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Spatial distribution and catchment-scale controls of potentially toxic elements, phosphorus and rare earth elements in the Koppány (Hungary) and Ledava (Slovenia) rivers

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Abstract

Rivers are subject to multiple pressures from chemical contaminants. In this study, we analysed seven potentially toxic elements (PTEs: Pb, Cd, As, Cr, Ni, Cu, Zn), phosphorus (P), and rare earth elements (REEs: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) in soils, river sediments, suspended particulate matter (SPM), and river water under the varying hydrological conditions. The investigation was conducted in two lithologically distinct catchments: the carbonate-dominated Koppány catchment in Hungary and the siliciclastic Ledava catchment in Slovenia. Total concentrations of PTEs in river water increased substantially during high-flow events due to the mobilization of SPM, whereas dissolved concentrations remained largely below the environmental quality standards of the EU Water Framework Directive. Most PTEs, with low bioavailability (acetic acid-extractable fraction less than 10%), indicated limited environmental risk. Enrichment factors revealed anthropogenic enrichment for Cd, Pb, and P. Elevated P levels in Koppány sediments and SPM were primarily linked to diffuse agricultural sources and point-source wastewater discharges, while Cd enrichment was more associated with urban runoff. Multivariate statistical analysis combined with REE geochemistry shows that element distribution across the different matrices is controlled by two main processes. The first is hydrodynamic sorting during fluvial transport, which selectively enriches fine-grained phases from soils through sediments to SPM. The second is primary lithological provenance, which distinguishes the carbonate-dominated, recycled, loess-derived Koppány catchment from the siliciclastic Ledava catchment across all three solid matrices. REE patterns further supported these interpretations, showing associations with Fe–Mn oxyhydroxides, aluminosilicate clay minerals, and heavy minerals, along with progressive enrichment in the fine-grained suspended fraction via surface complexation during transport. These results highlight that an integrated approach, incorporating PTEs and P as contaminants and REEs as tracers, provides a robust framework for distinguishing lithogenic sources, hydrodynamic processes, and anthropogenic inputs in geochemically complex river systems.

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Keywords Potentially toxic elements, Phosphorus, Rare earth elements, Soils, Bed sediments, Suspended particulate matter, River water, Catchment-scale controls, Provenance, Hydrological events

Introduction

Water is essential for life on our planet. It plays a fundamental role in economic growth and social development. Clean water is crucial for the functioning of ecosystems and the preservation of biodiversity. However, the rapid increase in fresh water demand for urban, agricultural, economic and industrial development has led to a release of contaminants into water bodies, including excess loads of potentially toxic elements (PTEs) [1–4] and nutrients such as phosphorus (P) [5, 6]. Among various contaminants, PTEs are of particular concern due to their significant contribution to the overall pollution of aquatic environments. To reduce pollution and improve the environmental status of surface waters, it is essential to understand the behaviour and spatial distribution of contaminants.

Elevated concentrations of PTEs in river water can originate from both natural and anthropogenic sources. One of the major factors affecting the river water quality is soil erosion. It is mainly driven by rainwater runoff that washes soil into the rivers, contributing to the formation of bed sediments and suspended particulate matter (SPM).Aggregates of minerals and natural organic matter are transported and deposited in riverbeds. While this process creates suitable habitats and supports the aquatic food webs, it also strongly influences the transport and accumulation of contaminants. Once introduced into river systems, PTEs may remain dissolved in the water column or become adsorbed onto the surfaces of SPM and sediments [7]. The extent of adsorption depends on the physical properties of SPM, such as specific surface area, as well as its chemical composition and the properties of individual dissolved PTE species. As adsorption increases, the dissolved fraction of PTEs decreases, promoting their accumulation in riverbed sediments [8]. Therefore, investigating water–sediment interactions, including both dissolved and suspended sediment-associated PTE fractions, is essential for understanding contaminant dynamics in riverine environments [2, 9].

Since PTEs are present in both dissolved and particulate forms, it is important to assess contamination in both river water and sediments. Hossain et al. [10] highlighted that river water and sediments reflect ongoing contaminant inputs and long-term accumulation processes. Analysis of the water phase provides insight into the current mobility and transport of PTEs, whereas sediment act as an important sink that reflects past pollution and can also release contaminants back into the water through remobilization. Elevated concentrations of metals such as Cd, Pb, Cr, and Ni have frequently been studied in river sediments, often linked to urban, industrial, and agricultural activities [11, 12]. Therefore, combined monitoring of sediment and water quality is essential for a comprehensive assessment of aquatic ecosystem contamination.

The amount of sediment reaching the riverbed depends on geological background, weathering, soil erosion, precipitation characteristics, and erosion processes within the riverbed itself [11, 13]. In addition, anthropogenic factors within the catchment, such as land use [14], industrial activities [15], and wastewater discharges [16], further influence the extent of river water and sediment pollution [17]. Within these systems, suspended and bottom sediments act as sinks and carriers of PTEs.

Since the terrestrial and aquatic compartments are closely interconnected, various environmental quality standards (EQS), based on biological effects, have been proposed to assess the environmental status of soils [18, 19], sediments [20–22], and SPM [20], all of which interact closely with river water and influence overall aquatic ecosystem health. In this context, achieving good ecological status in water bodies is a fundamental requirement of the European Commission (EC Water Framework Directive (WFD) as well as its related Directives [23–2827]

In addition to catchment characteristics and anthropogenic pressures, climate change–driven extreme events, especially floods and droughts, are increasingly recognized as key drivers of PTE mobility and redistribution across environmental compartments. These events can significantly enhance the release of PTEs from soils and sediments [29, 30]. Natural disturbances, like extreme rainfall, also disrupt geochemical conditions and promote desorption, mobilizing PTEs into the water column [31–37]. Investigating the interactions between water, sediments, and SPM, including dissolved PTEs and fractions bound to particulate matter, is essential for understanding contaminant dynamics in riverine systems [2, 9, 34]. Flooding can further transform contaminated soils from passive sinks into secondary pollution sources by increasing PTEs bioavailability and transport [30, 38]. This process is of particular concern in agricultural floodplains, where it may threaten crop safety, soil health, and downstream water quality under upcoming extreme hydrological scenario [29, 30, 33]. As rivers face

increasing pressure from altered flow regimes, studies on contaminant behaviour under varying hydrological conditions are becoming more important [2, 9, 34, 37, 39].

As outlined by the United Nations [40] in one of the seventeen Sustainable Development Goals, clean water must be accessible to all living beings by 2030. To achieve this goal, water pollution must be reduced and water resources managed and used sustainably [41]. Although rivers are under pressure from various sources of pollution, integrated approaches that address contamination processes and examine the fate of contaminants within river catchments have rarely been documented [20]. To assess the natural and anthropogenic input of PTEs in different environmental compartments, normalization procedures are widely employed. To distinguish background from contaminated samples, appropriate normalization can suppress the effects of changes in grain size, dilution by a predominant matrix phase and provenance [42]. Several studies have shown that the use of the enrichment factor (EF) concept is beneficial when a suitable background composition and immobile element have been selected that allow a reliable estimate of pollution [42–44].

Furthermore, rare earth elements (REEs) serve as robust geochemical tracers in fluvial systems due to their coherent behavior and affinity for the particulate phase [45]. However, factors such as grain-size effects, chemical weathering intensity, and organic matter complexation can modify fluvial REE compositions. Along the source-to-sink trajectory, REE-bearing phases are redistributed through sorting among soils, deposited sediments, and SPM [46, 47]. This redistribution can be influenced by catchment lithology,for example, siliciclastic systems tend to preserve primary provenance signatures that reflect mineralogical inheritance from bedrock sources [48]. The chemical signatures of REEs are often further shaped by their association with secondary minerals, such as Fe–Mn oxyhydroxides and clay minerals, which act as important reservoirs during transport [45, 49]. Complementary provenance information can be provided by REE anomalies. The Eu anomaly typically records plagioclase weathering and source rock inheritance, while the Ce anomaly reflects redox-controlled fractionation [50, 51]. Additionally, positive Gd anomalies are frequently used to identify anthropogenic contributions to fluvial systems [47, 52].

While total PTE concentrations and normalization procedures help identify contamination sources and extent, assessing the actual risk to organisms requires understanding element bioavailability. To evaluate the possible harmful effects of PTEs on terrestrial and aquatic organisms, it is not enough to determine the total concentration of PTEs, but also the fraction of easily soluble elements in soil and sediments. For this purpose, extraction in 0.11 mol/L acetic acid is commonly applied [2, 4, 9, 53, 54].

To assess the influence of contrasting catchment lithologies on river-water geochemistry and provide information relevant for river management, the environmental pathways of selected PTEs, including lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), nickel (Ni), copper (Cu), and zinc (Zn), as well as phosphorus (P) as a key indicator of agricultural nutrient inputs, were investigated in two geologically contrasting catchments: the carbonate-dominated Koppány catchment (Hungary) and the siliciclastic-dominated Ledava catchment (Slovenia). To achieve this, total and acetic acid–extractable concentrations of PTEs in soil and sediments were analysed, along with total contents in SPM, to estimate the influence of soil erosion on PTE presence in river water. REEs were used as geochemical tracers to determine soil provenance and the main processes influence their composition. EF analysis was employed to distinguish between natural and anthropogenic sources, while multivariate statistical analysis identified the main drivers of element transfer from terrestrial to aquatic compartments. Finally, to evaluate the impact of contaminants from various sources on river water quality, total and dissolved concentrations of PTEs were measured under both low- and high-flow conditions, capturing the dynamic nature of PTE mobilization and transport.

