 1.15 |
| 2022 | 0.88 | 0.92 | 0.92 | 0.40 | 1.33 | 0.74 | 1.04 |
| 2023 | 0.81 | 0.73 | 1.59 | 0.20 | 1.80 | 0.58 | 1.03 |

Milanovac (Vuković et al., 2014) so, this profile was used to assess the temporal trend of each HM. Temporal trends at this profile (Fig. 7) show decreasing concentrations of Pb, Zn, and Cu, suggesting gradual attenuation of historical pollution. In contrast, Cr, Cd, and As exhibit increasing or stable trends, indicating continued inputs or delayed accumulation associated with reservoir sedimentation processes. Nickel concentrations remained relatively stable, further supporting its predominantly geochemical origin.

Overall, the observed spatial and temporal patterns indicate that HMs distribution in Danube River sediments is controlled by both natural geochemical background and anthropogenic inputs, dam-induced sediment retention and tributary contributions playing a key role in contaminant accumulation. The spatial heterogeneity of geochemical background concentrations and associated anthropogenic pressures originates from the catchments of major tributaries: Sava, Tisa, and Velika Morava Rivers. These tributaries drain areas with diverse geological compositions and varying intensities of industrial, agricultural, and urban activities, which may contribute to spatial variability and distinct contamination signatures observed in Danube sediments.

## PCA

Principal component analysis (PCA) was applied to the dataset comprising HMs concentrations in surface sediments of the Danube River, integrating measurements from ten monitoring profiles over a 23-year period (2001–2023), to identify underlying patterns and potential controlling factors within the Serbian sector of the river. The PCA extracted latent factors which explained the main structure of the dataset, with rotated factor loadings presented in Table 4. Factor loadings represent the correlation between each metal and the extracted components, indicating their relative contribution to each factor. Loading values greater than 0.6 were considered significant and are highlighted in bold, reflecting strong associations between the respective metals and the corresponding principal components.

Three principal components were extracted, explaining a cumulative 67.98% of the total variance (Table 4). The first component (F1), accounting for 41.74% of the variance, showed strong positive loadings for Zn (0.785), Pb (0.744), Fe (0.738), Cr (0.718), Ni (0.676), and Cu (0.628), and a moderate loading for As (0.473). This factor represents the dominant geochemical control on sediment composition and reflects a common source or mostly geochemical background of these elements.

The strong association with Fe suggests a significant lithogenic contribution related to the natural mineral composition of sediments, while the presence of Pb, Zn, and Cu also indicates potential influence from anthropogenic inputs. The second component (F2), explaining 15.17% of the total variance, was primarily characterized by a strong positive loading for Cd (0.774), indicating a distinct source independent from the elements grouped in F1. This separation suggests that Cd may originate from Sava River specific inputs which is consistent with previous investigations conducted in the Belgrade region (Crnković et al., 2008) and reported a measurable influence of the Sava River on Danube sediment quality during the 2001–2005 period, particularly with respect to elevated cadmium concentration.

The third component (F3), accounting for 11.07% of the variance, was dominated by a strong positive loading for As (0.682) indicating a different source compared to other metals. This factor likely reflects specific localized anthropogenic inputs influencing arsenic distribution in the sediment.

The PCA biplot (Fig. 8) also demonstrates strong positive correlations among most investigated HMs, particularly Fe, Zn, Pb, Cu, Cr, and Ni, as indicated by their similar orientation and clustering along the F1 axis. In contrast, Cd and As exhibit distinct orientations and weaker associations with the main component axes, indicating different sources or geochemical controls compared to the other metals. This separation supports the interpretation of Cd and As as elements influenced by specific anthropogenic inputs or localized geochemical conditions, distinct from the dominant lithogenic or mixed sources controlling the distribution of the other metals.

The PCA biplot clearly distinguishes the upstream sampling profiles (NS and SB) which are located within the Pannonian Plain from the downstream profiles influenced by the Iron Gate Reservoir system. These altered geochemical, hydromorphological and hydrodynamic conditions promote different sedimentation rates and accumulation of sediment-associated contaminants.

