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Suspended Sediment Metal and Metalloid Composition in the Danube River Basin, Croatia

Dijana Oskoruš *, Sanja Kapelj, Saša Zavrtnik and Karlo Leskovar

Faculty of Geotechnical Engineering, University of Zagreb, 42000 Varaždin, Croatia
* Correspondence: dijana.oskorus@gfv.unizg.hr; Tel.: +385-99-211-6649

Abstract: The Water Framework Directive (WFD) 2000/60/EC established a framework for community action in the field of water policy. This Directive requires the monitoring of surface watercourses' quality, which is undoubtedly influenced by the sediment composition. Their function can serve the living and transport purposes of numerous microorganisms and algae, but sediment may be a medium for transmitting dangerous toxic substances that are harmful to all living organisms in the environment as well. Many substances (including chemical substances, metals, and nutrients) can accumulate in sediment over time and be released in water or contaminate aquatic species, thus potentially negatively affecting the ecological or chemical status. Furthermore, flood events as well as human interventions can remobilise deposited sediment and thus result in the downstream and cross-border transport of sediment-associated contamination. The purpose of this investigation was to calculate the daily values of chemical elements in the transmission of suspended sediment and its accumulation in the suspended matter collected at some hydrological stations in the Danube River Basin during high flow events. The joint vision for the "Mura-Drava-Danube" area is to use the Transboundary Biosphere Reserve (TBR) concept to maintain a living river ecosystem for biodiversity and ecosystem services and to promote nature-friendly economic development for the local communities of this rural region. Therefore, this region requires a permanent sediment quality monitoring program.

Keywords: environmental quality standards; suspended sediment; metal composition; contamination; pollution source; monitoring program

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1. Introduction

Together with the Water Framework Directive (WFD, 2008/105/EC) [1], the Environmental Quality Standards Directive (EQS, 2000/60/EC) [2] defines the good chemical status to be achieved by all EU Member States and gives the legal basis for monitoring the priority substances in sediment and biota. Good chemical status is defined in compliance with all the quality standards established for chemical substances in the European context. The Directive also provides a mechanism for renewing these standards and establishing new ones through a prioritisation mechanism for hazardous chemicals. This will ensure at least a minimum chemical quality everywhere in the Union, particularly in relation to very toxic substances [2].

The Guidance Document No: 25 for guidance on chemical monitoring of sediment and biota, EU 2010, gives a joint implementation strategy for the WFD [2]. This document addresses different requirements for compliance checking and temporal trend monitoring for biota and sediment considering the requirements of the EQS Directive. The recommendations in the guidance consider current scientific knowledge and should allow the harmonised implementation of sediment and biota monitoring across Europe. For most of the substances on the list of priority substances included in the Directive, the establishment of Environmental Quality Standards (EQS) at the community level has been limited to concentrations in the water column.

The recommendations address surveillance and operational and investigative monitoring and should be applied to the current list of 33 priority substances and 8 certain other pollutants included in the Directive as well as to specific river basin pollutants which tend to accumulate in sediment or biota. Based on the rule of thumb mentioned, a distinction has been made between monitoring substances:

Preferred (P)—monitoring is preferred in this matrix.

Optional (O)—monitoring can be performed in this matrix and other compartments/matrices; the choice will also be made based on the degree of contamination of a particular matrix.

Not recommended (N)—monitoring in this matrix is not recommended unless there is evidence of the possibility of accumulation of the compound in this matrix.

In some cases, sediment and biota are preferred matrices, and the choice should be made based on local contamination and the EQS derived. However, these criteria are not mandatory, and Member States can choose the appropriate matrix based on their knowledge, provided they keep in mind the indications of Directive 2008/105/EC. Chemicals used for the chemical status assessment were grouped for the WFD into four groups (heavy metals, pesticides, industrial pollutants, and other pollutants) by the Commission. Lists of the chemicals within the different pollutant groups are given in Table 1 [2].

Table 1. Grouping of chemicals into pollutant groups.

1. Heavy Metals	2. Pesticides	3. Industrial Pollutants	4. Other Pollutants
1.1 Cadmium	2.1 Alachlor	3.1 Anthracene	4.1 Aldrin
1.2 Lead	2.2 Atrazine	3.2 Benzene	4.2 Endrin
1.3 Mercury	2.3 Chlorpyriphos	3.3 Brominated diph. ether	4.3 Isodrin
1.4. Nickel	2.4 Chlorvefinphos	3.4 Carbontetrachloride	4.4 DDT Total
	2.5 Diuron	3.5 C10-13 Chloroalkanes	4.5 para-para-DDT
	2.6 Endosulfan	3.6 1,2-Dichloroethane	4.6 Fluoranthene
	2.7 Isoproturon	3.7 Dichloromethane	4.7 Hexachlorobenzene
	2.8 Hexachlorocyclphexane	3.8 Di (2-ethylexyl) phthalate (DEHP)	4.8 Hexachlorobutadiene
	2.9 Pentachlorobenzene	3.9 Naphthalene	4.9 Pentachlorophenol
		3.10 Nonylphenol	4.10 Polyaromatic hydrocarbons
	2.10 Simazine	3.11 Octylphenol	4.11 Indeno(1,2,3-cd)pyrene
	2.11 Trifluralin	3.12 Trichloroethylene	4.12 Tributyltin compounds
		3.13 Trichloromethane	4.13 Trichlorobenzenes (all isomers)

With the present study, the goals are as follows:

1. Provide the state of sediment contamination in four major rivers in Croatian heartlands.
2. Compare the concentrations and correlation of major contaminants in the sediment.
3. Discuss possible sources of the discovered contamination of the riverbed sediments.
4. Emphasise the importance of regular sediment monitoring and management in rivers.

2. Materials and Methods

2.1. Background

The main aim of the WFD is the achievement of good chemical status for all water bodies, but the Member States can decide on the matrix substances. For instance, sediment is a recommended matrix for assessing the chemical status of some metals and hydrophobic compounds in marine and lentic water bodies. In dynamic lotic water bodies, however, sediments do not often provide an appropriate matrix for compliance checking because of their high variability. Furthermore, in such water bodies, sediments can be either too perturbed to be representative or, in some cases, absent. In these cases, this assessment could be made by measuring suspended particulate matter (SPM) concentrations. In large lowland rivers, freshly deposited sediment collected by sedimentation traps can be used instead of SPM. However, the equivalence between SPM and freshly deposited sediment must be verified in the latter case. Horowitz (1991) suggested that suspended sediments are more physically and chemically variable compared to bottom sediment, and the quantity of the suspended sediment collected is not always sufficient for the

required analysis; consequently, bottom sediments are more suitable for monitoring. Bottom sediment characterises what is entering a water body from upstream, and suspended sediment indicates the transport of contaminants downstream to the next water body. In summary, both sediment types meet the monitoring requirements of the WFD for determining sediment quality [2].

Suspended sediment is essential in transporting natural and anthropogenic substances due to its large reactive surfaces for physical, chemical, and biogeochemical interactions. In addition, the fine clay fraction of suspended sediment has a solid ability to scavenge trace elements, which is attributed to its extensive absorption capabilities. Such fine particles are usually composed of clay minerals, organic matter, Fe/Mn oxyhydroxides, etc. The coarser part of sediment, silt, is mainly composed of resistant minerals (quartz, rutile, zircon, some feldspars, plagioclase, etc.) and tiny rock fragments or grains. Quantitative objectives for a selected primary purpose should, therefore, also be established for exploratory studies. Deposition areas with soft sediment characterised by a relatively high amount of fine fraction (fraction <0.063 mm, consisting of silt and clay) are preferred as sampling sites, whereas sampling of areas where the sediment contains peat, gravels or rock fragments, compacted sediments, or coarse sand should be discouraged [2].

The EU Member States shall determine the frequency of sediment or biota monitoring to provide sufficient data for reliable long-term trend analysis. As a rule of thumb, sediments should contain at least 5% fine fraction (<0.063 mm), information which may have to be obtained from preliminary trial surveys. Alternatively, especially in the cases of rivers without sediments or with perturbed sediments, SPM and freshly deposited sediment can be used to collect the desired fine fraction. Knowing that deposition of suspended particles from the water column is favoured in areas with relatively low energy in the water (waves and currents), the following general criteria can be provided for the selection of the sampling sites [2]:

- Temporal monitoring studies aim to detect temporal trends in the investigated matrix. Since sediment and biota are generally buffered in their reaction time to chemical stress (if compared to the water column), more extended time series covering several years are needed to detect significant changes.
- Spatial monitoring studies aim to identify spatial distribution patterns and anomalies. Normal distribution may be assumed, with sediment and biota monitoring being less subject to short-term variability.