Materials and methods

Study area

The study areas were the Koppány catchment in Hungary and the Ledava catchment in Slovenia. The Koppány catchment, covering 660 km^2 and located upstream of Tamási in Somogy County, represents the hilly regions of Hungary and receives an average annual precipitation of approximately 630 mm [55]. Geologically, it is situated within the Pannonian Basin and is dominated by Neogene carbonate-rich sediments (limestone, marl, and dolomite) overlain by Quaternary loess and alluvial deposits. The Ledava catchment, with an area of 388 km^2, situated in northeastern Slovenia, is a representative example of the flat Pannonian Prekmurje region. It receives about 800 mm of precipitation annually [55, 56]). The Ledava catchment is characterized by siliciclastic sediments derived from the Alpine foreland, consisting predominantly of Tertiary clays, silts, sands, and gravels with occasional volcanic influences in the upper reaches [57]. The contrasting geological characteristics of the two study areas provide a basis for investigating the influence of lithology on river-water chemistry. Differences in weathering processes associated with carbonate and siliciclastic sediments are expected to affect the release,

transport, and mobility of elements, enabling assessment of lithological controls on river-water geochemistry.

The sampling sites in the Koppány and Ledava River catchments, covering soil, sediment, SPM, and river water samples, are shown in Fig. 1. These sites were selected to represent the main geographical characteristics and land use types in both basins. In the Koppány catchment, river water and SPM were sampled at two main river sites with continuous flow and water level measurements, while tributary sites were near their confluence to represent the characteristics of each tributary. Bed sediments were collected to reflect local hydrodynamics and sediment sources. In the Ledava catchment, river water, SPM, and sediments were sampled at two main river sites and one main tributary with continuous hydrological data. Soil sampling across both catchments captured the characteristics of agricultural, forest, and pasture soils in the region. Sampling codes, along with site coordinates (latitude and longitude) and the main characteristics of each catchment, are provided in Table S1 (Supplementary material).

Sampling procedures

Sampling of soil

Agricultural, forest, and pasture soil samples were taken from nine locations in the Koppány and Ledava river catchments to represent different types of land use (information on the sampling locations is provided in Fig. 1 and Table S1). At each sampling location, at least five subsamples were collected from points within a 5 m×5 m square (top 30 cm, approximately 1 kg per subsample) and pooled to form a composite sample [58]. This composite sample was then reduced to 0.5 kg using the quartering procedure to obtain a representative sample. The samples were dried at 40 °C, sieved through a 2 mm sieve, and then through a 150 µm sieve. The fraction < 150 µm was used for chemical analysis of elements in soils [59].

Sampling of sediment

Sediment samples were collected from the river beds (grab sampling, top 10 cm layer) at the same locations as the river water samples, during low-flow conditions.

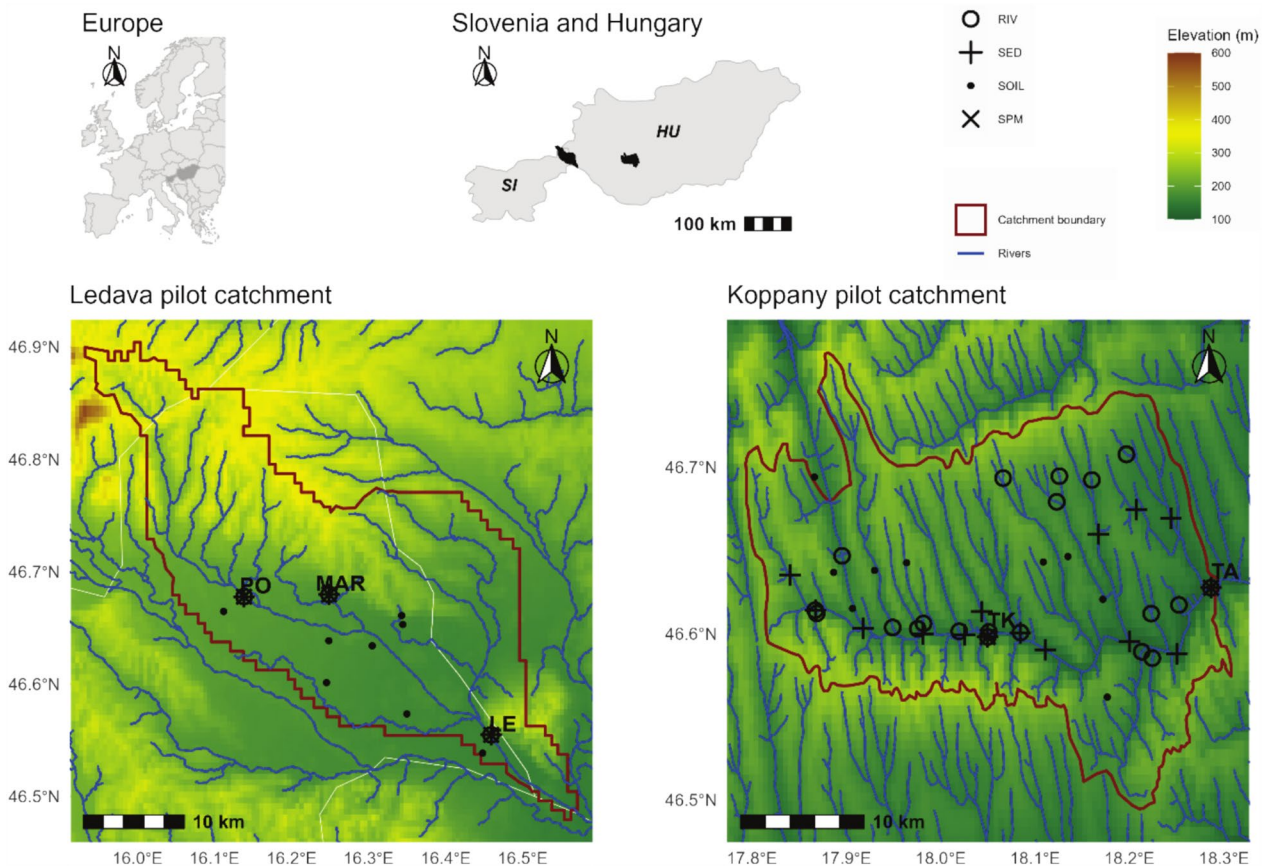


Fig. 1 Sampling sites in the Ledava River (SI) and Koppány River (HU) catchments. The sampling codes, latitude and longitude coordinates of the sampling sites in both river catchments, as well as the main characteristics of each catchment, are provided in Table S1. Sampling stations in Slovenia: PO – Polana sampling station; MAR – Martjanski Potok sampling station; LE –Lendava/Čentiba sampling station. Sampling stations in Hungary: TK Törökkoppány sampling station; TA Tamási sampling station

Fifteen sediment samples were collected from the Koppány catchment area and three from the Ledava catchment area (information on the sampling locations is provided in Fig. 1 and Table S1). The samples were wet sieved through a 1 mm sieve, followed by sieving through a 63 µm sieve, and then freeze-dried. The < 63 µm fraction was used for the chemical analysis of elements in sediments [24].

The percentage of the < 63 µm sediment fraction was determined gravimetrically from the masses of the < 63 µm and 63 µm–1 mm fractions (Table S2).

Sampling of SPM

SPM samples were collected during different heavy rainfall events at the same locations as the river water samples in the Ledava catchment (three sampling sites), and at the two main river stations in the Koppány catchment (information on the sampling locations is provided in Fig. 1 and Table S1). Sampling was performed using a simple time integrated modified (slightly larger outlet diameter: 10 mm, much larger inlet of 2.4 cm) Phillips sampler [60]. At the Ledava sites, 10 L of river water were collected, filtered through 0.45 µm filter, and the SPM content on the filter was freeze-dried. Fifteen SPM samples were collected from the Koppány catchment area, and three from the Ledava catchment area.

Sampling of river water

River water sampling was conducted over the course of one year in the Koppány (two main stations) and Ledava (three stations) catchments, under low- and high-flow conditions (information on the sampling locations is provided in Fig. 1 and Table S1). At low-flow conditions, grab sampling was performed, while at high-flow conditions, either grab sampling or flow-proportional sampling was carried out using various automatic samplers. The water discharges under high-flow and low-flow conditions along with pH, electrical conductivity and total alkalinity are presented in Table S3. At the main river sampling sites in the Koppány catchment, water discharges under high-flow conditions ranged from 0.3 to 9.3 m^3/s, and in the Ledava catchment from 0.12 to 9.7 m^3/s. Under low-flow conditions, discharges ranged from 0.08 to 1.98 m^3/s at Koppány and from 0.02 to 5.5 m^3/s at Ledava. 15 tributaries in the Koppány watershed were sampled during a campaign measurement, which was done under low-flow conditions. Samples were collected in bottles pre-cleaned with 20% nitric-acid solution. For the determination of dissolved concentrations of PTEs, 50 mL of water samples were filtered (0.45 µm filter) into 50 mL LDPE bottles and acidified to a pH below 2 by adding 75 µL of concentrated HNO_3 (67–70%) per 50 mL of sample [25, 28, 61]. To determine total elemental concentrations, 250 mL of unfiltered water samples were acidified to pH < 2 by adding 375 µL of concentrated HNO_3. All acidified samples were frozen at − 20 °C and thawed prior to analysis. Filtration blanks did not exceed 3% of the measured PTE concentrations by ICP–MS and were generally below the LODs.