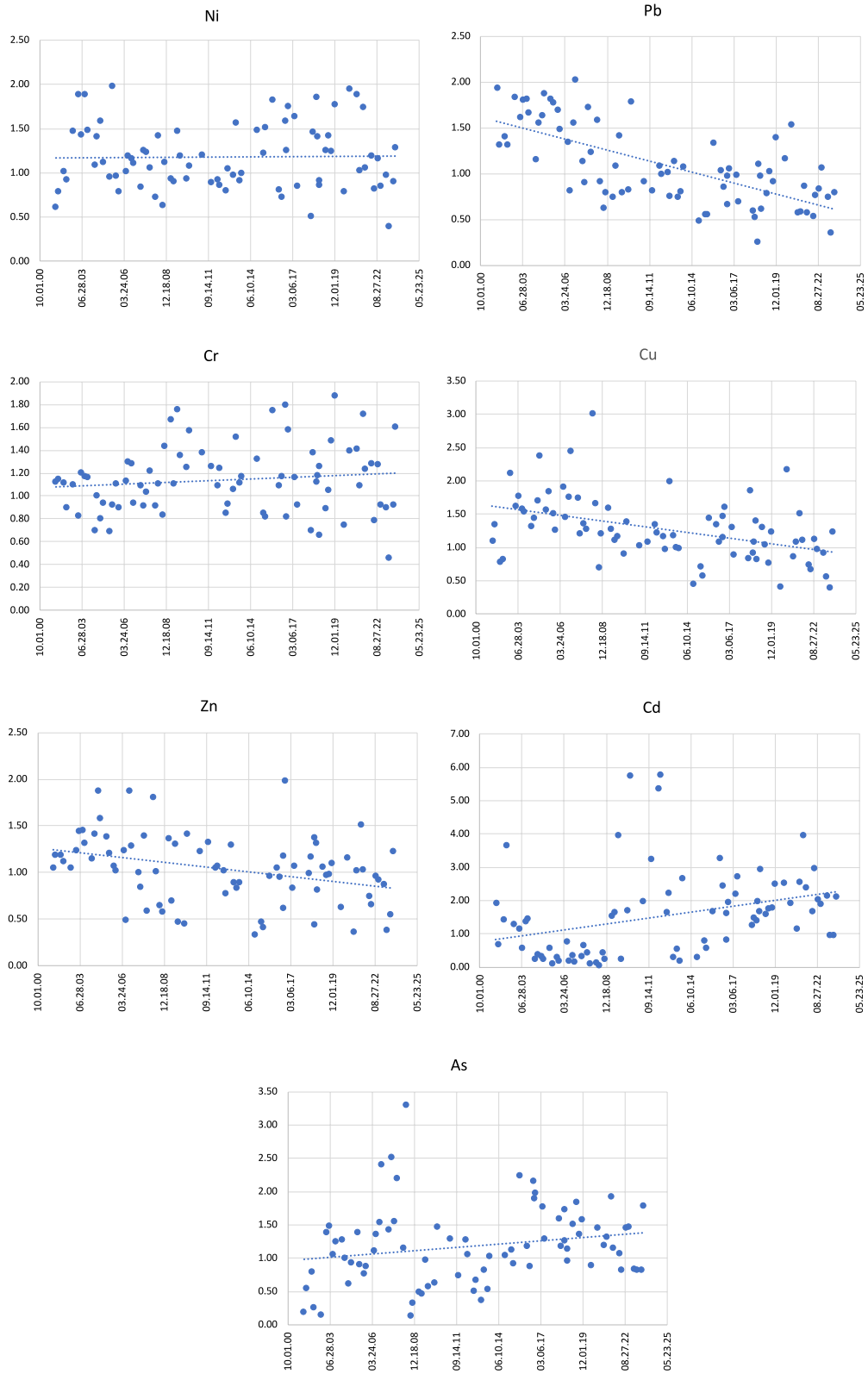
## Sediment toxicity and ecological risk

To estimate the probability of toxic biological effects on aquatic organisms comparison of concentrations of HMs in the studied sediments with the Threshold Effect Concentration (*TEC*) and Probable Effect Concentration (*PEC*) values as SQGs was applied. Percentage of sediment samples with values higher than *TEC* and *PEC* are presented in Table 5.

The contaminant concentrations in sediments revealed distinct ecological risks patterns based on exceedances of *TEC* and *PEC* values (Table 5). *TEC* exceedances were observed from 60% for Cd to 88% for Zn indicating widespread contamination and a high likelihood of toxic ecological effects supporting the need for continued monitoring. In contrast, Cd and As are the HMs with the highest percentage of samples below *TEC* thresholds, implying lower ecological concern of all HMs.

*PEC* exceedances were also observed. A total of 86% of samples exceeded the *PEC* threshold for Ni, identifying it as the only heavy metal clearly associated with expected toxic effects. In contrast, only 1–5.6% of samples surpassed *PEC* values for Zn, Cu, Pb, Cd, and As, indicating that while such exceedances are relatively occasional, they may still pose localized but potentially significant ecological risks.