Many scientists worldwide in recent decades have found suspended matter to be a transport mode for many toxic substances, including heavy metals, throughout rivers and other water environments. Their efforts were associated with studies of the sources of toxic elements and behaviour within and between all parts of the aquatic environment, water, biota, and sediment [3–7]. Toxic elements are a severe threat not only to human health but also to the whole ecossystem. That is why in recent years, more and more attention has been paid to the risk assessment of heavy metals and other toxic substances in sediment [3,8]. During the last decade, there have been several published papers with results about the suspended matter (SM) or suspended particulate matter (SPM) of the rivers of the Croatian part of the Pannonian Basin—the Sava and Danube Rivers [9–13]. Unfortunately, the Drava, Bednja, and Mura Rivers' suspended sediments and their capabilities for transporting heavy metals and metalloids have not been studied until today.

2.2. Methodology

Suspended sediment concentrations (SSCs) in open watercourses in the Republic of Croatia are monitored by the Croatian Meteorological and Hydrological Service at 22 locations, so-called hydrological stations included in the hydrological monitoring program [14]. Water samples are taken manually from the surface of the watercourse once a day and analysed in a lab using the traditional filter method (ISO 4365:2005; ISO 13317-4:2014). In addition, to determine the daily concentrations of the suspended sediment, the sample is poured over filter paper with a density of 0.045 mm. To filter samples, "Munktell" filter

paper 100/N, with a diameter of 320 mm and an area density of 85 g/m^2, is used. Based on the daily SSC (g/m^3), the daily, monthly, and annual amounts of suspended sediment load transport SSLT (t) in rivers are calculated [15].

$$\text{SSLT } (t/\text{day}) = \text{SSC } \left(g/m^3\right) \cdot Q \left(m^3/s\right) \cdot 0,0864 \quad (1)$$

where 1 t (ton) equals 1000 kg (kilograms), hence the 0.0864 conversion factor, and Q is the mean daily flow rate.

This traditional calculation method is imprecise and does not give a realistic value of the temporal and spatial concentration distribution, especially in the case of high turbidity during peak flow, because it is based on one discrete sample per day. Therefore, recent work has improved monitoring by introducing continuous turbidity measurements through optical turbidity sensors.

In addition to monitoring from one point, profile measurements of the suspended sediment (g/m^3) and current SSLT (kg/m/s) are carried out occasionally on the Danube River and its largest tributaries: the Sava River, Mura River, and Drava River. These measurements are used to define the regression between the mean profile value of the SSC and the concentration from one point to obtain the correction coefficient of daily discrete point values [15].

$$\text{SSCprof} = k \cdot \text{SSCpoint} \quad (2)$$

where SSCprof is the mean profile suspended sediment concentration SSC (g/m^3), SSCpoint is the suspended sediment concentration of a water sample from one point (g/m^3), and K is the regression coefficient.

Monitoring of water and sediment quality in Croatia is regulated by the Water Quality Standard F [16]. For priority substances that tend to accumulate in sediments and/or biota, only long-term trends are analysed, as class boundaries have not yet been established. The frequency of monitoring is set to provide sufficient data for reliable analysis of trends, and it is carried out once every three years. At the approximately forty sampling points used for monitoring sediments in rivers and lakes, nutrients, TOC, and priority substances are analysed once a year [17].

The Joint Danube Surveys characterised the sediment quality in the Danube several years ago and concluded that contaminated sediment was an existing problem in the Danube River Basin (DRB). However, the DTP countries did not have enough institutional capacity (information, guidelines, and methods) to build a transnational sediment monitoring network for HS trend assessment. Therefore, a significant contribution to the Sediment Quality Evaluation methods under the Water Framework Directive (WFD) was made by the project SIMONA [18]—Sediment-quality Information, Monitoring and Assessment System—to support transnational cooperation for joint Danube Basin water management (Interreg Transnational Program (start 1 January 2018, end 30 November 2021)). As part of the project, two protocols were issued which will contribute significantly to better compliant monitoring on cross-border basins:

1. A sediment quality sampling protocol for hazardous substances (HSs) [18].
2. A sediment quality laboratory protocol for hazardous substances (HSs) [19].

The purpose of SIMONA [18,19] protocols is to give practical guidance for sediment quality monitoring data evaluation in compliance with the EU Water Framework Directive (WFD, EC 2000 [1]), focusing on the use for the Danube Basin countries. After testing the protocols and the results from laboratory analyses, further comments regarding the need for monitoring suspended sediments have been given.

2.3. Study Area

The Danube River is the second largest river in Europe. It constitutes the most important freshwater resource of the largest lowland basin of Central Europe, the Carpathian Basin. One of the most important tributaries of the Danube is the Drava River. The most

significant tributary of the Drava is the Mura River. UNESCO designated the Mura-Drava-Danube Transboundary Biosphere Reserve in 2021 along these three rivers, extending 631,460.71 ha (395,860.71 ha in Croatia and 235,600 ha in Hungary). The water regime of the rivers determines biodiversity and human uses as well [20].

Bearing in mind that the regular SS monitoring program in Croatia consists mostly of quantitative analysis but not chemical analysis, this paper presents an SS analysis to obtain the chemical composition of suspended sediment. The samples used for this research were taken for daily SSC analysis at hydrological stations on different Danube River Basin (DRB) rivers, as shown in Figure 1.

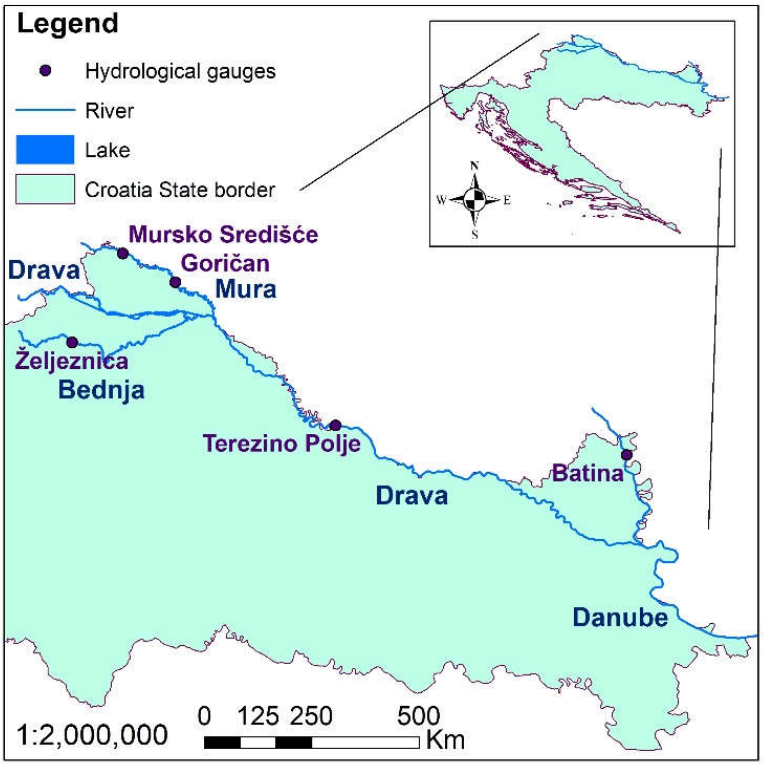


Figure 1. Cartographic presentation of the observed hydrological stations and corresponding rivers.

The Mura River originates in the Hohe Tauren National Park, Austria, and flows through Slovenia and northern Croatia before mounding in the Drava River near Legrad. It flows mostly through rural and forested areas—in the upper stream through hilly regions, while in the lower course through lowlands. The Bednja River originates in northwestern Croatia, flowing through mostly rural agricultural, overly lowland areas, and is also a tributary of the larger Drava River. The Drava River originates in the Italian Alps, near Dobbiaco; flows through Austria, Slovenia, and Croatia; and mounds to the Danube River near Aljmaš. The Mura and Drava Rivers are both employed for hydropower production with multiple power plants and dams. Of the mentioned rivers, in Croatia, only on the Drava River can three hydroelectric reservoirs (dams) and hydropower plants be found, all upstream of the confluence with the Bednja and Mura Rivers. The Danube is the second longest river in Europe and originates in the Schwartzwald region in Germany; in Croatia, it presents a natural border with Serbia on the east. All the rivers pass multiple major or minor towns and cities on their course.

3. Results

Samples with the highest SSCs collected during peak flow events were chosen. Eighteen samples were included in the analysis to obtain their chemical composition, as shown in Table 2.

Table 2. List of locations with main hydrological characteristics.

