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ASSESSMENT OF RIVER SEDIMENT QUALITY ACCORDING TO THE EU WATER FRAMEWORK DIRECTIVE IN LOWLAND FLUVIAL CONDITIONS. A CASE STUDY IN THE DRAVA RIVER AREA, DANUBE RIVER BASIN

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Abstract: The EU Water Framework Directive requires the monitoring and evaluation of surface water sediment quality based on the assessment of risk posed by contamination on the biotic receptors. Fluvial sediments are important receptors of hazardous substances (HSs) pollution from the upstream catchment areas in the Danube River Basin (DRB). For the development of systematic sediment quality monitoring and evaluation, the Drava River region on the border of Hungary and Croatia was selected as a test area representative of lowland hydromorphological conditions. Overbank (floodplain) sediments and river bottom sediments (stream sediments) were sampled at two depths at 9 locations in the test area. Eight heavy metal(oid)s were analyzed As, Cd, Cr, Cu, Hg, Ni, and Zn as hazardous substances. The sediment quality assessment was carried out according to the 2013/39/EU Directive and EU Water Framework Directive standards. Most of the analysed HS concentrations in river bottom sediment and overbank (floodplain) sediments fall within the limits of environmental quality standards (EQS). Results show that there is no significant differences in metal(oid) HS concentrations among the various sediment types and between shallow (0-5cm) and deeper (stream sediment: 5-10cm; floodplain sediment: 40-50cm) sediment which suggests that the large lowland Drava River fluvial system is an extensive single fluvial system with homogeneous distribution of sediments and the associated contaminants. Specifically, the studied sediments in the tributaries of the Drava River do not seem to be contaminated with metal(oid) hazardous substances but at certain sites concentrations are elevated above the environmental limit values, especially for As and Zn, and to lesser extent for Cr. The data analysis techniques used enabled the identification of sites with anthropogenic pollution and the recognition of regional pattern in HSs distribution.

Keywords: environmental quality standards (EQS), hazardous substances, heavy metals, monitoring, priority substances, SIMONA, geological background, anthropogenic activities, Drava River.

1. INTRODUCTION

The objective of this investigation is the investigation of sediment quality in surface waters in the Drava River area according to the SIMONA Sediment Quality Sampling Protocol (Šorša, 2019)

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and the SIMONA Sediment Quality Sampling Manual (Jordan & Humer, 2021), and to the Sediment Quality Laboratory Protocol for HSs (Šorša, 2019; Čaić Janković & Šorša, 2019).

The Sediment-quality Information, Monitoring and Assessment System to Support Transnational Cooperation for Joint Danube Basin Water Management (SIMONA) project (https://www.interreg-danube.eu/approved-projects/simona) was established in 2018 as a project of the EU Danube Transnational Programme aiming at delivering a ready-to-deploy sediment-quality monitoring system for the effective and comparable measurements and assessment of sediment quality in surface waters in the DRB in accordance with the EU Water Framework Directive (EC 2000).

The scope of this study is limited to fluvial (river) sediments including river bottom sediment (stream sediment) and overbank sediment (floodplain sediment). Stream and river bottom sediments are considered as synonyms in the present study and in this paper the term stream sediment is used (Salminen et al., 2005; Šorša, 2019). It is hypothesised that the monitoring of the HSs in stream sediments characterises the baseline concentration values and current contamination. The analysis of the HSs in overbank (floodplain) sediments is expected to reflect natural background values and historical contamination, especially at greater depth.

2. STUDY AREA

Drava is the third largest river in the Carpathian Basin, Europe (749 km), with a unique and diverse riverine ecosystem. Its source area is in the Alps in San Candido, South Tirol in northern Italy, and it runs across Austria, Slovenia, Hungary and Croatia, discharging into River Danube eventually (Figure 1). The section with the tributaries investigated in this study runs along the Hungarian-Croatian border and it is surrounded by regularly (1-2 times a year) flooded alluvial plains covered mostly with agricultural lands (CLC, 2018, 2019; Kiss & Andrási, 2019; Figure 1). More specifically, according to the European Corine land cover data (CLC, 2018), the land cover is Non-irrigated arable land at sampling sites SDR02, SDR04, SDR08, and SDR09, while Broad-leaved forest dominates at sites SDR05 and SDR06. 'Transitional woodland-shrub', 'Pastures and Land principally occupied by agriculture' together with significant areas of 'Natural vegetation' cover the land at sampling sites SDR01, SDR03, and SDR07, respectively.