The *TRI* values in sediments ranged from 1.87 to 24.80, with an average of 11.11, indicating conditions from no toxic risk to very high toxic risk (Table 6). Based on these criteria, the lowest ecotoxicological impact of the analyzed HMs was observed at the Novi Sad and Stari Banovci profiles, where all samples fell within the no to low toxic risk categories. In contrast, the remaining profiles were dominated by samples exhibiting moderate toxic risk, reflected in elevated *TRI* values. The highest proportions of samples classified under significant toxic risk (10–15%) were recorded at Tekija, Kladovo, and Kusjak. Overall, only 5% of the sediment samples were categorized as posing no toxic risk to aquatic life, while 30% indicated a low potential for toxic effects. The majority of


Ni
Pb
Cr
Cu
Zn
Cd
As
10.01.00
06.28.03
03.24.06
12.18.08
09.14.11
06.10.14
03.06.17
12.01.19
08.27.22
05.23.25

◂**Fig. 7** Long-term trends in HMs concentrations (mg/kg) at the Donji Milanovac Profile, 2001–2023

samples (56%) exhibited moderate toxic risk, whereas significant and very high toxic risk levels were observed in 8% and 1% of the samples, respectively.

**Table 4** Factor loadings for HMs measured in surface Danube River sediments from 2001–2023

| | F1 (41.74%) | F2 (15.17%) | F3 (11.07%) |
|---|---|---|---|
| Fe | **0.738** | −0.044 | −0.326 |
| Zn | **0.785** | −0.192 | −0.155 |
| Cu | **0.628** | −0.456 | −0.302 |
| Cr | **0.718** | 0.304 | 0.200 |
| Pb | **0.744** | −0.396 | −0.068 |
| Ni | **0.676** | 0.053 | 0.463 |
| Cd | 0.177 | **0.774** | −0.376 |
| As | 0.473 | 0.089 | **0.682** |

Loading values greater than 0.6 were considered significant and are highlighted in bold

## Conclusions

This study provides a comprehensive long-term assessment of HMs contamination in surface sediments of the Serbian sector of the Danube River. Based on a large dataset (about 620 samples) spanning 23 years and multiple monitoring profiles background concentrations of each HMs are proposed. The results highlight the combined influence of geochemical background, anthropogenic inputs, tributary contributions, and hydromorphological modifications, particularly dam-induced sediment retention, on the spatial and temporal distribution of HMs in Danube River sediments. Although sediment quality in the main Danube stream remains generally good, reservoir environments represent the most important zones of contaminant accumulation.

Descriptive statistical analysis, box plot evaluation and applied SQGs revealed predominantly low to moderate HMs concentrations across most profiles, with occasional elevated values indicating localized contamination events. The observed variability and the presence of outliers, generally suggest episodic or site-specific pollution inputs. Dominant influence of