Instrumentation

Concentrations of elements were determined by ICP–MS, using instrument Agilent 7700x (Agilent Technologies, Tokyo, Japan). ICP–MS operating parameters are presented in Table S4. Data were extracted using the Agilent 5.1 MassHunter software and further processed with Microsoft Excel 2019 MSO (Redmond, WA, USA).

A CEM Corporation (Matthews, NC, USA) MARS 6 Microwave System was used for sample digestion. A Mettler AE 163 (Zürich, Switzerland) analytical balance was used for all weighing. During the extraction procedure, the samples were mechanically shaken on a Vibromix 40 orbital shaker (elliptical table shaker) (Tehtnica, Železniki, Slovenia). Sample extracts were centrifuged on a Hettich Universal 320 Centrifuge (Hettich GmbH & Co., KG, Tuttlingen, Germany).

Reagents and materials

Ultrapure 18.2 MΩ cm water obtained from a Direct-Q 5 system (Millipore, Watertown, MA, USA) was used for preparation of samples and reagents. Suprapur nitric acid (67–70% HNO_3) was obtained from Carlo Erba Reagents (Val-de-Reuil, Normandie, France). Suprapur hydrochloric acid (30% HCl), suprapur hydrofluoric acid (40% HF), suprapur hydrogen peroxide (30% H_2O_2), suprapur boric acid (H_3BO_3) and glacial acetic acid (CH_3COOH) of analytical reagent grade were purchased from Merck (Darmstadt, Germany). ICP multi-element standard solution XVI (21 elements in diluted nitric acid, 100 mg/L), rare earth element mix for ICP and stock standard solutions of scandium (Sc), germanium (Ge), yttrium (Y), rhodium (Rh) and indium (In) (1000 ± 2 mg/L in 2–3% HNO_3) obtained from Merck, were used to prepare calibration curves and internal standards for the determination of elements by ICP–MS. Samples were filtered using 0.45 µm Minisart cellulose nitrate membrane filters (Sartorius, Goettingen, Germany). SPM was collected by vacuum filtration using 0.45 µm nitrocellulose Millipore Membrane Filters, purchased from Merck. The water samples were collected in 250 mL and 50 mL low-density polyethylene (LDPE) wide-mouth bottles obtained from BRAND (Wertheim, Germany). The certified standard reference material SPS-SW1 (Reference material for measurements of elements in surface waters) obtained from Spectrapure Standards (Oslo, Norway) and the certified reference materials CRM 320R Trace Elements

in Channel Sediment, Community Bureau of Reference (Geel, Belgium) were used for the accuracy check.

Analytical procedures

Analytical procedures for the determination of total elements contents in soil, sediment and SPM

Approximately 0.2 g of freeze-dried soil, sediment, or SPM sample was weighed into a Teflon vessel, and 2 mL of H_2O_2, 4 mL of HNO_3, 1 mL of HCl, and 2 mL of HF were added. The resulting mixture was subjected to a two-step microwave-assisted digestion. After the first digestion step, 12.5 mL of a 4% aqueous H_3BO_3 solution was added to dissolve sparingly soluble fluorides (e.g., calcium fluoride) and to complex excess HF, followed by the second digestion step. The digest was then transferred into 50 mL graduated PE tubes. The concentrations of selected major and trace elements (Na, Mg, Al, K, Ca, Sc, Ti, V, Mn, Fe, Co, Sr), lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), PTEs (Pb, Cd, As, Cr, Ni, Cu and Zn), and P were determined in samples diluted 100- or 1000-times using ICP–MS [4]. Selected major and trace elements, along with the full set of REEs, were analysed to choose suitable normalizers and better understand anthropogenic impacts, geographic origin, and lithological controls.

Analytical procedure for the determination of acetic acid–extractable concentrations of PTEs

To determine of acetic acid extractable concentrations, 0.5 g of soil, sediment or SPM was shaken with 20 mL of 0.11 mol/L acetic acid on a mechanical shaker (300 rpm) for 16 h. Samples were then centrifuged (10,000 rpm, 20 min), filtered through 0.45 µm membrane filter and concentrations of PTEs were determined by ICP–MS [2].

Analytical procedure for the determination of PTEs and phosphorous concentrations in river water

To determine the total concentrations of PTEs and P in river water, 3 mL of HNO_3, 1 mL of HCl, and 0.1 mL of HF were added to 10 mL of sample, and the resulting mixture was subjected to microwave-assisted digestion. After digestion, the samples were diluted 10-times, and the concentrations of PTEs were determined by ICP–MS.

To determine the dissolved concentrations of PTEs and P, the river water samples were analysed directly by ICP–MS.

All the analyses were performed in triplicate.

Quality control and limits of detection

The certified standard reference material SPS-SW1 and the certified reference material CRM 320R were used to verify analytical accuracy. The analyses were performed using the same procedures as those applied to the investigated samples. The results obtained for SPS-SW1 and CRM 320R are presented in Table S5. Good agreement was observed between the determined elemental concentrations and the certified values, with differences not exceeding ± 3%, confirming the accurate determination of PTE concentrations in river water, soil, sediment, and SPM samples by ICP–MS.

The limits of detection (LODs) for the determination of total and dissolved elemental concentrations in river water samples, total elemental concentrations in soils, sediments, and SPM, as well as acetic acid (0.11 mol/L) extractable elemental concentrations in soils, sediments, and SPM, were calculated as the concentrations corresponding to a signal equal to 3 *s* of the blank sample. For LOD calculation, eight blank samples were analysed by ICP–MS. The LOD values for the elements analysed in each sample matrix are provided in Table S6.

Statistical analyses

Multidimensional Scaling Analysis

Multidimensional Scaling (MDS) analysis was performed to visualize multivariate relationships and clustering patterns among sample groups based on their elemental compositions. Prior to analysis, data were centered log-ratio (clr) transformed separately for each dataset to address the compositional nature of geochemical data and to minimize closure and grain-size effects [62]. MDS is an ordination technique that transforms the original multidimensional data into a lower-dimensional space while preserving the relative distances between samples. The analysis used Euclidean distance matrices, and the first two MDS dimensions were plotted to represent the main sources of variation in the dataset. Element loadings were calculated to identify which variables contributed most to the ordination patterns and sample differentiation.

Enrichment factor analysis

Robust algorithms were favoured in the geochemical data exploration due to their reduced susceptibility to outliers when compared to ordinary least squares methods [43]. The multivariate linear robust regression (MLRR) approach utilizing the MM-estimator was employed to predict simultaneously the relationship between multiple independent variables (lithogenic elements) and a single dependent variable (PTE) in sediment and SPM samples [63]. The MLRR analysis was conducted using a stepwise procedure, beginning with the inclusion of

all lithogenic elements as explanatory variables and progressively eliminating those failing to achieve statistical significance in the t-test at P = 99%. In cases where only one element remained statistically significant, univariate robust regression was applied instead of the multivariate approach. The resulting empirical background functions,

$$E_{BN} = f(E_{REF}), \quad (1)$$

were used to calculate enrichment factors,

$$(EF = E/E_{BN}), \quad (2)$$

where E_{BN} represents the background concentration derived from the relationship between target PTEs and multiple conservative lithogenic elements [42, 44]. To distinguish statistically anomalous enrichment from natural geochemical variability, EF thresholds were established using Shapiro–Wilk normality testing. For normally distributed elements, the mean plus two standard deviations was applied, while the 90th percentile was used for elements with significant positive skewness ($p \leq 0.05$). The resulting thresholds for sediment were: As = 1.25, Cd = 1.39, Cr = 1.08, Cu = 1.32, Ni = 1.07, Pb = 1.08, Zn = 1.19, and P = 1.25; and for SPM: As = 1.23, Cd = 1.49, Cr = 1.30, Cu = 1.10, Ni = 1.08, Pb = 1.28, Zn = 1.24, and P = 1.28.

REE analyses

Concentrations of REEs and yttrium (REY; La to Lu, including Y) were normalized to the estimated average composition of European Shale (EUS) following Bau et al. [64]. EUS normalization was selected over Post-Archean Australian Shale (PAAS) based on empirical testing, as it provided more consistent normalized patterns for the lithologies in the study area. REEs were divided into light (LREEs: La, Ce, Pr, Nd), middle (MREEs: Sm, Eu, Gd, Tb, Dy), and heavy rare earth elements (HREEs: Ho, Er, Tm, Yb, Lu). Fractionation was quantified using the ratios LREE/HREE and MREE/LREE, calculated from the respective EUS-normalized groups. Ce, Eu, and Gd anomalies were calculated as:

$$Ce/Ce* = 2\,x\,Ce_N/(La_N \times Pr_N), \quad (3)$$

$$Eu/Eu* = 2\,x\,Eu_N/(Sm_N \times Gd_N), \quad (4)$$

$$Gd/Gd* = 2\,x\,Eu_N/(Sm_N \times Tb_N), \quad (5)$$

where subscript N denotes concentrations normalized to EUS. Before calculating anomalies, both linear and semi-logarithmic (geometric) interpolation methods were evaluated empirically [65]. Linear interpolation produced more consistent results and was therefore used throughout.

Results and discussion

Spatial distribution of PTEs and phosphorus in the Koppány and Ledava catchments

Despite growing concern over riverine contamination, the spatial variability and catchment-scale controls of PTEs and P remain poorly understood in smaller Central European rivers. This study investigates the Koppány and Ledava river catchments to assess the factors governing the spatial distribution of PTEs (Pb, Cd, As, Cr, Ni, Cu, and Zn) and P in soils, sediments, SPM, and river water. Samples were analysed following the procedures described in Section *Analytical procedures*. Element concentrations were evaluated against relevant EQS and guideline values.