Settlements and some industries are found in the study area influencing the chemical composition of the sediments and soils, but historical mining and smelting in the upstream Alpine region are the most important contamination sources in the region (Halamić et al., 2003; Peh et al., 2008; Šajn et al., 2011).

The geological background in the upper section of the river, especially around Bleiberg (Austria) and in the catchment of the Meža River (Slovenia), is composed of rocks rich in Pb-Zn (Cu, As, Cd) ore deposits and occurrences. The erosion, mining, and tailings of these rocks cause geogenic and anthropogenic release of heavy metals (metal(oid)s), which are then being carried downstream by the river and deposited. Additionally, floods also contributed to a wider area of the material deposition. Developed industrial and agricultural production along the corridor of the Drava River contributes to the release of heavy metals. The heavy metals are transported downstream as suspended sediment and deposited as stream and overbank (floodplain) sediment in the lower course of the Drava River.

The sources of the metals in the river Drava alluvium are for some elements ambiguous, but as a general rule it is considered that As mainly originates from intensive agricultural activities (pesticides), Hg has an anthropogenic source (e.g. fossil fuel combustion), Cr, Cu, and Ni are predominantly of natural origin with week anthropogenic impact. The elements Cd, Pb, and Zn are of geogenic and anthropogenic origin derived by weathering ore deposits and mine waste such as tailings upstream in the Meža River valley in Slovenia and Bleiberg in Austria (Halamić et al., 2003; Šajn, 2006; Peh et al. 2008; Šajn et al., 2011; Halamić et al., 2012).

In this study, nine tributaries of Drava River with known water or sediment pollution were investigated (Figure 1).

3. METHODS AND MATERIALS

The locations of the nine sampling sites were selected according to proposition of the SIMONA Sampling Protocol and other recommendations (Fig. 1; Šorša, 2019; Jordan & Humer, 2021). The seven types of sediment samples were collected with five different types of sampling devices. This study presents the results of stream sediment samples collected at depths of 0-5 cm (top layer) and 5-10 cm (bottom layer) using a vacuum corer and overbank (floodplain) sediment samples collected at depths of 0-5 cm (top soil) and 40-50 cm (bottom soil) using standard soil sampling procedures in a sampling pit.

All types of sediment samples were collected as composite samples. A composite sample of stream