No.	Sample	Date	Hydro Station	H (cm)	Q (m^3/s)	SSC (g/m^3)	SSLT (t/day)
1	M 321-9	17 November 2019	Mura River Mursko Središće	196	324	182	5095
2	M 322-9	18 November 2019		182	350	237	7167
3	M 323-9	19 November 2019		172	550	257	12,213
4	L 150-9	30 May 2019	Mura River Goričan	288	423	344	12,572
5	L 175-9	24 June 2019		240	328	556	15,757
6	L 323-9	19 November 2019		294	435	535	20,107
7	L 324-9	20 November 2019		324	498	517	22,245
8	P 130-9	2 June 2019	Drava River Terezino polje	55	1306	107	12,074
9	P 131-9	3 June 2019		0	1117	64	6177
10	P 133-9	5 June 2019		−65	910	181	14,231
11	Ma 148-9	28 May 2019	Bednja River Željeznica	33	2.66	477	110
12	Ma 169-9	18 June 2019		46	4.68	247	100
13	Ma 174-9	23 June 2019		66	8.94	198	153
14	Ma 313-9	9 November 2019		117	22.5	494	960
15	Ma 320-9	16 November 2019		161	36.6	285	901
16	B 133-9	24 June 2019	Dunav River Batina	353	3399	270	79,292
17	B 254-9	18 September 2019		81	1709	245	36,176
18	B 262-9	26 September 2019		−24	1132	357	34,916

H (cm) is the mean daily water level; Q (m^3/s) is the mean daily flow; SSC (g/m^3) is the suspended sediment concentration in the water; SSLT (t/day) is the suspended sediment load transport.

The original intention of this research was to analyse SS samples during the same events; however, given the nature of individual watercourses and the hydrological conditions on the basins, this was not possible because the maximum concentrations of the SS in the water did not always coincide with the same event (Figure 2). As shown in Table 2, in the case of the Mura River, samples affected during the same hydrological event were analysed, where the most significant transmission of SS was in the period of 17–20 November, as shown in Figure 2a,b. Although this water wave with the highest annual flow was also recorded on the Drava, the concentrations of the SS were more elevated in June, according to Figure 2c. Therefore, samples of suspended sediment during the water wave on the Drava River in June were selected for analysis. In the case of the Danube, the samples with the highest concentrations of SS appeared in June and September 2019, as shown in Figure 2e. Samples from the small tributary Bednja River were taken in May, June, and September 2019, represented in Figure 2d.

3.1. Sample Analysis

The Laboratory for Environmental Geochemistry at the Faculty of Geotechnical Engineering, University of Zagreb, analysed adequate samples with suspended matter. Filters with satisfactory suspended matter (SM) were acquired from the Croatian Hydrological and Meteorological Service and were selected for further handling. Then, aqua regia, a mixture of hydrochloric and nitric acids in a ratio of 3:1, 20 mL each, was added to an individual sample. The samples in the glasses were sealed with parafilm, placed in a Grant JB Academy JBA5 water bath, put in a fume cupboard, and heated at 50 °C for 6 h with occasional stirring. A reagent blank was prepared in the same way. The samples decomposed in this way were filtered through a Munktell blue ribbon filter of 90 mm and funnels for rapid filtration into labelled volumetric flasks of 100 mL. The remaining sediment in the glasses and on the filter paper was washed with ultrapure water (type 1), with which the volumetric flasks with the filtrate were filled up to the mark after the end of the filtration. Ultrapure or deionised water was obtained by a Millipore Direct-Q 3 UV system and had a conductivity of 0.05 µS/cm. Thus, disintegrated and prepared samples were analysed on a PerkinElmer Atomic Absorption Spectrometer Analyst 800. The elements analysed were Cu, Au, Zn, Cr, Mn, Fe, K, Na, Mg, Ca, Pb, Cd, Ni, As, Co, Se, Al, and Hg. Three techniques were used for the analysis: the elements Cu, Au, Zn, Cr, Mn, Fe, K, Na, Mg, and Ca were analysed by the flame technique (FAAS); the elements Pb, Cd, Ni, As, Co, Se, and Al were analysed by the graphite furnace technique (GFAAS); and Hg was analysed by the

hydride technique (FIAS). Compressed air was used as the oxidant and acetylene 2.6 as the carrier gas for the flame technique. In the graphite furnace technique, argon 5.0 gas was used, which was also used for the hydride technique. Appropriate HCL or EDL lamps were used as radiation sources of a known wavelength for individual elements.

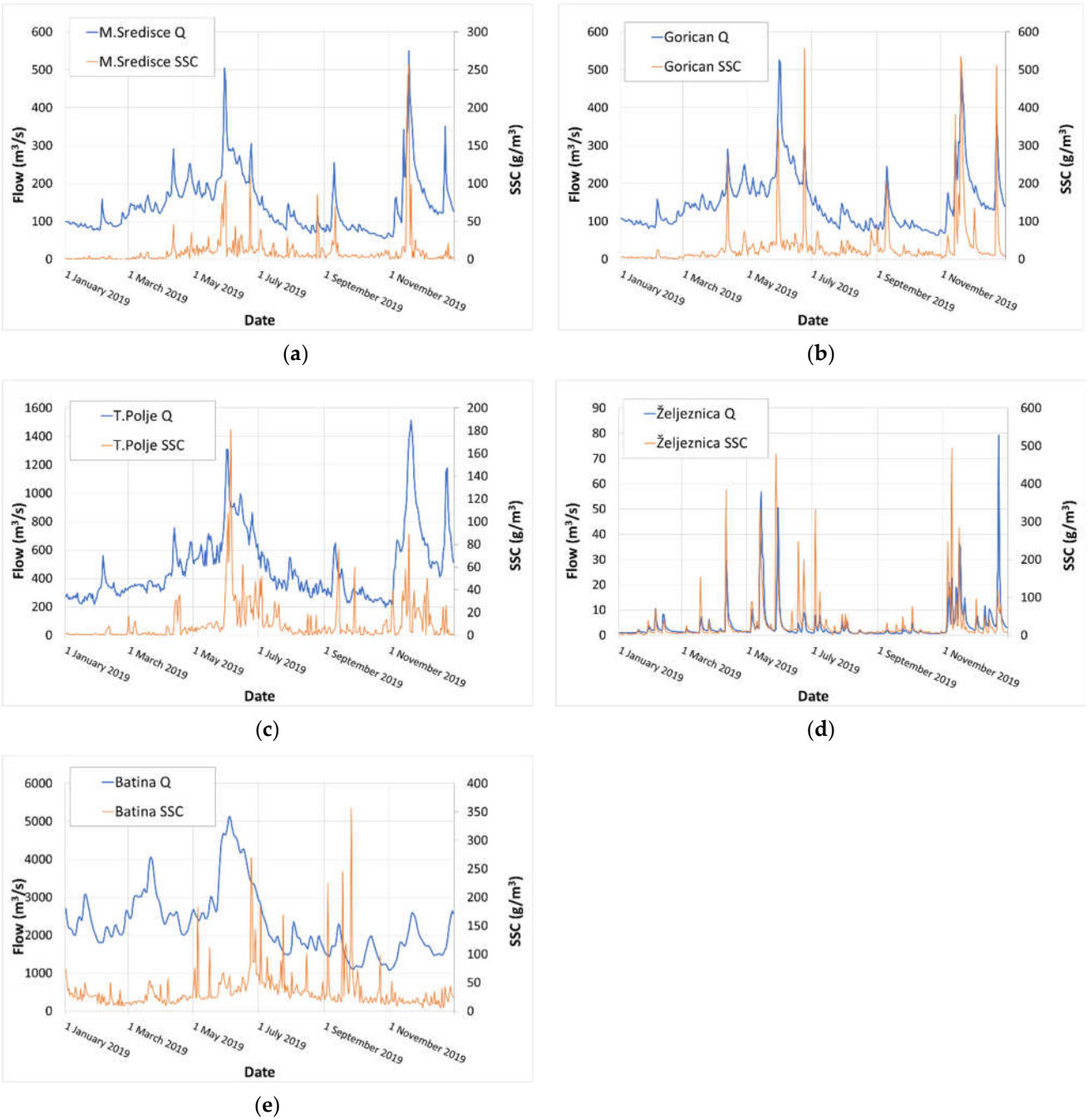


Figure 2. Daily flow and SSC distribution in 2019: (**a**) HS Mura-Mursko Sredisce; (**b**) HS Mura-Goričan; (**c**) HS Drava-Terezino Polje; (**d**) HS Bednja-Željeznica; (**e**) HS Dunav-Batina.

Standard solutions of known concentrations required for calibration were made from certified reference standard Inorganic Ventures or PerkinElmer Pure reagent solutions with a concentration of 1000 µg/mL, diluted to the required concentration with ultrapure water. These standard solutions were used to create calibration curves for which unknown sample concentrations were determined. During the calibration, the value of the reagent blank was also considered. PerkinElmer Pure matrix modifier solutions of 10,000 mg/L Pd (Pd $(NO_3)_2$

in 15% HNO_3), 10% NH4H2PO4, and 10,000 mg/L Mg (Mg $(NO_3)_2$) were used for graphite furnace analyses. A nitric acid solution of 0.2% obtained from Merck ultrapure nitric acid 60% was also used for washing the autosampler. In the hydride technique analysis, a 0.2% $NaBH_4$ solution obtained from Merck sodium borohydride p.a. was used as well as a 3% HCl solution obtained from Merck ultrapure hydrochloric acid 60%. Values derived by an atomic absorption spectrometer expressed in mg/L regarding the weight of an individual sample were converted into mg/kg of dry matter.