The analytical results for PTEs and P are presented in Fig. 2. Concentrations measured in each sample matrix, together with the corresponding EQS or target values, are provided in the Supplementary Material (Tables S7–S11), while the minimum, median, and maximum concentrations are presented in Tables 1, 2 and 3. Data from the Hungarian and Slovenian pilot areas are also available in the ARP data repository [66]. The concentrations obtained in this study are further compared with literature data, summarized in Table 4.

Results from Fig. 2, Table 1, and Table S7 show that median concentrations of PTEs and P in soils are comparable between the Koppány and Ledava catchments. Approximate values are 20 mg/kg for Pb, 0.3 mg/kg for Cd, 10 mg/kg for As, 70 mg/kg for Cr, 30 mg/kg for Ni, 20 mg/kg for Cu, 65 mg/kg for Zn, and 700 mg/kg for P. In these predominantly agricultural soils, Pb and Cd likely to reflect background levels. As may be influenced by both natural soil composition and historical pesticide use. Cr and Ni are predominantly associated with parent material, with potential minor anthropogenic contributions. Cu and Zn may be linked to fertilizer and manure application, while P is likely related to intensive use of fertilizers.

Element concentrations in sediments are generally higher than in soils (Fig. 2, Table 1, and Table S8). Median values for the Koppány and Ledava catchments are: Pb 21 and 35 mg/kg, Cd 0.28 and 0.42 mg/kg, As 14 and 22 mg/kg, Cr 72 and 91 mg/kg, Ni 39 and 53 mg/kg, Cu 25 and 35 mg/kg, Zn, 76 and 161 mg/kg, and P 1350 and 1175 mg/kg, respectively. In the Koppány catchment, SPM (Fig. 2, Table 1, and Table S9) exhibits substantially higher concentrations than sediments, with median values of 34.8 mg/kg for Pb, 0.43 mg/kg for Cd, 24.8 mg/kg for As, 97.7 mg/kg for Cr, 58.5 mg/kg for Ni, 40.4 mg/kg for Cu, 131 for mg/kg Zn, and 1615 mg/kg for P. In the Ledava catchment, SPM exceeds sediment concentrations for Cr, Ni, Cu, and P (132, 57.5, 42.6, and 1199 mg/kg, respectively), but is slightly lower

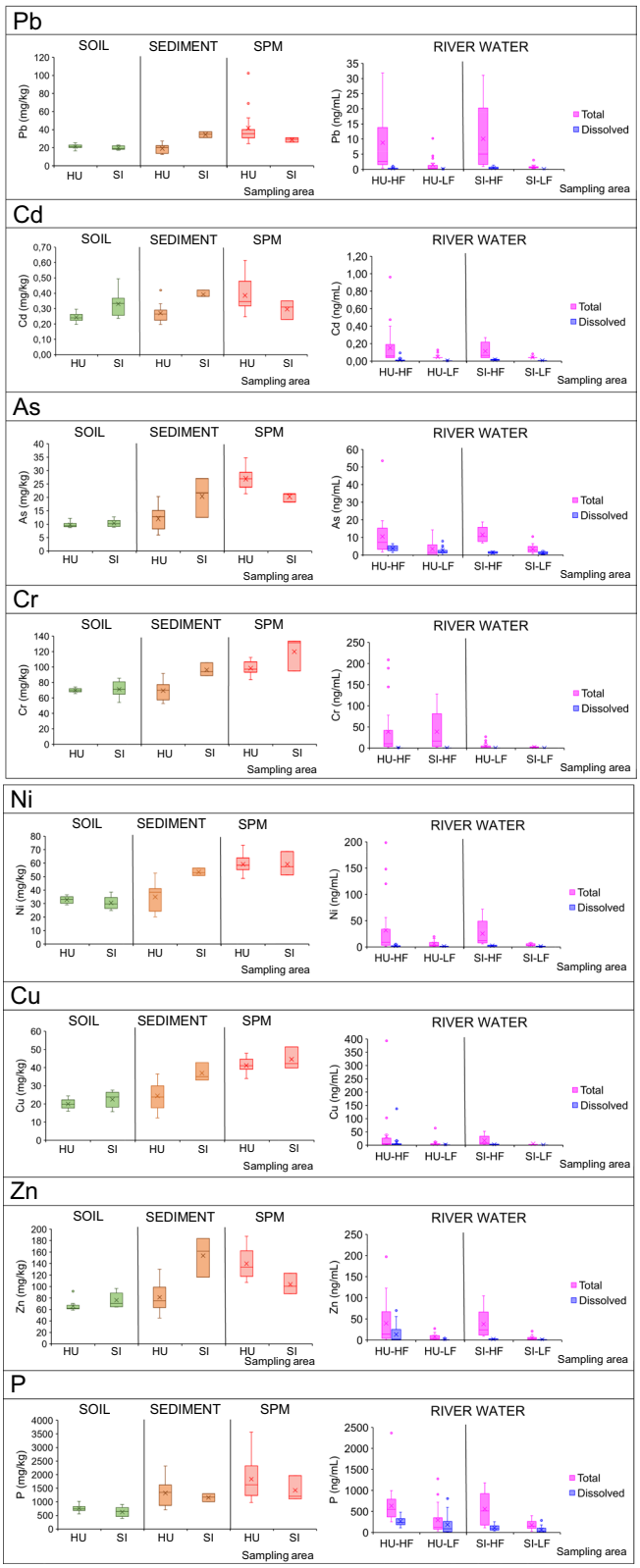


Fig. 2 Box plots showing elemental concentrations in soil, sediment, SPM, and river water from Hungarian (HU) and Slovenian (SI) sampling areas. The boxes represent the interquartile range, the horizontal line inside each box indicates the median, and the whiskers show the full data range. Outliers are displayed as individual points. In river water, HF denotes high-flow conditions and LF denotes low-flow conditions

Table 1 Minimum, median, and maximum concentrations of PTEs and P in soil, sediment and SPM samples from the Koppány, Hungary (HU) (n = 9) and Ledava, Slovenia (SI) (n = 9) river catchments, determined by ICP–MS

	Pb (mg/kg)	Cd (mg/kg)	As (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	P (mg/kg)
Soil HU								
Min.	16.4	0.197	8.77	65.6	29.1	16.0	58.7	548
Median	20.9	0.239	9.36	69.4	33.2	19.8	61.7	739
Max.	25.3	0.295	12.1	74.1	36.5	24.4	91.5	1017
Soil SI								
Min.	17.1	0.236	8.80	54.1	24.8	15.7	63.8	377
Median	18.8	0.333	10.1	71.2	29.7	23.8	70.3	635
Max.	22.7	0.493	12.7	85.4	38.6	27.6	96.7	896
Sediment HU								
Min.	13.6	0.222	6.91	56.3	23.1	12.2	45.6	719
Median	21.2	0.276	14.1	71.8	39.1	24.5	75.7	1346
Max.	27.6	0.418	20.5	92.4	52.5	36.2	111	2300
Sediment SI								
Min.	31.1	0.377	12.6	89.8	50.8	33.0	116	1015
Median	34.8	0.378	21.8	94.7	52.9	34.9	161	1175
Max.	37.4	0.419	27.3	106	56.3	42.7	183	1301
SPM HU								
Min.	24.8	0.274	21.3	84.3	49.1	34.1	107	963
Median	34.8	0.430	24.8	97.7	58.5	40.4	131	1615
Max.	102	0.616	35.1	113	73.1	46.6	187	3560
SPM SI								
Min.	26.6	0.229	18.0	95.1	51.5	40.0	88.1	1092
Median	29.6	0.309	21.2	132	57.5	42.5	101	1199
Max.	31.3	0.350	21.3	134	68.5	51.6	123	1957

for Pb, Cd, As, and Zn (29.6, 0.31, 21.3, and 101 mg/kg, respectively). These differences reflect catchment-specific controls on element distribution. In the Koppány catchment, the sediment fraction < 63 µm, which is readily resuspended during heavy rainfall, accounts for a median of 60% of total sediment, compared to only 2.3% in the Ledava catchment (Table S2). The higher proportion of fine particles in the Koppány catchment likely promotes greater trace element accumulation in SPM, given that soil erosion and surface runoff are major pathways for the transfer of contaminants from soils to rivers, where trace elements accumulate in bed sediments and SPM. These findings indicate that soil erosion and surface runoff are major pathways for the transfer of contaminants from soils to rivers, where trace elements accumulate in bed sediments and SPM. This is consistent with previous studies of Barhoumi et al. [11] and Jaskuła and Sojka [13].

Comparison with soil EQS [18], Table S7) and quality target values for sediments and SPM [20], Tables S8 and S9) showed some exceedances. As slightly exceeded the soil threshold of 10 mg/kg in 6 of 18 samples. The sediment and SPM target value of 20 mg/kg for As was exceeded in 3 sediment samples and 17 SPM samples. Ni exceeded the 50 mg/kg threshold once in Hungarian sediments and in all Slovenian sediments and was notably elevated in most SPM samples. Cr slightly exceeded the 100 mg/kg threshold once in Slovenian sediments and in five Hungarian and two Slovenian SPM samples. No exceedances were observed for the other elements. No EQS exist for P, as it is considered a nutrient rather than a toxic element.

The partitioning of trace elements between dissolved and particulate phases in rivers is largely controlled by hydrological conditions, element-specific properties, pH and the amount of organic matter [10]. Data from Fig. 2, Tables 2 and 3, and Tables S10 and S11 show that, under low-flow conditions, total elemental concentrations are generally comparable to dissolved concentrations, suggesting that the dissolved phase predominates. In contrast, during high-flow conditions, dissolved concentrations are markedly lower than total concentrations, reflecting the preferential association of trace elements with particulate matter. This is consistent with the findings of Milačič Ščančar et al. [2, 9], Lučić et al.