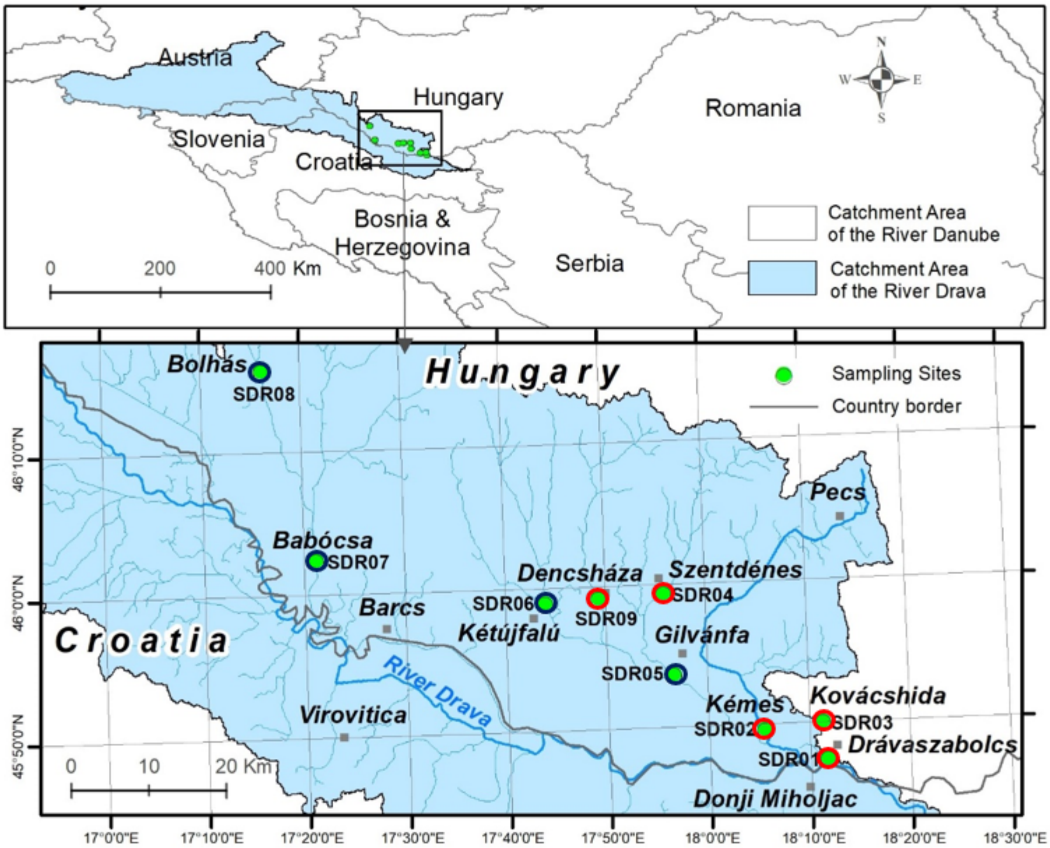

Figure 1. Geographical position of the Drava River research area. Solid green dots show the nine sampling sites located in the tributaries of the Drava River. Red circle shows Group 1 sites; Blue circle shows Group 2 sites. Compare to Figure 5. See text for details.

sediment consists of five sub-samples collected at approximately equal intervals (50 m) along a 250 m section of river. If only shorter river sections were available, at least three sub-samples were collected. For overbank (floodplain) sediment sampling, five 50 cm deep holes were dug along the 250 m section of the river aligned along a line parallel to the river bank on the active floodplain, and samples were collected using a spade and soil sampling knife.

Proposed field measurements in river water chemistry (EC, T, pH, redox potential, dissolved oxygen, turbidity) and in stream sediment (EC, T, pH, redox potential) were made. Field documentation included field photographs and videos and the standard SIMONA Sampling protocol field sheets were completed in the field.

All the sediment samples were stored in glass sample containers transported and stored cooled at 5-8 ℃ from immediately after sample collection to the laboratory analysis.

The laboratory analyses were performed in the SIMONA project reference laboratory Bálint Analitika Ltd. Sample preparation included drying at 40°C until constant weight, sieving to <2 mm fraction, homogenisation by mixing and shaking for 1 minute. In this study, 8 metal(oid)s as hazardous substances (EQS, 2018) were selected for analysis.

The eight metal(oid)s (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) (Table 1) were analysed with inductively-coupled plasma mass spectrometry (ICP-MS) after aqua regia extraction Čaić & Šorša (2019).

4. RESULTS AND DISCUSSION

This study discusses the concentrations of selected metal(oid) hazardous substances in the sediments of tributaries of the Drava River catchment located in Hungary (Figure 1; Table 1). International and national environmental standards according to the SIMONA Evaluation Protocol (Dudás et al., 2021) were used to evaluate the level of contamination of the sediments in the Drava study area.

4.1. Metal(oid)s in sediments

4.1.1 Arsenic

Arsenic concentrations detected in sediment samples ranged from 2.41 mg/kg at sampling site SDR09 in stream sediment at 0-5 cm depth to 183 mg/kg at sampling site SDR08 in the same sediment type (Tables 1 and 2; Figure 2A). The highest As concentrations were found at SDR08 among all sediment types sampled. Depending on sediment type, the highest values and most variables of As were measured in shallower stream sediments and the lowest in deeper (5-10 cm) stream sediments. Land use at site SDR08 is Non-irrigated arable land (CLC, 2018) and higher concentrations of As are likely due to intensive agricultural activities (Halamić et al., 2003; Šajn et al. 2011). Altogether 10 sediment samples exceed the Hungarian limit value (15 mg/kg).

4.1.2. Cadmium

Cadmium levels range from 0.31 mg/kg in floodplain sediment 0-5 cm depth at site SDR05 to 0.89 mg/kg also in floodplain sediment 0-5 cm depth at site SDR09 (Tables 1 and 2). Despite the high Cd concentrations found in the Drava River floodplain sediments by previous studies (Šajn et al., 2011), the cadmium concentrations measured in the tributary sediments remain below the Hungarian limit value (1 mg/kg) in all the studied sediments (Figure 3A). This suggests that ore mining is not a major source of cadmium in this environment, unlike in the nearby large Drava River floodplain areas (Halamić et al., 2003).

4.1.3. Chromium

Chromium concentrations vary from the minimum of 9.37 mg/kg in stream sediment bottom layer to the maximum of 111 mg/kg floodplain top layer (Tables 1 and 2; Figure 3C). Altogether 5 sediment samples exceed the Hungarian limit value (55 mg/kg), of which 3 samples are from the SDR02 site representing the Pécs-víz tributary well-known for its wide-spread pollution originating from the upstream industrial areas of at the town of Pécs (Figure 1). These polluted sediments are all top layers of active stream and floodplain sediments indicating the recently still ongoing pollution processes.