3.2. Results

Eighteen SM samples from different locations were obtained using an atomic absorption spectrometer, and eighteen values of elements expressed in mg/L with respect to the weight of each sample were converted to mg/kg. The analysed metals were Cu, Au, Zn, Cr, Mg, Fe, K, Na, Mn, Ca, Pb, Cd, Ni, Co, Al, and Hg, and the metalloids were As and Se.

The graphical presentation in Figure 3 shows the concentration values in the analysed suspended dry matter. As shown on the map (Figure 1) and the list of locations (Table 2), the first seven values belong to the Mura River (three from cross-border HS Mursko Sredisce and four from cross-border HS Goričan). The next three are from the Drava River, cross-border HS Terezino Polje, and five samples are from the small Drava tributary, the Bednja River. Finally, at least three samples are from the Danube River, at HS Batina, close to the Republic of Croatia (HR) and the Republic of Hungary (HU) state border. The average concentrations of the elements are shown in Figure 3.

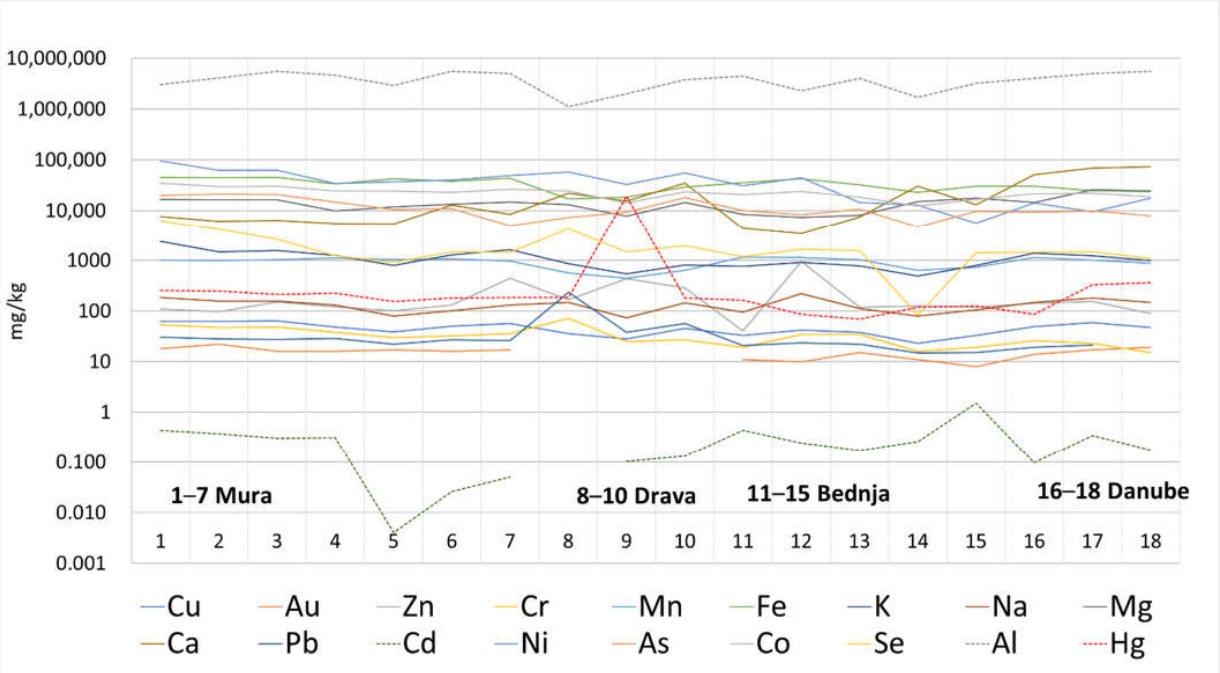


Figure 3. The concentration values in suspended dry matter in mg/kg: Samples 1 to 3, HS Mura-Mursko Sredisce; 4 to 7, HS Mura-Goričan; 8 to 10, HS Drava-Terezino Polje; 11 to 15, HS Bednja-Željeznica; 16 to 18, HS Dunav-Batina.

4. Discussion

Due to mutual relations, for this research, it was necessary to refer to previous studies of heavy metals (Hg, Pb, Zn, Cu, etc.) (Figure 4) and metalloids (As) in the shallow soil layer (topsoil). In the river alluvium, due to occasional flooding, the surface of the terrain is covered with suspended river sediment [21,22]. The Drava and Mura Rivers drain the mountain massifs of the Alps, which contain mineralisation and mineral deposits of Pb and Zn. Exploitation of the mentioned heavy metals in Austria and near Mežice in Slovenia can cause an anthropogenic anomaly in the topsoil of the Drava and Mura River

alluvium. The content of As, Cd, Cu, and Hg in the soils of the Drava River valley is higher than the calculated baseline values (Figures 4 and 5), while Pb and Zn contents are anomalous. As, Pb, and Zn have higher concentrations than permitted for ecological food production as prescribed by Croatian regulations. An elevated Hg concentration was established in the urban area of the city of Varaždin, primarily because of traffic and fossil fuel combustion. The performed study has also shown that the mentioned metals' content decreases with the soil's depth to concentration values recorded before mining activity [21,23]. The Bednja River catchment also partly belongs to the Pb–Zn ore mineralisation area of Mt. Ivanščica, located in the Middle Triassic carbonate rocks near the town of Ivanec, Hrvatsko Zagorje [24]. Additionally, there is a long-standing tradition of gold panning in the Mura and Drava alluvium area. Tiny grains of gold originated from mining activities of gold and silver ore deposits in the Austrian Alps province of Carinthia [25].

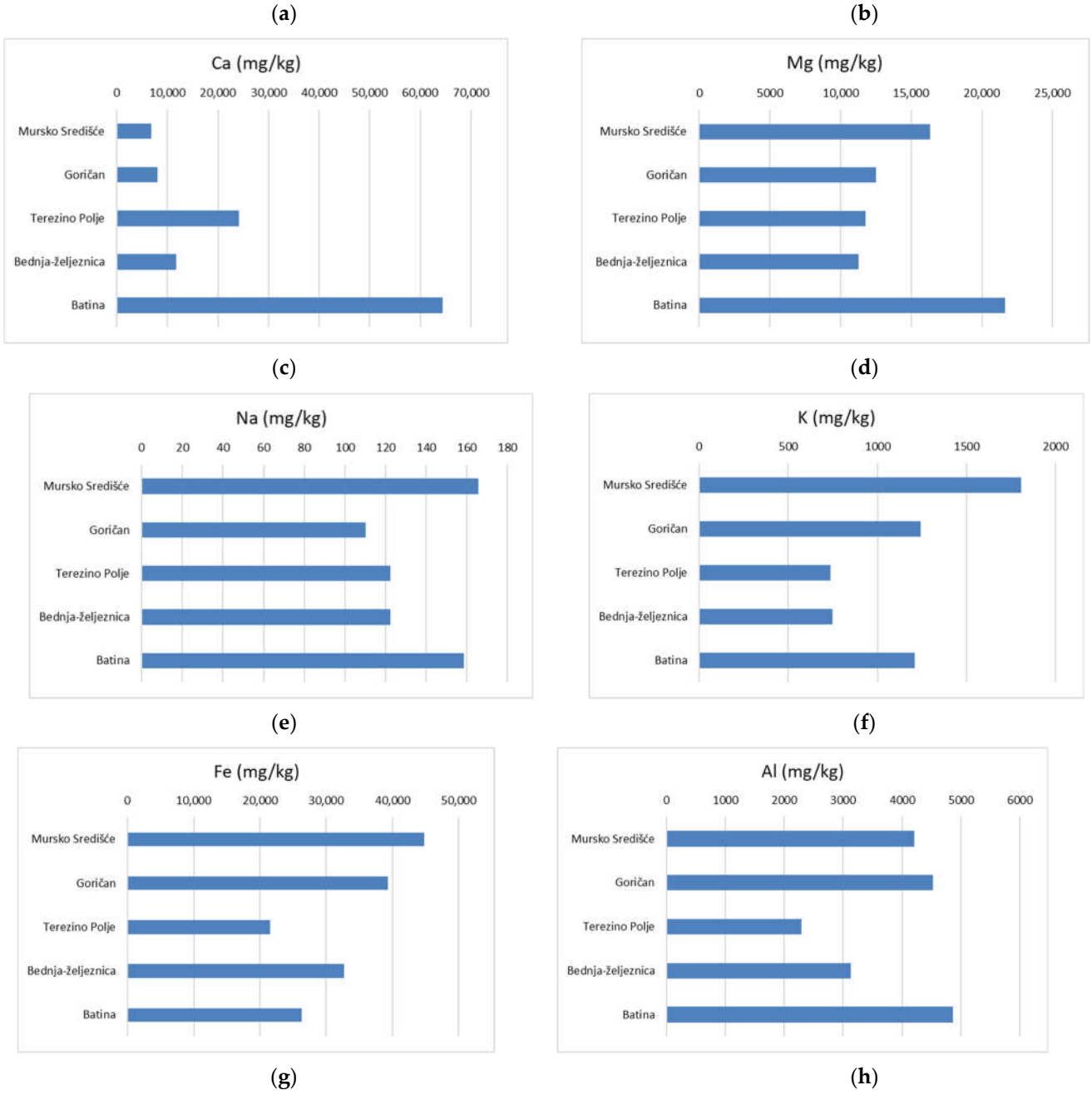


Figure 4. *Cont.*



Figure 4. The average concentrations of Ca (**a**), Mg (**b**), Na (**c**), K (**d**), Fe (**e**), Al (**f**), As (**g**), and Se (**h**) in suspended sediments.