Table 2 Minimum, median, and maximum total concentrations of PTEs and P in river water samples from the Koppány, Hungary (HU) and Ledava, Slovenia (SI) catchments at high (n = 24 and 6, respectively) and low (n = 28 and 18, respectively) water flow conditions, determined by ICP–MS

	Pb (ng/mL)	Cd (ng/mL)	As (ng/mL)	Cr (ng/mL)	Ni (ng/mL)	Cu (ng/mL)	Zn (ng/mL)	P (ng/mL)
River water HF-T HU								
Min.	0.372	< 0.04	1.79	1.25	1.35	1.59	< 0.70	255
Median	2.76	0.059	7.19	10.3	8.84	5.44	14.1	549
Max.	99.8	0.962	53.6	209	199	393	197	2367
River water HF-T SI								
Min.	0.949	< 0.04	6.88	2.18	5.86	3.17	9.33	112
Median	5.02	0.066	10.5	16.6	12.0	7.91	24.1	512
Max.	31.1	0.269	18.8	128	71.8	52.3	105	1179
River water LF-T HU								
Min.	< 0.15	< 0.04	< 0.10	0.117	1.35	0.288	< 0.70	38.2
Median	0.327	0.040	1.47	1.52	3.01	1.55	4.06	126
Max.	10.6	0.127	14.3	26.9	21.7	64.6	31.0	1287
River water LF-T SI								
Min.	0.224	< 0.04	0.828	0.837	0.250	1.31	< 0.70	30.3
Median	0.718	0.040	2.81	2.26	3.05	2.10	3.27	151
Max.	3.08	0.083	10.5	4.41	22.0	61.7	21.1	400

Table 3 Minimum, median, and maximum dissolved concentrations of PTEs and P in river water samples from the Koppány, Hungary (HU) and Ledava, Slovenia (SI) catchments at high (n = 24 and 6, respectively) and low (n = 28 and 18, respectively) water flow conditions, determined by ICP–MS

	Pb (ng/mL)	Cd (ng/mL)	As (ng/mL)	Cr (ng/mL)	Ni (ng/mL)	Cu (ng/mL)	Zn (ng/mL)	P (ng/mL)
River water HF-D HU								
Min.	0.016	< 0.004	1.39	0.125	0.954	1.07	0.622	112
Median	0.177	0.006	3.99	0.214	1.88	2.71	1.95	237
Max.	1.17	0.094	6.47	1.13	5.31	137	69.9	484
River water HF-D SI								
Min.	0.090	0.007	0.716	0.115	1.28	1.33	1.34	37.3
Median	0.321	0.015	1.31	0.500	2.16	1.48	2.52	91.0
Max.	1.37	0.029	2.21	0.888	3.69	4.04	3.32	257
River water LF-D HU								
Min.	< 0.015	< 0.004	0.177	< 0.006	0.452	0.087	< 0.070	8.09
Median	0.015	0.004	1.53	0.241	0.988	0.995	0.070	88.8
Max.	0.431	0.014	8.77	1.50	2.56	6.92	4.71	826
River water LF-D SI								
Min.	< 0.015	< 0.004	0.365	0.044	0.200	0.509	< 0.070	7.62
Median	0.025	0.006	1.06	0.13	1.26	0.891	0.665	36.1
Max.	0.294	0.011	2.63	0.434	2.18	1.47	3.93	289

Table 4 Concentrations of PTEs and P in soils, sediments, and SPM, as well as total and dissolved element contents in the river waters under high-flow (HF) and low-flow (LF) conditions, compared with literature data

River/Location	Sample matrix	Pb	Cd	As	Cr	Ni	Cu	Zn	P	Reference
Sava River	Soil (mg/kg)	21.1–83.6	0.13–3.11	7.59–29.3	36.3–283	15.6–168	17.9–149	91.6–328	/	[67]
Sava River/Slovenia, Croatia (average concentrations)	Soil (mg/kg)	49.2	0.60	12.8	61.1	/	27.3	89.9	/	[42]
	Sediment (mg/kg)	54.2	0.63	12.3	89.9	/	32.6	170		
	SPM (mg/kg)	58.4	0.86	15.7	99.5	/	51.1	235		
Western European rivers (1945–2020)	Sediment (mg/kg)	20–60	0.2–8.0	/	30–80	15–60	15–70	30–800	/	[68]
	SPM (mg/kg)	50–300	0.3–11	/	80–150	50–100	50–200	110–1100	/	
Danube Delta/Romania/Ukraine—JDS 2	Sediment (mg/kg)	97–343	0.6–0.75	/	76–102	144–205	60–105	134–150	/	[36]
				/					/	
Someşu Mic River, Romania	Sediment (mg/kg)	12.3–132	0.04–0.35	/	9.39–43.2	14.7–47.7	7.22–65.6	42.1–237	/	[11]
Bug River catchment/Poland	Sediment (mg/kg)	3.01–15.4	0.03–0.75	/	0.87–8.13	3.12–14.3	0.55–8.05	5.11–53.9	/	[69]
47 rivers in Poland	Sediment (mg/kg)	0.50–7.59	0.025–1.67	/	0.854–113	0.79–50.8	0.20–84.3	4.41–414	/	[12]
Oder, Vistula Rivers, Poland	Sediment (mg/kg)	1–579	0.5–17	/	1.5–538	0.85–500	0.40–105	0.50–637	/	[13]
Lower Lee catchment, London, United Kingdom	Sediment (mg/kg)	50.0–322	0.47–5.64	/	/	1.34–51.1	32.6–294	164–777	/	[31]
	River water total (ng/mL)	0.21–13.3	0.02–0.44	/	/	0.66–55.1	1.04–32.5	1.25–62.7	/	
Zagyva, Koppány Rivesr/Hungary	River water dissolved (ng/mL)	< 0.015–1.15	< 0.004–0.038	1.05–10.3	0.076–4.44	0.903–3.26	0.998–6.98	< 0.070–14.4	/	[61]
Sava River/Slovenia, Croatia	River water dissolved (ng/mL)	0.035–0.235	0.008–0.067	0.294–0.830	0.143–2.13	0.269–1.61	0.314–3.72	0.843–12.4	/	[39]
Sava River/Sava catchment	Sediment (mg/kg)	20–70	0.10–1.5	4.0–30	20–200	10–100	10–40	30–300	/	[2]
	River water total (ng/mL)	< 0.15–2.0	< 0.04–0.05	0.20–3	0.50–12	1–35	0.40–6.0	0.40–8.0	/	
	River water dissolved (ng/mL)	< 0.015–0.30	< 0.004–0.015	0.02–1.5	0.10–0.50	0.1–5.5	0.2–2.0	0.2–5.0	/	
Evrotas River/Greece	Sediment (mg/kg)	10–60	< 0.06–0.40	2.0–28	120–280	50–150	20–100	50–180	/	[9]
	River water total (ng/mL)	< 0.15–0.25	< 0.04–0.070	< 0.10–0.18	0.02–0.8	0.20–24	0.20–0.50	0.80–6.0	/	
	River water dissolved (ng/mL)	< 0.015–0.050	< 0.004–0.070	< 0.01–0.015	0.2–0.7	0.10–6.0	0.015–0.20	< 0.07–0.15	/	
Danube River catchment	Sediment (mg/kg)	13.7–85	0.72–1.95	< LOQ–17.1	9.8–101	5.1–69.2	< LOQ–527	23–199	/	[20]
	SPM (mg/kg)	< 0.20–48.7	0.21–1.16	8.4–27.6	37.0–76.1	29.0–69.3	26.8–86.7	100–246	/	
	River water dissolved (ng/mL)	0.20–8.1	< 0.01–1.1	1.1–5.3	0.29–67.1	0.78–230	1.1–283	1.0–60.7	150–700	
Agricultural catchments/Sweden	Sediment (mg/kg)	/	/	/	/	/	/	/	~1200	[5]
	SPM (mg/kg)	/	/	/	/	/	/	/	~1200	
Koppány catchment, Hungary	Soil (mg/kg)	16.4–25.3	0.197–0.295	8.77–12.1	65.6–74.1	29.1–36.5	16.0–24.4	58.7–91.5	550–1020	This study
	Sediment (mg/kg)	13.6–27.6	0.222–0.418	6.91–20.5	56.3–92.4	23.1–52.5	12.2–36.2	45.6–111	720–2300	
	SPM (mg/kg)	24.8–102	0.274–0.616	21.3–35.1	84.3–113	49.1–73.1	34.1–46.6	107–187	960–3560	
	River water total (ng/mL) HF	0.372–99.8	< 0.04–0.962	1.79–53.6	1.25–209	1.35–199	1.59–393	< 0.70–197	255–2370	
	River water total (ng/mL) LF	< 0.15–10.6	< 0.04–0.127	< 0.10–14.3	0.117–26.9	1.35–21.7	0.288–64.6	< 0.70–31.0	40–1290	
	River water dissolved (ng/mL) HF	0.016–1.17	< 0.004–0.094	1.39–6.47	0.125–1.13	0.954–5.31	1.07–137	0.622–69.9	110–480	
	River water dissolved (ng/mL) LF	< 0.015–0.431	< 0.004–0.014	0.177–8.77	< 0.006–1.50	0.452–2.56	0.087–6.92	< 0.070–4.71	8–820	

Table 4 (continued)