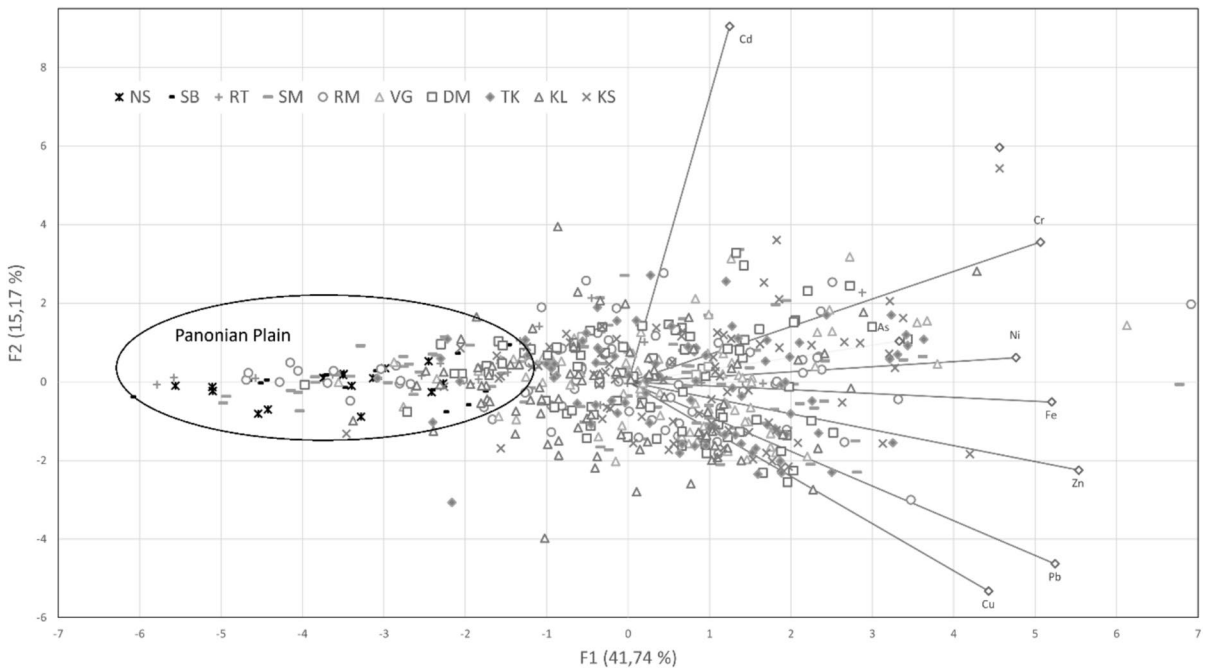



**Fig. 8** The PCA biplot (scores and loadings) of HMs concentrations in the Danube River Sediments (Serbia) from Novi Sad to Kusjak, 2011–2023

**Table 5** Percentage of sediment samples higher than SQGs

| | | Zn | Cu | Cr | Pb | Ni | Cd | As |
|---|---|---|---|---|---|---|---|---|
| *TEC** | mg/kg | 121 | 31.6 | 43.4 | 35.8 | 22.7 | 0.99 | 9.79 |
| *PEC** | mg/kg | 459 | 149 | 111 | 128 | 48.6 | 4.98 | 33 |
| $C_i < TEC$ | % | 6.4 | 12.7 | 7.5 | 15.1 | 2.4 | 38.3 | 24.6 |
| $TEC < C_i < PEC$ | % | 88.1 | 86.0 | 80.4 | 83.5 | 11.3 | 58.2 | 72.7 |
| $C_i > PEC$ | % | 5.6 | 1.3 | 12.1 | 1.4 | 86.3 | 3.50 | 2.7 |

*Consesus-based values proposed by MacDonald et al. (2000)

**Table 6** Percentage of sediment samples based on the *TRI* values for each profile and for whole Danube River (total)

| Profile (Number of samples) | No toxic risk $TRI < 5$ | Low toxic risk $5 < TRI < 10$ | Moderate toxic risk $10 < TRI < 15$ | Significant toxic risk $15 < TRI < 20$ | Very high toxic risk $TRI > 20$ |
|---|---|---|---|---|---|
| | Percentage of sediment samples | | | | |
| NS (15) | 47 | 53 | 0 | 0 | 0 |
| SB (15) | 40 | 60 | 0 | 0 | 0 |
| RT (21) | 20 | 45 | 35 | 5 | 0 |
| SM (84) | 7 | 32 | 54 | 6 | 1 |
| RM (73) | 8 | 26 | 57 | 8 | 1 |
| VG (85) | 0 | 20 | 71 | 7 | 2 |
| DM (80) | 1 | 27 | 62 | 9 | 0 |
| TK (86) | 0 | 21 | 70 | 11 | 0 |
| KL (85) | 0 | 45 | 45 | 10 | 0 |
| KS (76) | 0 | 23 | 64 | 15 | 0 |
| Total (620) | 5 | 30 | 56 | 8 | 1 |

natural geochemical processes was observed for most of HMs. Only Cd and As exhibited higher variability and enrichment, indicating stronger anthropogenic control and localized contamination sources. Principal component analysis further supported these findings, identifying a dominant geochemical component controlling Fe, Zn, Cu, Cr, Pb, and Ni distribution, and distinct components associated with Cd and As, reflecting specific anthropogenic for As and tributary-related inputs for Cd. Temporal trend analysis indicated an overall improvement in sediment quality at several upstream and midstream profiles, including Ritopek, Smederevo, and Ram. Profiles downstream of Veliko Gradište showed relatively stable or slightly increasing contamination levels, reflecting the long-term accumulation of contaminants in low-energy depositional environments.

Overall, this study provides the first comprehensive long-term reconstruction of HMs contamination trends in Danube River sediments in Serbia. These findings provide valuable scientific support for sediment quality monitoring, environmental risk assessment, and sustainable river basin management in large transboundary river systems such as the Danube River. This study highlights the importance of long-term monitoring for identifying one-time or continuous contamination, hot spots, persistent and transient contamination sources. Although this study primarily focused on the characterization of HMs, future research should integrate sediment physicochemical properties and additional organic pollutants (e.g., PAHs, PCBs, PFAS) to develop correlation models for predicting sediment quality based on site-specific monitoring data, thereby supporting more effective future sediment management plans for the Danube River environments.

**Author contributions** All authors contributed to the study conception and design. The first draft of the manuscript was

written by Tatjana Mitrović and Marija Perović. All authors read and approved the final manuscript.

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**Data availability** No datasets were generated or analysed during the current study.

**Declarations**

**Conflict of interest** The authors declare no conflict of interest.

**Ethics approval** This study did not require ethics approval.

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