The main mineralogical composition of the Drava River alluvium is quartz, feldspar, plagioclase, carbonate (calcite) and dolomite of carbonate rock grains (limestone and dolomite), kaolinite, chlorites, magnetite, rutile, zircon, etc. [25,26].

The concentrations of Ca, Mg, Na, K, Fe, and Al (Figures 4 and 5) in the suspended sediments (Figures 3 and 4) are mainly the consequence of weathering of the Mura, Drava, and Bednja Rivers' deposits rich in carbonate components (Ca and Mg). In contrast, the highest values in the SS of the Danube River near Batina village reflect an increased concentration of ferromagnesium minerals in clastites of alluvium deposits in the recharge area.

In addition, the higher Na and K contents reflect the enrichment of minerals having a high concentration of sodium (plagioclase) and potassium micaceous minerals, probably muscovite, according to the values present in soils of flooding plains [22]. The concentrations of Fe and Al in SS are comparable with their content in the topsoil of the Mura, Drava, and Bednja Rivers' flood plains. The average highest concentration of Al measured in SS from the Danube River could result from the prevailing content of fine-grained clay fraction in the SS [22].

The average As and Se contents in the SS (Figure 4) followed the same distribution and could be of geogenic and anthropogenic origin (As) somewhere elevated, as the concentrations could indicate the past use of some pesticides/insecticides, but the obtained values are in the range of concentrations found in the topsoil layer of flood plains of rivers.

The concentrations of Co, Cr, Ni, and Cu in SS (Figures 4 and 5) are linked with the heavy metal fraction, but only the Cu concentration increased because of possible anthropogenic input from different sources (phosphate fertilisers, application of cuprum blue in vineyards, and industry). The SS sample analysis results showed an extremely high mercury concentration in sample No. 9, as seen in Figure 3. This sample of water and suspended sediment was taken on 3.6.2019 at HS Drava-Terezino Polje during the maximum water wave between 2 and 3 June (Table 2, Figure 2c). The region of the Mura, Drava, and Danube alluvium has the highest values of Pb in topsoil in Croatia, which relates to lead deposit mining upstream in Slovenia and Austria (Mežice and Bleiburg) over the last two centuries. The flood plain of the Danube River is also enriched with Pb, but is mainly due to anthropogenic impact from different sources somewhere in the Republic of Hungary. The mentioned metals' concentration ranges are similar to the ranges obtained in the topsoil of rivers of alluvium flood pains.

The primary purpose of this investigation was to calculate the daily values of a particular chemical element in the suspended sediment load transport (SSLT). The total amount of each element is based on the results of its concentration obtained by the analysis of the filters (Figure 3) and the total daily suspended sediment load transport (SSLT) (Table 1). The daily amounts of metal (Cu, Au, Zn, Cr, Mn, Fe, K, Na, Mn, Ca, and Al) in tonnes are shown in Table 3 and Figure 6. In addition, the daily amounts of heavy metals and metalloids (Pb, Cd, Ni, As, Co, Se, and Hg) transferred downstream in kg/day are shown in Table 4 and Figure 7.

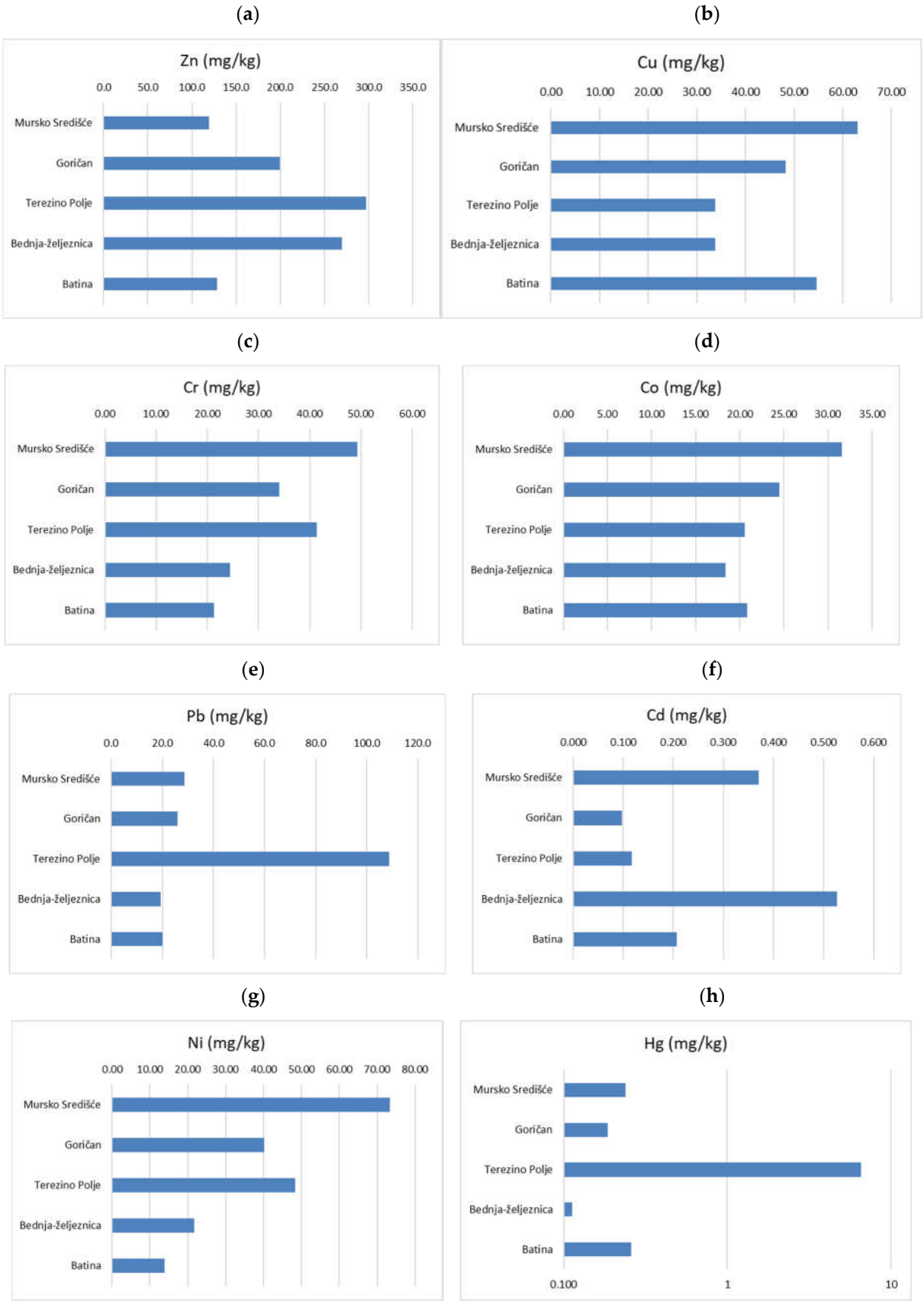


Figure 5. The average concentrations of Zn (**a**), Cu (**b**), Cr (**c**), Co (**d**), Pb (**e**), Cd (**f**), Ni (**g**), and Hg (**h**) in suspended sediment.

Table 3. The total amount of metals (t/day) in SSLT.