River/Location	Sample matrix	Pb	Cd	As	Cr	Ni	Cu	Zn	P	Reference
Ledava catchment, Slvenia	Soil (mg/kg)	17.1–22.7	0.236–0.493	8.80–12.7	54.1–85.4	24.8–38.6	15.7–27.6	63.8–96.7	380–900	
	Sediment (mg/kg)	31.1–37.4	0.377–0.419	12.6–27.3	89.9–106	50.8–56.3	33.0–42.7	116–183	1015–1300	
	SPM (mg/kg)	26.6–31.3	0.229–0.350	18.0–21.3	95.1–134	51.5–68.5	40.0–51.6	88.1–123	1090–1960	
	River water total (ng/mL) HF	0.949–31.1	< 0.04–0.269	6.88–18.8	2.18–128	5.86–71.8	3.17–52.3	9.33–105	110–1100	
	River water total (ng/mL) LF	0.224–3.08	< 0.04–0.083	0.828–10.5	0.837–4.41	0.250–22.0	1.31–61.7	< 0.70–21.1	30–400	
	River water dissolved (ng/mL) HF	0.090–1.37	0.007–0.029	0.716–2.21	0.115–0.888	1.28–3.69	1.33–4.04	1.34–3.32	40–260	
	River water dissolved (ng/mL) LF	< 0.015–0.294	< 0.004–0.011	0.365–2.63	0.044–0.434	0.200–2.18	0.509–1.47	< 0.070–3.93	8–290	

[39], Ollivier et al. [70], and Trostle et al. [71], who demonstrated that variations in river discharge significantly influence the partitioning, mobilization, and transport of PTEs, with higher flows promoting their association with SPM. Median total and dissolved element concentrations are generally lower in the Koppány than in the Ledava catchment under both high- and low-flow conditions, except for dissolved As, P, and Cu, which are higher in the Koppány River. This is likely attributed to the carbonate-rich geology of the Koppány area, reflected in higher alkalinity (7.2 and 9.2 mmol/L under high- and low-flow conditions, respectively) compared to the Ledava catchment (1.9 and 3.1 mmol/L). Higher amounts of carbonate raise river water pH, giving the Koppány a median pH of 8.2 versus pH 7.4 in the Ledava watershed (Table S3). The higher pH and alkalinity promote formation of insoluble hydroxides and carbonates for Cd^{2+}, Pb^{2+}, Cr^{3+}, Ni^{2+}, and Zn^{2+}, and reduce solubility [72]. Consequently, their dissolved metal concentrations in the Koppány are lower than in the Ledava watershed. At neutral to slightly alkaline pH, dissolved As and P in river water primarily exist as negatively charged oxyanions AsO_4^{3-} and PO_4^{3-}, respectively. As pH rises, sedimentary Fe and Al oxides gradually lose their positive surface charge, reducing the adsorption of AsO_4^{3-} and PO_4^{3-} onto the surface of particulate matter [73]. This leads to higher solubility and mobility of As and P in the Koppány River compared to the Ledava River. Cu readily forms carbonate and organic (e.g., fulvate) complexes at neutral to alkaline pH, which increases its dissolved fraction and mobility in river water [2, 74]. Consequently, higher alkalinity and amount of carbonate in the Koppány River result in higher dissolved Cu concentrations than in the Ledava River.

According to the WFD [23, 25, 27] exceedances of EQS for dissolved PTEs were rare (Table S11). Ni and Pb slightly exceeded EQS limits of 4 and 1.2 ng/mL, respectively, in one Hungarian and one Slovenian sample. A markedly elevated dissolved Cu concentration (137 ng/mL) was observed in another Hungarian water sample, substantially exceeding the EQS level of 30 ng/mL. The same sample also exhibited a high total Cu concentration (393 ng/mL; Table S10) and was identified as an outlier. No other exceedances of dissolved PTEs concentrations were observed. Phosphorous, used as an indicator of ecological status, frequently exceeded WFD guideline values (< 100 ng/mL for good status), reflecting strong agricultural influence.

To evaluate the mobility of PTEs in environmental compartments, acetic acid–extractable concentrations (0.11 mol/L), expressed as the percentage of extractable PTEs relative to their total concentrations in soils and sediments, were determined. The results are presented in Table S12. Since there are no legally defined EQS for P

in soils and sediments, and because P is not considered a toxic element but rather an essential nutrient, its acetic acid–extractable concentrations were not determined. As evident from the data in Table S12, the very low mobility of Cr and Pb in soils and sediments (< 0.5% and < 2% of their total amounts, respectively), together with the relatively low mobility of Cu, As, and Ni (< 10%), suggests that river waters in the Koppány and Ledava catchments are not significantly contaminated with these elements. Although Cd and Zn show moderate mobility (up to 52% and 20% of their total amounts, respectively), their relatively low concentrations in soils and sediments in both catchments result in dissolved concentrations in river waters that remain well below EU WFD thresholds.

Literature data and data from this study, shown in Table 4, indicate that Pb, Cd, As, Cr, Ni, Cu, and Zn in soils from the Koppány and Ledava catchments are generally lower than those reported for the Sava River in industrially impacted areas [42, 67]. In sediments, concentrations of these elements are generally comparable to or lower than those reported for major European watersheds, including the Sava, Danube, and Western European rivers, as well as for sediments from the Danube Delta and other European rivers [2, 9, 11, 20, 31, 36, 42, 68]. Compared with other European regions, sediment concentrations are generally similar to or lower than those reported for rivers in Poland and the Evrotas River, with only minor element-specific deviations [12, 13, 69]. In SPM, concentrations of Pb, Cd, As, Cr, Ni, Cu, and Zn are generally comparable to or lower than those in the Sava, Danube, and Western European rivers [20, 42, 68]. Phosphorus contents in sediments and SPM are notably higher than those reported for agricultural catchments in Sweden, indicating elevated P levels relative to comparable rural European areas [5].

River water data further show that total concentrations of Pb, Cd, As, Cr, Ni, Cu, and Zn are generally higher than those reported for the Sava, Evrotas, and Lee rivers [2, 9, 31], while dissolved concentrations exhibit greater variability. Pb, Cd, Cu, and Zn are comparable to regional rivers, e.g., Zagyva and Koppány [61] but often exceed Sava and Evrotas River dissolved concentrations [2, 9], while remaining lower than those in the Danube River [20]. Arsenic concentrations fall within the range of major European rivers and are generally higher than in the Evrotas River, whereas dissolved concentrations of Cr and Ni are comparable to regional rivers but lower than those reported for the Danube River [2, 9, 20, 39].

The results of the present study indicate that the Koppány catchment exhibits slightly higher contamination with PTEs and P than the Ledava catchment in most soil, sediment, and SPM samples, as well as higher dissolved concentrations of As, P, and Cu in river water. Overall, comparison with previous studies suggests that the investigated Koppány and Ledava catchments exhibit low to moderate contamination levels with PTEs and P relative to major European rivers, with variations primarily reflecting differences in anthropogenic inputs and natural geochemical background.

Provenance signatures and major processes in the catchments

To determine the geochemical controls on element partitioning and distinguish between provenance signatures and transport processes, multidimensional scaling (MDS) analysis was performed. The first two dimensions explained 64.7% of the total variance (43.1% for MDS1 and 21.6% for MDS2), indicating that the main sources of geochemical variability in the dataset are captured within a two-dimensional ordination space (Fig. 3). Along MDS1, REEs (LREEs, MREEs, HREEs), Y, Ti, U, and Cd load on the negative side. These elements, typically found in heavy minerals and the aluminosilicate matrix, are largely immobile during weathering and transport and may therefore represent the conservative lithogenic fraction [42, 51]. Their negative loading is reflected in the tight clustering of soils at strongly negative MDS1 values, where Koppány soils form a particularly homogeneous group with the geochemically uniform composition of the loess-derived material [75, 76], while Ledava soils show greater dispersion, reflecting heterogeneous source lithologies [57]. In contrast, As, Ni, Mn, Cu, Zn, and Pb load positively. These elements are frequently associated with anthropogenic inputs and show preferential sorption to fine-grained phases such as clay minerals, Fe–Mn oxyhydroxides, and organic matter, resulting in their enrichment during transport in shallow suspended load [77, 78]. Koppány sediments are notably stretched along this axis in the soil-to-SPM direction, indicating possible compositional modification through increasing contributions from fine reactive phases during transport, whereas Ledava sediments and SPM occupy largely overlapping positions, suggesting similar composition. Along MDS2, Sr loads positively, reflecting its partitioning into carbonate minerals and the influence of carbonate-rich source material [76]. P also loads positively on this axis, likely recording a combination of diffuse agricultural inputs and potential geogenic mobilization from soluble carbonate bedrock, where phosphate commonly co-precipitates with calcite [6, 79]. Co, Cr, Fe, Ba, and V load negatively on MDS2, reflecting Fe-phyllosilicate-rich weathering products derived from the siliciclastic lithologies that dominate the Ledava catchment [80]. This clear separation between the two catchments along MDS2 persists across all

solid matrices (soils, sediments, and SPM), confirming that the carbonate versus siliciclastic lithological contrast is the primary provenance signal throughout the source-to-sink system. The siliciclastic nature of the Ledava catchment is further supported by its characteristically lower alkalinity compared to the carbonate-dominated Koppány catchment, as silicate weathering generates significantly less bicarbonate than carbonate dissolution (Table S3). However, several Koppány samples plot toward negative MDS2 values, close to Fe and Co, indicating occasional mobilization of Fe-phyllosilicate-bearing material that locally overprints the otherwise dominant carbonate geochemical signature of this catchment.