4.1.4. Copper

Copper content ranges from 3.36 to 97.9 mg/kg at sites SDR07 and SDR03, respectively, both samples coming from floodplain sediment top layer (0-5cm) (Tables 1 and 2). Only the above-mentioned maximum concentration value at site SDR03 exceeds the Hungarian limit value (75 mg/kg) indicating that the studied sediments are not polluted for copper (Figure 3B).

4.1.5. Mercury

The lowest mercury concentration 0.04 mg/kg was found in the deep floodplain layer of site SDR05 and the highest value 0.83 mg/kg in floodplain sediment (0-5 cm) of site SDR09 (Tables 1 and 2). Only the above-mentioned maximum concentration value at site SDR09 exceeds the Hungarian limit value (0.5 mg/kg) indicating that the studied sediments are not polluted for mercury (Figure 3D). Site SDR09 seems to be polluted by a combination of hazardous metal(oid)s most probably originating from the industrial areas at Szigetvár located upstream of the sampling point.

4.1.6. Nickel

All the samples have Ni concentrations well below the Hungarian limit value (40 mg/kg) (Tables 1 and 2; Figure 2C). Nickel most probably represents the regional geochemical background in this area (Šajn et al. 2011).

4.1.7. Lead

The lowest lead concentration of 1.18 mg/kg was measured in stream sediments (5-10cm) sampled at site SDR05, and the highest values of 28.3 mg/kg were measured in floodplain sediments (40-50 cm) at site SDR01. Similar to Ni, all the measured lead concentrations remain well below the relevant environmental standard value (100 mg/kg) (Tables 1 and 2; Figure 2D).

4.1.8. Zinc

The lowest (16.5 mg/kg) and highest (92.2 mg/kg) zinc concentrations were recorded in the same samples as those for lead. Altogether 20 sediment samples exceed the Hungarian limit value (40 mg/kg).

In summary it can be stated that, apart from a few exceptions, the studied stream sediments (river bottom sediments) and floodplain sediments (overbank sediments) are not polluted with respect to the metal(oid) hazardous substances. However, As and Zn pollution seems to be widely dispersed having 10 and 20 sediment samples with concentrations above the environmental standards, respectively. Chromium follows with 5 polluted sediment samples, while mercury and copper have elevated concentration at 1 site each, only. Three metals, Ni, Pb and Cd concentrations remain below the limit values for all the investigated sediments. Sites SDR02, SDR03, SDR08 and SDR09 seem to be the most polluted as indicated by the number of polluted sediment samples.

Perhaps the most interesting pattern is the uniform concentration levels for all the sample types, independently from the depth and the character (stream sediment and floodplain sediment) (Figures 2 and 3). The homogeneity of the medians shown in Figures 2 and 3 is confirmed by the Kruskal-Wallis Test at 95% confidence level. A further apparent feature is that the lowest concentrations are found in the deep layer (5-10cm) of the stream sediments.

Table 1. Concentrations of metal(oid) hazardous substances in the studied fluvial sediments. Colours from green-yellow-orange-red show increasing metal concentration from the lowest concentration (green) to the highest (red)