Samp.	Total SSLT	Al	Cu	Au	Zn	Cr	Mn	Fe	K	Na	Mg	Ca
No.	t/Day	t/Day	T/Day	T/Day	t/Day	t/Day	t/Day	t/Day	T/Day	t/Day	t/Day	t/Day
1	5094.84	15.53	0.321	0.092	0.560	0.270	5.20	230.08	12.19	0.932	84.95	39.11
2	7166.88	29.29	0.444	0.158	0.695	0.337	7.05	316.06	10.50	1.13	115.83	43.67
3	12,212.64	67.19	0.782	0.195	1.84	0.586	12.57	550.09	19.11	1.91	198.46	78.54
4	12,572.24	58.51	0.603	0.201	1.53	0.478	14.02	422.24	15.72	1.65	125.37	69.12
5	15,756.60	46.01	0.615	0.268	1.59	0.473	16.18	667.35	12.49	1.24	187.03	85.34
6	20,107.44	111.72	1.01	0.322	2.65	0.643	21.37	763.92	26.06	2.03	269.68	257.84
7	22,245.06	110.81	1.25	0.378	9.88	0.801	21.69	964.90	36.55	2.89	329.32	186.41
8	12,073.71	13.57	0.435	-	2.02	0.869	6.87	206.76	10.35	1.79	158.77	265.84
9	6176.56	12.20	0.173	0.130	2.69	0.154	2.73	113.23	3.32	0.457	48.21	94.29
10	14,230.94	53.68	0.640	-	4.11	0.384	9.09	412.68	11.54	2.06	204.70	501.93
11	109.63	0.491	0.004	0.001	0.004	0.002	0.128	3.90	0.084	0.010	0.927	0.478
12	99.87	0.231	0.004	0.001	0.094	0.003	0.113	4.28	0.090	0.022	0.731	0.341
13	152.94	0.612	0.006	0.002	0.018	0.005	0.158	4.89	0.119	0.017	1.23	1.14
14	960.34	1.62	0.022	0.011	0.122	0.015	0.611	21.87	0.471	0.077	14.43	28.89
15	901.24	2.88	0.030	0.007	0.107	0.017	0.661	27.34	0.718	0.095	15.89	11.69
16	79,291.87	318.32	3.89	1.11	11.34	2.06	90.08	2391.68	111.09	11.81	1158.14	4021.68
17	36,176.11	182.02	2.13	0.615	5.53	0.832	36.61	904.29	44.64	6.48	932.26	2507.26
18	34,916.31	194.43	1.64	0.663	3.11	0.524	30.69	831.22	34.78	5.17	857.68	2551.65

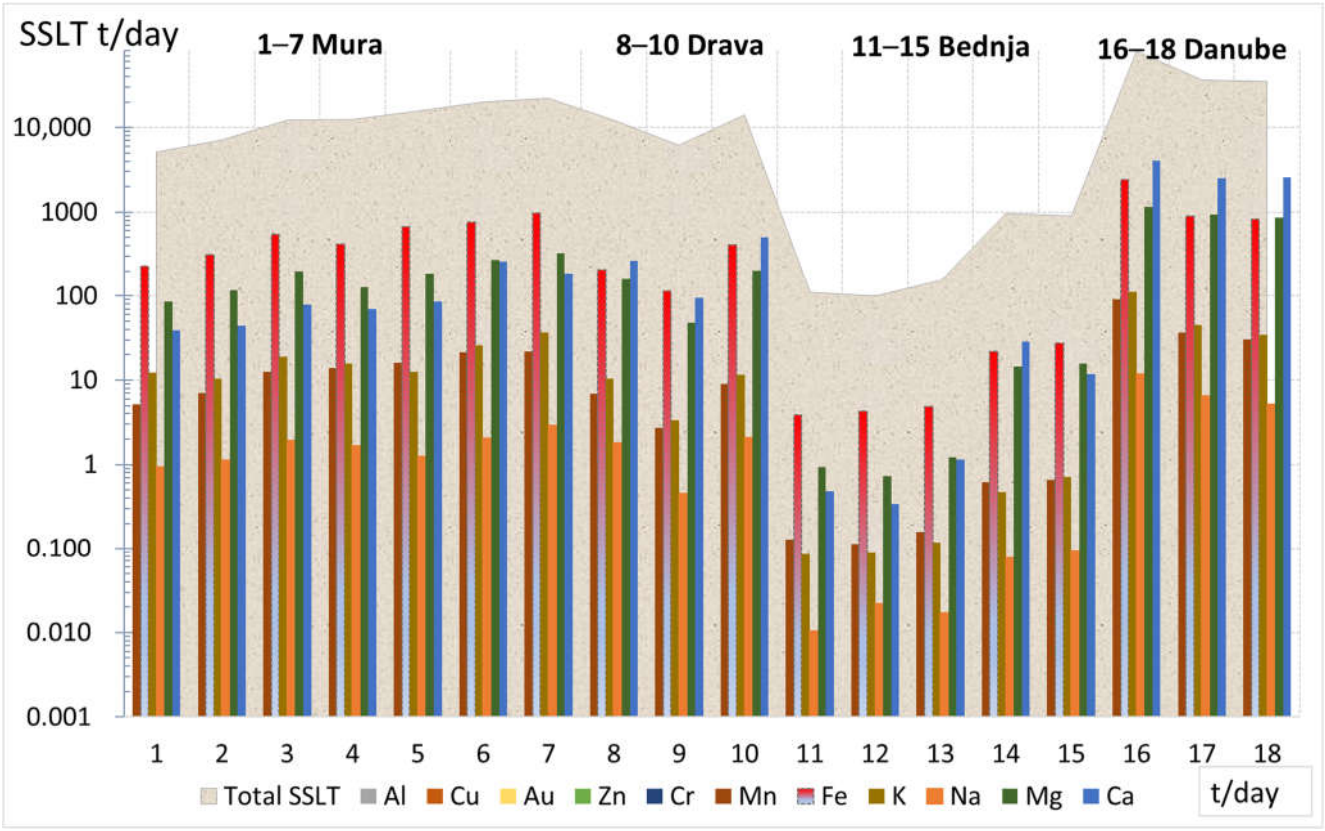


Figure 6. The total amount of metals (t/day) in daily SSLT.

Table 4 and the graphic in Figure 7 highlight the extreme daily value of mercury of 119 kg in Terezino Polje on 3 May 2019. Due to the high flow of the Danube River and the significant daily amounts of SSLT at HS Batina, the concentration of mercury increased during the peak flow in June and ranged between 11.78 and 12.74 kg per day. Unlike other cross-border rivers, in the Bednja tributary in the profile of HS Željeznica (samples No. 11–15), the values of mercury concentration were minimal and ranged from 0.009 to 0.114 kg per day.

Table 4. The total amount of metals (kg/day) in daily SSLT.

Sample	Total SSLT	Pb	Cd	Ni	As	Co	Se	Hg
No.	t/Day	kg/Day	kg/Day	kg/Day	kg/Day	kg/Day	kg/Day	kg/Day
1	5094.835	154.40	2.21	482.96	101.10	176.93	31.65	1.30
2	7166.880	201.07	2.69	447.54	151.62	211.40	30.15	1.78
3	12,212.640	337.56	3.71	765.89	255.28	373.38	32.55	2.58
4	12,572.237	357.03	3.91	428.91	184.60	308.52	15.58	2.80
5	15,756.595	348.52	0.063	581.09	164.81	381.77	14.26	2.41
6	20,107.440	537.83	0.523	810.45	220.08	464.46	29.98	3.64
7	22,245.062	581.11	1.11	1091.85	112.18	582.09	32.08	4.14
8	12,073.709	2801.32	-	690.54	89.36	292.61	51.76	2.21
9	6176.563	234.84	0.636	202.92	58.03	87.82	9.15	**119.08**
10	14,230.944	806.37	1.88	782.70	255.39	331.57	27.82	2.58
11	109.626	2.29	0.047	3.41	1.11	2.30	0.130	0.018
12	99.875	2.33	0.025	4.47	0.826	2.37	0.166	0.009
13	152.938	3.36	0.027	2.20	1.63	2.79	0.240	0.011
14	960.336	14.09	0.249	12.26	4.54	11.86	0.079	0.114
15	901.238	13.73	1.37	5.11	8.72	15.12	1.27	0.113
16	79,291.872	1513.44	7.77	1124.99	741.62	1716.11	115.53	6.82
17	36,176.112	772.69	12.41	340.60	358.69	792.84	52.93	11.79
18	34,916.314	677.27	6.22	618.33	276.33	661.28	38.16	12.74