Distinguishing geogenic from anthropogenic inputs of PTEs

To distinguish between natural and anthropogenic sources of PTEs, EFs were calculated for all elements in sediments and SPM. The EF approach reduces grain-size effect, which is the major driver of element concentration variability in river samples, thereby improving discrimination between geogenic and anthropogenic contributions [42, 44]. The MLRR identified V, Fe, Mn, and Co as the most suitable normalizing elements for sediments (Table S13), while Mn, Fe, and V were optimal for SPM (Table S14). The predominance of these elements as normalizers reflects the role of Fe–Mn oxyhydroxide phases and clay minerals in governing the natural distribution of PTEs in these catchments [77, 78]. Applying the determined thresholds, Cd, Pb, and P were identified as elements with evidence of potential anthropogenic enrichment, while As, Cr, Cu, Ni, and Zn remained within the range of background geochemical variability in the majority of samples (Tables S15 and S16). Cd showed moderate enrichment, with EF values reaching 2.12 in SPM (TA-4-HF-AS) and slight enrichment (EF 1.66–1.87) in several other SPM samples. Pb was enriched in two SPM samples (TA-2-LF-GS, EF = 2.34; TK-3-LF-GS, EF = 1.63). The most systematic enrichment was observed for P, with EF values exceeding the threshold in multiple sediment samples along the Koppány River (IRSA: 2.57, KOBO: 2.17, KOFI: 2.26, KOGE: 1.98, KOKI: 2.17) and several SPM samples (TK-3-LF-GS: 2.18, TK-4-LF-GS: 1.83), likely reflecting diffuse agricultural inputs from phosphorus-based fertilizer applications and point-source wastewater discharges [6, 81]. Notably, Cd and P enrichment do not occur at the same locations, suggesting their sources are at least partially independent. A previous study by Jolankai et al. [81] identified Cd, together with Zn and Cu, as predominantly associated with urban runoff rather than agricultural sources. Comparison of the two sample matrices reveals

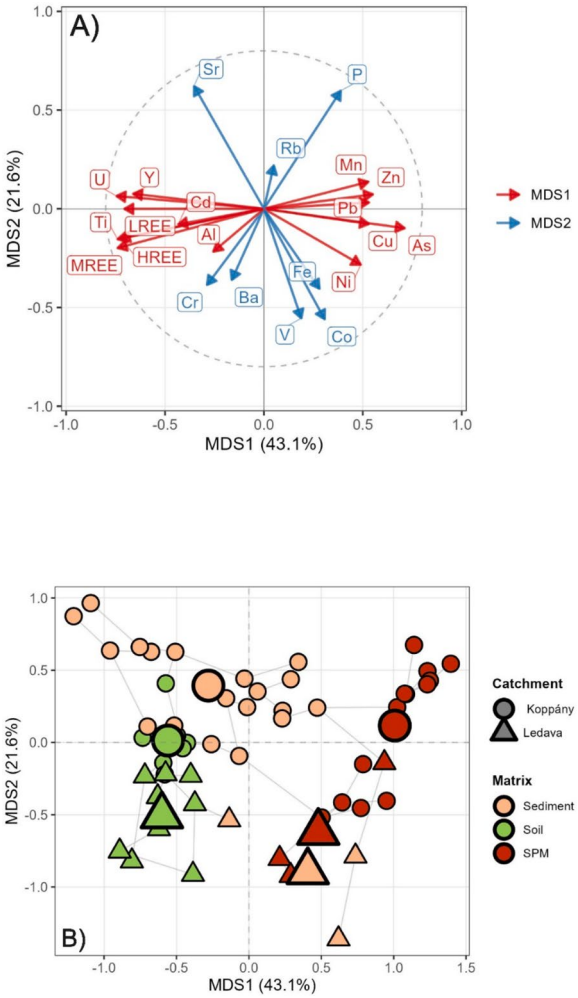


Fig. 3 Multidimensional scaling (MDS) ordination of clr-transformed geochemical data [62] from soil, sediment, and suspended particulate matter (SPM) samples. **A** Biplot showing the contribution of individual elements and element groups to the first two MDS dimensions. **B** Sample scores colored and shaped by catchment and sample matrix

differences in enrichment patterns between sediments and SPM. Cd and Pb show higher EF values in SPM than in sediment, due to their preferential adsorption by Mn and Al oxides and organic material [82]. In contrast, P enrichment is more pronounced in sediments. This may imply a geochemical tendency for P retention through sorption onto Fe-oxyhydroxides, co-precipitation with Ca, and subsequent accumulation in the sediment [6, 79]. In both matrices, the data indicate greater anthropogenic influence in the Koppány than in the Ledava catchment, with diffuse agricultural inputs, urban runoff, and point-source wastewater discharges representing the dominant pressures on the concentrations of PTEs.

Geochemistry of REE

The sum concentrations of REEs (ΣREEs) are broadly comparable across environmental matrices, with mean values in the Koppány catchment ranging from 160.7 mg/kg (144.4–182.2 mg/kg) in soils, 159.0 mg/kg (144.7–184.8 mg/kg) in river sediments, and 172.0 mg/kg (151.8–197.3 mg/kg) in SPM (Table 5).

This lack of significant enrichment from soils to SPM may reflect homogenization of the geochemical signal through sorting processes [78, 83], or the uniform distribution of REE-bearing mineral phases with similar concentrations across grain-size fractions. Such patterns are also common in river systems like the Danube, where sediment concentrations are influenced by a mixture of similar geological sources, leading to relatively stable REE profiles across different locations [84]. This contrasts with PTEs, which show enrichment from soil to SPM due to grain-size effects that concentrate these elements in finer fractions (Fig. 2). In Slovenia, an accumulation pattern is observed, with concentrations of ΣREEs ranging from 153.4 mg/kg (119.0–200.6 mg/kg) in soils, 214.1 mg/kg (177.6–233.6 mg/kg) in river sediments, and 180.6 mg/kg (144.6–199.9 mg/kg) in SPM. The maximum value for the Ledava River exceeds the maximum of 170 mg/kg reported by Dragun et al. [85] in the nearby Croatian section of the Mura River and is comparable to the findings of Lučić et al. [47] in the Sava River, where a maximum of 197 mg/kg was observed in the sediments. This may result from preferential REE accumulation in the settled mineral phases [77]. Across all compartments and both countries, LREEs consistently dominated (mean value of 147 mg/kg) the REEs budget, followed by MREEs (mean value of 18.9 mg/kg) and HREEs (mean value of 6.3 mg/kg).

Geochemical controls on REE associations

Examining the relationships between REEs and other elements provided insight into the dominant mineral phases controlling REE associations across both catchments. Across all matrices, REEs showed statistically significant correlations with Fe, Co, and V ($r > 0.53$; $p < 0.05$), while additional associations with Mn, Al, and Ti were observed in certain matrices (Tables S17 and S18). This pattern reflects the adsorption capacity of Fe–Mn oxyhydroxides and clay minerals such as illite, chlorite, and smectite for REEs due to their negative surface charges and large specific surface area [86], with MREEs and HREEs showing preferential adsorption onto clay minerals driven by increasing surface complexation constants with atomic number [87]. In the Koppány catchment, these associations strengthen progressively toward the sediment and SPM, where Ti, Al, Fe and particularly Co and V exhibited constant correlations with REEs ($r = 0.55–0.75$, $p < 0.05$, reflecting the sorting and enrichment of fine-grained reactive mineral phases in the finer fraction of fluvial material. Notably, in SPM of Koppány, all REE groups show negative correlations with P ($r = -0.60$ to -0.70; $p < 0.05$ and Mn ($r = -0.60$ to -0.80; $p < 0.05$, contrasting with positive association between Mn and REEs in soils. The negative correlation between REEs and Mn in SPM likely reflects partial dissolution of Mn-oxyhydroxide phases under reducing conditions within the sampler during sample collection [78], while the negative REE-P association may reflect dilution of the lithogenic REE signal by P-bearing carbonate phases, which is in align with the well-documented tendency of phosphorus to co-precipitate with calcite in carbonate-dominated systems [6, 79]. Additionally, MREE in SPM shows a negative correlation with Sr ($r = -0.66$, $p < 0.05$, suggesting dilution of the MREE signal by carbonate-associated Sr-bearing phases. In the Ledava catchment, the stable correlation between Co and REEs across all matrices ($r = 0.85–0.93$; $p < 0.05$ suggests their co-release from primary minerals during weathering in the headwaters [88].

REE fractionation patterns and anomalies

Average REE abundance patterns in soil, sediment, and SPM, normalized to EUS, are shown in Fig. 4.

The graphs display a consistent "hump-shaped" MREE enrichment, reflecting the combined influence of Fe–Mn oxyhydroxide and phosphate phases (e.g., apatite) that preferentially concentrate MREEs [49, 86]. While this shape is shared, the catchments differ in variability. In the Koppány, soils, sediments, and SPM produce nearly superimposed curves, indicating that provenance, transport, and sorting do not transform the REE signal. This geochemical stability matches the soils in the Koppány catchment, which mainly developed on loess and reworked sedimentary material [76]. These materials have undergone many cycles of weathering, erosion, and redeposition. Over time, sorting processes average out the original differences in REE patterns from different rock types, resulting in a very similar REE distribution regardless of the starting rock material [75]. In contrast, in the Ledava catchment, the patterns of soil, sediment, and SPM are more distinct, with soils showing LREE depletion and a positive Eu anomaly, while sediments plot substantially higher across all REEs. This differentiation likely reflects the geologically heterogeneous terrain, but also the hydrodynamic sorting, which preferentially concentrates REE-rich heavy minerals in the coarse-dominated Ledava sediment fraction given the very low fine fraction content of deposited sediments (0.5–9.1% less than 63 µm,Table S2, driving elevated total REE concentrations in sediments relative to both soils and SPM.