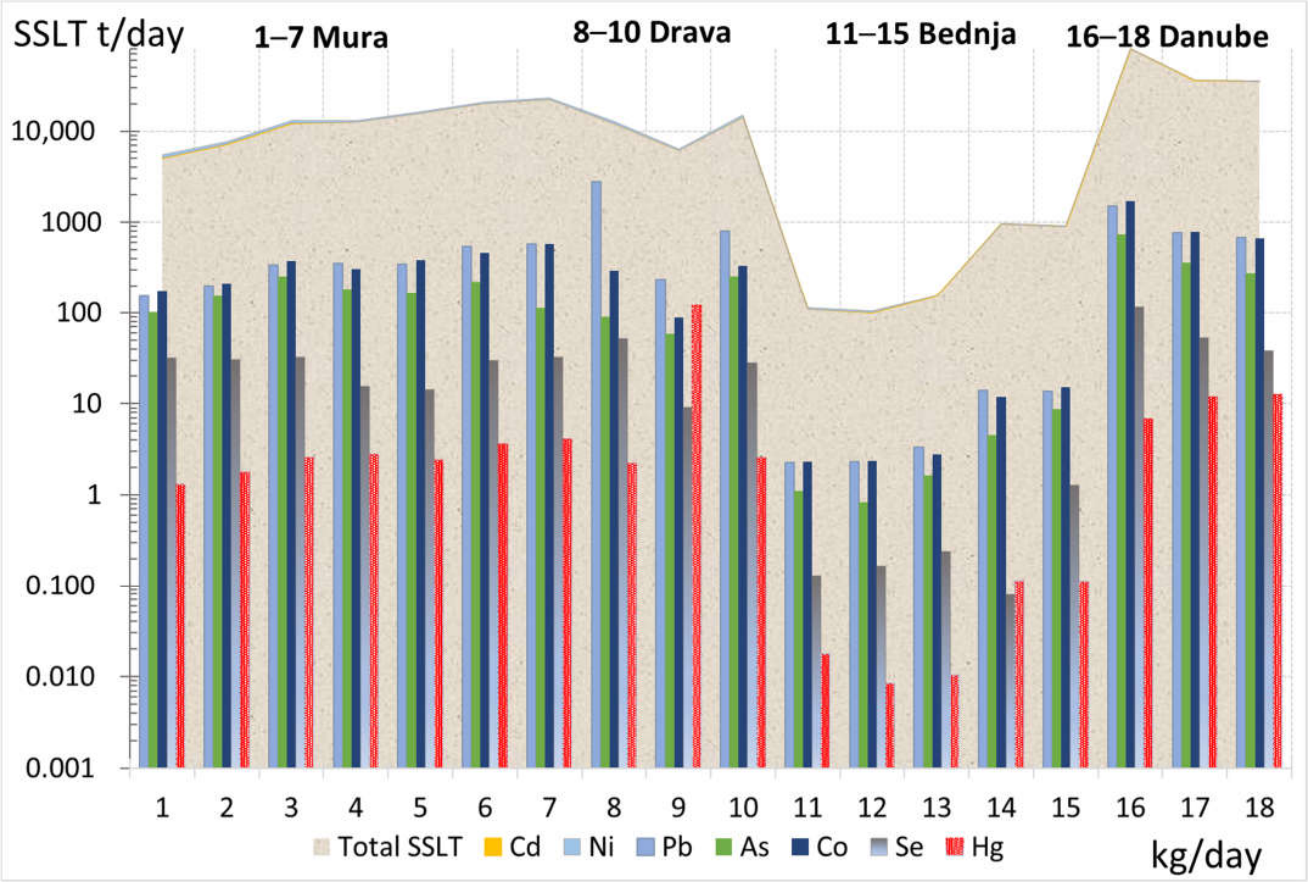


Figure 7. The total amount of metals (kg/day) in daily SSLT.

However, given their toxicity, large amounts of dangerous heavy metals such as lead, nickel, and cobalt and the metalloid arsenic are of particular concern. From Table 4 and Figure 7, it can be seen that a considerable amount of lead (Pb) is transported in suspended sediment in the Mura River (HS Goričan), Drava River (HS Terezino Polje), and Danube River. The highest value of 2801.32 kg/day was measured at HS Drava-Terezino Polje during peak discharge Q = 1306 m^3/s, followed by 1513.44 kg/day at HS Dunav-Batina,

on the recession site of the highest peak flow hydrograph (Figure 2e). At HS Batina, large quantities of aluminium (182–318 t), calcium (2507–4021 t), and other elements such as iron (Fe), manganese (Mn), and magnesium (Mg) were carried through the Danube River.

4.1. Correlation Analysis

A correlation analysis was conducted by calculating the Pearson correlation coefficient (Figure 8) for each metal contaminant in the suspended matter. For this purpose, a simple Python 3 script was written based on the popular Pandas, Matplotlib, and Seaborn libraries. This analysis aimed to identify the patterns of behaviour between contaminants.

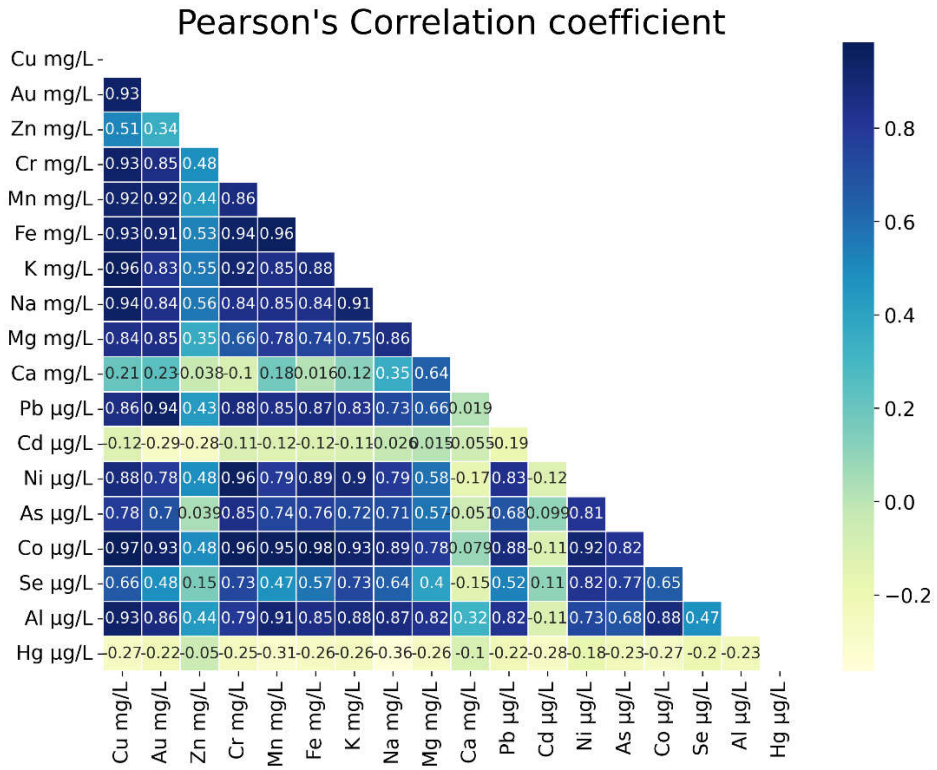


Figure 8. Pearson correlation coefficients.

Pearson's correlation coefficient measures how strong the linear relationship between two random variables is; in other words, it is the ratio between the covariance and the products of the standard deviations (Equation (3)).

$$r = \frac{n\sum xy - (\sum x)(\sum y)}{\sqrt{\left[n\sum x^2 - (\sum x)^2\right]\left[\sum y^2 - (\sum y)^2\right]}} \quad (3)$$

The coefficient value varies between −1 and +1, where a value of +1 indicates a perfect degree of association between two observed variables, 0 shows no correlation, and −1 means a negative relationship. A positive correlation indicates that with an increase in pollutant A, the concentration of pollutant B also increases. Meanwhile, a negative correlation indicates that when pollutant A's concentration increases, the concentration of pollutant B decreases.

According to the Pearson correlation coefficients (Figure 6a), most of the metal contaminants found in the suspended matter correlated rather well, except mercury (Hg), cadmium (Cd), calcium (Ca), and zinc (Zn). Mercury (Hg) was the only element showing only a negative correlation with other metals, and cadmium (Cd) also followed such a trend. However, some of the correlations with cadmium (Cd) were positive—for example, with arsenic (As) and selenium (Se). Calcium (Ca) had an even degree of positive and

negative correlations, while zinc (Zn) had mostly lower positive values of correlation, only showing a negative correlation with cadmium (Cd), mercury (Hg), and calcium (Ca). Most of the other elements showed relatively high values of correlation, with only selenium (Se) standing out, where some above average correlation values were observed and lower negative correlations with calcium (Ca) and mercury (Hg).

4.2. Source of Pollution

The fine-grained fraction (silt and clay) is transported by rivers in suspension, where saturation depends mainly on the rock and soil erosion compliance and water velocity. The saturation of suspended sediments varies with changes in current velocity. Upstream areas are typically regions characterised by high-velocity water flows and, consequently, high erosion. Thus, the composition of a river's suspended sediment depends mostly on the lithology and its mineralogical composition. Downstream in lowland rivers with slower flow rates, the composition of suspended sediment is generally influenced less by the parent material and more by anthropogenic input.

The value of the geochemical background is necessary to assess the current state of pollution in sediment. The baseline value refers to the concentration of an HS in a drainage basin, and the concentrations of HSs in an unpolluted basin should be equal or close to the background values [26].

Contaminants can reach surface waters via point and diffuse sources, airborne deposition, and potentially in the form of inadvertent spills. Many of these contaminants are on the priority substances list of the WFD (2000/60/EC [2,3]). In addition, there are emerging concerns about river basin-specific pollutants and other potentially relevant contaminants that must be addressed. All measured elements mainly belong to the same mineralisation sources as the alluvial flooding terraces of the Drava, Mura, and Danube Rivers. Other inputs can be a consequence of agricultural activity (mineral fertilisers and pesticides), the combustion of fossil fuels, waste deposits, wastewater from industrial facilities, urban settlements, etc.

According to the obtained results of the correlation analysis, most elements, including heavy metals and metalloids, had a strong positive correlation between themselves, implying common sources, mainly situated in upstream countries far away from the monitoring locations. The concentration ranges are very similar to ranges in the topsoil of flooding river terraces. The mercury concentration in all samples of SS was very low, but one of them, from HS Terezino Polje, showed only one very high value, which could result from some pollution. Such high results can partly be obtained as a result of correlation. Another reason may be the very complex behaviour of mercury in the water environment compared with other analysed elements that transport mercury throughout the water, such as in suspended sediments, inorganic or organic complexes, or incorporated within the tissue of biota, etc., which is very efficient in all forms and phases. The negative correlation of selenium with calcium and the low correlation with cadmium and zinc indicate its transport mainly as a part of the organic fraction. At this study phase, the obtained results are insufficient for a more detailed interpretation.

5. Conclusions

Where human activities interfere with sediment quantity or quality, sediment management at the river basin becomes necessary. Earlier documents have already defined [1,2] that all the elements of analysis must be set out in a plan for the river basin—a so-called River Basin Management Plan (RBMP). The goal is to produce a detailed account of how the objectives set for the river basin (ecological status, quantitative status, chemical status, and protected area objectives) are to be reached within the timescale required. The plan will include all the results of the above analysis: the river basin's characteristics, a review of the impact of human activity on the status of water in the basin, an estimation of the effect of existing legislation and the remaining "gap" to meeting these objectives, and a set of measures designed to fill the gap [15].

Therefore, the topic of sediment has been included in the work program of ECOSTAT for 2022–2024 [27]. In 2022, a technical document titled "Integrated sediment management—Guidelines and good practices in the context of the Water Framework" was developed [27]. This technical document has been developed through a collaborative framework (the Common Implementation Strategy (CIS)) involving the Member States, EFTA countries, and other stakeholders including the European Commission. The document was developed in the year before the finalisation of the draft RBMPs for the third cycle, and Member States are expected to consider the extent to which the recommendations in this document can be included in the context of this cycle and in subsequent steps.

This valuable document will help to include an integrated sediment management plan in the RBMPs. Applying "integrated sediment management planning" requires a preliminary analysis of the sediment dynamics in the river basin. It is generally recommended to start by setting objectives at the catchment scale and then derive them at more local scales. Identifying measures at the local scale without assessing both the cause of the problem and the effects of the measures at the larger scale risks being counterproductive, as the measures may not bring the expected benefits. It is also recommended, where relevant, to address both sediment quantity and contamination aspects, as these may be closely linked.

Therefore, the scoping phase of sediment quality should include the following components:

- An assessment and classification of contaminated sediment.
- An inventory of the relevant amounts and sediment contamination in the areas of investigation.
- An assessment of remobilisation risk due to floods, wind, and anthropogenic impacts (dredging, redeposition, navigation, etc.).

The presented study provides the following few conclusions.

1. The state of sediment contamination in four major rivers in the Croatian heartland

The analysed SS samples were taken from several hydrological stations on major Croatian rivers: the Mura River, Drava River, and Danube River. Due to their length and geopolitical significance, these rivers have a cross-border character and international basins. Therefore, SS quality monitoring is even more critical according to the WFD. In addition, for comparison purposes, one smaller tributary of the Drava River, namely the Bednja River, whose basin extends through a less populated area without industry, was included in the SS chemical status analysis.

At the analysed locations, large amounts of dangerous heavy metals such as lead, nickel, and cobalt and the metalloid arsenic were of particular concern. Table 4 and Figure 7 show that a considerable amount of lead (Pb) was transported in suspended sediment in the Mura River (HS Goričan), Drava River (HS Terezino Polje), and Danube River. The highest value of 2801.32 kg/day was measured at HS Drava-Terezino Polje during peak discharge Q = 1306 m^3/s, followed by 1513.44 kg/day at HS Dunav-Batina, on the recession site of the highest peak flow hydrograph (Figure 2e).

At HS Batina, large quantities of aluminium (182–318 t), calcium (2507–4021 t), and other elements such as iron (Fe), manganese (Mn), and magnesium (Mg) were found to be carried through the Danube River.

2. Comparison of the concentrations and correlation of major contaminants in the sediment

According to the results of the correlation analysis, most elements, including heavy metals and metalloids, had a strong positive correlation between themselves, implying common sources, mainly situated in upstream countries far away from the monitoring locations. The concentration ranges were very similar to ranges in the topsoil of flooding river terraces. The mercury concentration in all SS samples was very low, but one of them, from HS Terezino Polje, showed one very high value, which could have resulted from some pollution. Such high results can partly be influenced as a result of correlation. Another reason may be the very complex behaviour of mercury in the water environment compared with other analysed elements that transport mercury throughout the water, such as in suspended sediments, inorganic or organic complexes, or incorporated within the tissue

of biota, etc., which is very efficient in all forms and phases. The negative correlation of selenium with calcium and the low correlation with cadmium and zinc indicate its transport mainly as part of the organic fraction. At this study phase, the obtained results are insufficient to provide a more detailed interpretation.

3. A discussion about possible sources of the discovered contamination in the river sediments

Human activities in the river basin affect natural processes and may create imbalances due to a deficit or surplus of sediments, which can compromise the integrity of aquatic systems and the multiplicity of ecosystem services provided by them. In addition, discharge of pollutants in the environment can lead to sediment contamination, which may represent a threat for decades. Furthermore, flood events as well as human interventions can remobilise deposited sediment and by that result in downstream and cross-border transport of sediment-associated contamination.

This study mainly observed large amounts of mercury and lead in Croatian cross-border big rivers. Mercury is highly toxic for humans, plants, and animals. Mercury poisoning in people can provoke mutagenic, carcinogenic, and teratogenic effects; damage to the immune system, blood vessels, and central nervous system; deformation of DNK; reduced reproduction, and interference with child growth and development. The uses of mercury are varied: in measuring techniques, in dental and medical equipment, in the production of insecticides and fungicides, in gold mines, and in the production of caustic soda and chlorine. It comes into the environment (water in particular) from chemical industry waste, precipitation onto water and soil, and through waste mud, industrial and household wastes, and pesticides based on mercury [19]. Lead is a heavy metal and one of the most infamous environmental pollutants. It is used widely in producing batteries and electrodes, paints, glass, ceramic alloys, and tires as a shield against radiation. However, unfortunately, lead is very toxic and causes neurological damage, kidney and liver diseases, increased blood pressure, anaemia, cancer, and reproduction problems [19].

The HSs in sediments may represent a risk to the environment, and consequently, they should be monitored. Monitoring HSs includes sampling, chemical analyses, and producing risk assessments of the sediments. Whatever the water body, sediments should be sampled at sites representative of the water body or cluster of water bodies. This requires understanding the hydrological and geomorphological characteristics and pollution sources. For example, high direct pollutant inputs into waters and diffuse pollutants washed from the watershed negatively impact the sediment quality in the Danube RB. Older polluted sediments in lower sediment layers are partly remobilised by floods, navigation, or dredging and thus enter the flowing water and impact downstream river sections.

4. Emphasis on the importance of regular monitoring and management of the river sediments

Successful sediment management requires an appropriate governance framework and the support of relevant stakeholders. Therefore, a joint effort from ministries, public authorities, protected area administrations, universities, local communes, and NGOs is needed to save valuable sites and achieve harmonised, sustainable regional development [27].

Covering a substantial section of the European Green Belt, the Mura, Drava, and Danube (MDD) Rivers form a dynamic and interconnected lifeline in Central Europe. In 2021, the MDD area became the world's first five-country UNESCO Biosphere Reserve as a model region for connecting nature conservation and sustainable development. In response, the joint vision for the "Mura-Drava-Danube" area is to use the Transboundary Biosphere Reserve (TBR) concept to maintain a living river ecosystem for biodiversity and ecosystem services and to promote nature-friendly economic development for the local communities of this rural region [20].

Based on several individual samples, it is impossible to conclusively determine the origin of the high concentration of mercury and other heavy metals at the analysed locations. Since heavy metals are highly toxic, a continuous monitoring program with a specific spatial

and temporal resolution is required to monitor this phenomenon adequately. According to the Environmental Quality Standards Directive recommendations (2008/105/EC), this research could be the starting point for defining a preliminary sampling program, which can be useful in providing relevant information for designing the final sampling program. The conclusion is that additional investigations regarding the quantification of sediment balance and sediment quality are needed to identify the critical hotspots of contamination, achieve better sediment management for the Danube on a basin-wide scale, and propose appropriate measures for improving the situation [27].

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