Table 5 Mean REE concentrations (in mg/kg), fractionation ratios, and anomalies in the investigated samples. Fractionation indices and REE anomalies were normalized to European Shale (EUS; [64]) values

	Koppány (HU)			Ledava (SI)		
	Soil	Sediment	SPM	Soil	Sediment	SPM
Y	19.3	19.7	23.4	18.2	26.0	21.0
La	34.6	32.3	34.8	27.5	43.1	37.0
Ce	70.9	65.5	71.6	57.0	88.8	75.2
Pr	8.21	7.88	8.20	6.91	10.2	7.37
Nd	30.5	29.9	31.4	35.9	40.3	33.1
Sm	6.08	5.85	6.30	6.26	7.95	6.35
Eu	1.21	1.25	1.39	1.18	1.74	1.52
Gd	5.59	5.45	5.99	6.06	7.37	6.32
Tb	0.78	0.78	0.85	0.96	1.03	0.96
Dy	4.26	4.11	4.79	5.30	5.68	5.17
Ho	0.81	0.81	0.91	0.77	1.11	1.01
Er	2.29	2.31	2.64	2.23	3.07	3.03
Tm	0.33	0.32	0.34	0.32	0.43	0.47
Yb	2.14	2.07	2.38	2.75	2.77	2.72
Lu	0.32	0.32	0.33	0.31	0.43	0.44
ΣREE	168.0	159.0	172.0	153.4	214.0	180.6
LREE	144.2	135.7	146.1	127.2	182.4	152.6
MREE	17.9	17.4	19.3	19.8	23.8	20.3
HREE	5.89	5.83	6.59	6.38	7.81	7.67
LREE/HREE*	0.94	0.90	0.87	0.83	0.89	0.72
MREE/MREE*	0.82	0.80	0.88	0.90	1.08	0.93
Ce/Ce*	1.03	1.01	1.04	1.01	1.03	1.10
Eu/Eu*	0.96	1.02	1.04	0.88	1.05	1.11
Gd/Gd*	1.06	1.05	1.07	1.02	1.07	1.06

The analysis of REE anomalies provides further insights into provenance and weathering intensity across the two catchments. In all samples, Ce/Ce* ranges from 0.99 to 1.18, Eu/Eu* from 0.84 to 1.15, and Gd/Gd* from 0.97 to 1.18, with the greatest variability in Eu/Eu* reflecting differences among soils, sediment, SPM, and catchments (Table 5). Along the Ledava River, the positive correlation between Sr and Eu/Eu* ($r = 0.90$; $p < 0.05$) suggests that plagioclase abundance in the parent lithology primarily controls the Eu signature (Table S18). The Eu anomaly in bulk soils (Eu/Eu* = 0.84–0.92 in Ledava) most likely reflects inheritance from the source rock rather than pedogenic modification [52]. The loss of correlation between Sr and Eu/Eu* in the Ledava sediment and SPM dataset likely reflects the combined influence of lithological heterogeneity and sorting, as hydrodynamic sorting preferentially retains plagioclase in coarser settled fractions, while finer suspended fractions become increasingly dominated by clay minerals and Fe-oxyhydroxides with contrasting Eu signature. Furthermore, soils show associations of Mn and V with Gd/Gd*, consistent with Fe–Mn oxyhydroxide adsorption of MREEs [52]. In the loess-derived soils of the Koppány catchment, K shows a positive correlation with the Eu anomaly ($r = 0.72$, $p < 0.05$, identifying K-feldspar as a probable detrital Eu carrier. This signal is partially preserved in river sediments ($r = 0.67$; $p < 0.05$, indicating that K-feldspar remains an active REE host in the settled fraction, which does not differ from source soil samples. However, this correlation disappears in SPM. This may imply the preferential concentration of K-bearing clay minerals and micas over K-feldspar in the suspended load, which effectively decouples the K signal from the Eu anomaly originally hosted in the soil and sediment fractions.

These findings indicate that REE fractionation in the Ledava catchment is primarily controlled by mineralogical inheritance from siliciclastic bedrock sources in the soils, while in the fluvial material, REE distribution becomes increasingly governed by hydrodynamic sorting that selectively concentrates REE-rich heavy minerals and secondary mineral phases during the transport. In the Koppány catchment, the geochemically stable and identical REE patterns across all compartments reflect the uniform composition of the multi-recycled loess-dominated

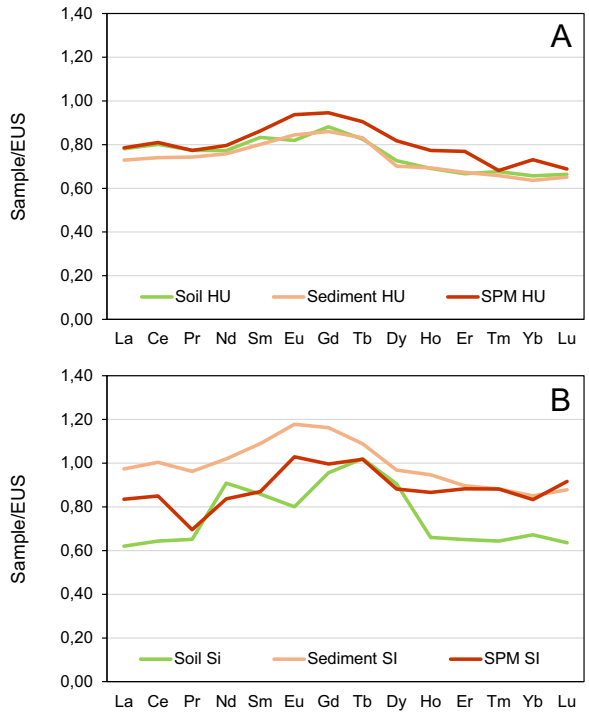


Fig. 4 Average EUS-normalized REE patterns of different sample types from **A** the Koppány and **B** the Ledava River catchments

source material, within which transport and sorting negligibly transform the inherited REE signal [75, 83].

Conclusions

The spatial distribution of selected PTEs, P, and REEs investigated in the Koppány (Hungary) and Ledava (Slovenia) river catchments showed that the concentrations of PTEs in soils, sediments, and SPM were generally slightly higher in the Koppány catchment than in the Ledava catchment. Hydrological conditions strongly controlled element partitioning in both river systems. PTEs were mobilized from soils through erosion, accumulate in bottom sediments, and were subsequently remobilized as SPM during high-flow events, resulting in elevated total concentrations in river water. Under low-flow conditions, PTEs and P exist predominantly in dissolved forms, whereas during high-flow events their dissolved concentrations decreased substantially due to preferential association with particulate matter. Both total and dissolved concentrations of these elements were generally lower in the Koppány river, likely due to the higher water alkalinity and pH, which promotes the formation of insoluble hydroxides and carbonates of Cd^{2+}, Pb^{2+}, Cr^{3+}, Ni^{2+}, and Zn^{2+}, thereby reducing their solubility. In contrast, under higher alkaline conditions, As and P, which exist as oxyanions of AsO_4^{3-} and PO_4^{3-}, are more mobile in the Koppány catchment. Moreover, Cu, which readily forms soluble complexes with carbonates is also more soluble in the Koppány River. Although some soil, sediment, and SPM samples contained elevated total concentrations of As, Cr, and Ni that exceeded EQS and quality target values due to lithological controls, their mobile fractions remained low (< 10%). As a result, dissolved concentrations in river water remained below EU WFD threshold levels, indicating low risk to water quality. Both rivers exhibit low to moderate pollution levels comparable to European agricultural catchments without major industrial or mining influences.

Cd, Pb, and P were identified as the main elements with anthropogenic signatures. P enrichment was attributed to diffuse agricultural inputs and wastewater discharges in the Koppány catchment, while the urban runoff is suggested as the probable source of Cd. This study shows that the total and dissolved concentration measurements under varying flow conditions provide essential data for implementing and validating pathway-oriented emission models in water quality management.

The integrated multielement approach combining EF analysis, multivariate ordination, and REE fingerprinting, offers a framework for resolving both natural and anthropogenic controls on element cycling in geochemically complex fluvial systems and may be applicable to similar agricultural-urban river systems. It also provides a reproducible template for source discrimination in environments where lithological heterogeneity, hydrodynamic sorting, and diffuse anthropogenic inputs occur simultaneously.

Supplementary Information

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Supplementary Material 1

Author contributions

R.M.Š.: Conceptualisation, Methodology, Supervision, Project administration, Funding acquisition, Investigation, Data curation, Validation, Visualisation, Writing – Original Draft, Writing – Review and Editing; J.Š.: Investigation, Methodology, Data curation, Validation, Visualisation, Writing – Review and Editing; K.K.: Formal analysis, Data curation; Writing – Review and Editing; M.Š.: Formal analysis, Data curation; Writing – Review and Editing; M.L.: Methodology, Supervision, Data curation, Investigation, Validation, Visualisation, Writing – Original Draft, Writing – Review and Editing; Z.J.: Investigation, Writing – Review and Editing; M.K.K.: Investigation, Writing – Review and Editing; A.C.: Conceptualisation, Methodology, Supervision, Project administration, Funding acquisition, Investigation, Writing – Review and Editing.

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Data availability
Data will be made available upon request to the corresponding authors.

Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Competing interests
The authors declare no competing interests.

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