Site ID	River	Site	Sample type	Sample Type ID	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
					mg/kg							
					Detection limit							
					0.005	0.003	0.03	0.1	0.005	0.005	0.005	0.1
SDR01	Fekete-víz (Régi)	Drávaszabolcs	stream sediment 5 cm	BS_CR_TL	7.11	0.37	57.1	25.9	0.34	28.1	8.00	58.9
SDR01	Fekete-víz (Régi)	Drávaszabolcs	stream sediment 5-10 cm	BS_CR_BL	6.20	0.32	23.6	3.55	0.35	10.0	4.41	32.1
SDR01	Fekete-víz (Régi)	Drávaszabolcs	floodplain sediment 5 cm	FS_SP_TS	8.62	0.45	61.6	12.1	0.41	20.7	22.3	86.5
SDR01	Fekete-víz (Régi)	Drávaszabolcs	floodplain sediment 40-50 cm	FS_SP_BS	8.76	0.50	84.4	14.5	0.30	22.2	28.3	92.2
SDR02	Pécsi-víz	Kémes	stream sediment 5 cm	BS_CR_TL	8.19	0.41	97.7	11.3	0.38	16.0	12.3	64.0
SDR02	Pécsi-víz	Kémes	stream sediment 5-10 cm	BS_CR_BL	12.0	0.39	93.4	11.2	0.29	15.1	10.5	60.6
SDR02	Pécsi-víz	Kémes	floodplain sediment 5 cm	FS_SP_TS	9.46	0.40	111	19.2	0.25	27.1	12.4	73.6
SDR02	Pécsi-víz	Kémes	floodplain sediment 40-50 cm	FS_SP_BS	8.15	0.33	34.6	10.3	0.25	15.8	7.06	41.6
SDR03	Egerszegicsatorna	Kovácshida	stream sediment 5 cm	BS_CR_TL	19.9	0.41	39.1	19.1	0.32	23.1	12.0	61.4
SDR03	Egerszegicsatorna	Kovácshida	stream sediment 5-10 cm	BS_CR_BL	9.80	0.31	23.4	8.34	0.21	14.1	6.27	39.0
SDR03	Egerszegicsatorna	Kovácshida	floodplain sediment 5 cm	FS_SP_TS	7.88	0.33	33.2	97.9	0.24	16.8	7.19	45.6
SDR03	Egerszegicsatorna	Kovácshida	floodplain sediment 40-50 cm	FS_SP_BS	9.60	0.35	41.1	14.1	0.26	24.2	8.31	55.3
SDR04	Okor-Bükkösdi víz	Szentdénes	stream sediment 5 cm	BS_CR_TL	11.4	0.37	41.2	13.3	0.19	24.0	11.1	61.7
SDR04	Okor-Bükkösdi víz	Szentdénes	stream sediment 5-10 cm	BS_CR_BL	10.2	0.34	39.7	13.7	0.32	23.8	11.4	61.8
SDR04	Okor-Bükkösdi víz	Szentdénes	floodplain sediment 5 cm	FS_SP_TS	13.9	0.41	52.9	18.1	0.38	29.1	14.6	72.1
SDR04	Okor-Bükkösdi víz	Szentdénes	floodplain sediment 40-50 cm	FS_SP_BS	13.5	0.41	49.9	20.1	0.13	27.8	14.7	73.5
SDR05	Bükkösdiárapasztó	Gilvánfa	stream sediment 5 cm	BS_CR_TL	8.37	0.26	28.4	10.6	0.11	14.9	5.50	39.4
SDR05	Bükkösdiárapasztó	Gilvánfa	stream sediment 5-10 cm	BS_CR_BL	7.63	0.29	26.6	7.22	0.37	11.4	5.77	35.6
SDR05	Bükkösdiárapasztó	Gilvánfa	floodplain sediment 5 cm	FS_SP_TS	9.26	0.31	30.4	9.58	0.08	13.1	5.35	35.4
SDR05	Bükkösdiárapasztó	Gilvánfa	floodplain sediment 40-50 cm	FS_SP_BS	8.03	0.26	18.3	4.67	0.05	7.11	1.68	25.2
SDR06	Egyesült-Gyöngyös	Kétújfalú	stream sediment 5 cm	BS_CR_TL	16.9	0.28	99.9	6.14	0.09	8.70	3.10	26.5
SDR06	Egyesült-Gyöngyös	Kétújfalú	stream sediment 5-10 cm	BS_CR_BL	11.7	0.27	19.9	5.83	0.12	7.46	2.61	27.0
SDR06	Egyesült-Gyöngyös	Kétújfalú	floodplain sediment 5 cm	FS_SP_TS	18.1	0.32	26.8	8.78	0.11	12.8	5.13	38.0
SDR06	Egyesült-Gyöngyös	Kétújfalú	floodplain sediment 40-50 cm	FS_SP_BS	12.7	0.34	36.6	10.5	0.11	19.1	6.82	41.8
SDR07	Babócsai-Rinya	Babócsa	stream sediment 5 cm	BS_CR_TL	17.9	0.25	11.4	3.36	0.09	3.49	1.18	16.5
SDR07	Babócsai-Rinya	Babócsa	stream sediment 5-10 cm	BS_CR_BL	16.4	0.26	9.37	3.81	0.07	3.87	1.33	19.8
SDR07	Babócsai-Rinya	Babócsa	floodplain sediment 5 cm	FS_SP_TS	24.3	0.28	14.7	5.45	0.1	5.59	2.62	25.7
SDR07	Babócsai-Rinya	Babócsa	floodplain sediment 40-50 cm	FS_SP_BS	13.6	0.26	12.5	3.84	0.06	4.83	1.48	19.3
SDR08	Taranyi-Rinya	*Bolhás	stream sediment 5 cm	BS_CR_TL	183	0.36	24.8	10.2	0.25	11.6	6.18	44.7
SDR08	Taranyi-Rinya	*Bolhás	stream sediment 5-10 cm	BS_CR_BL	21.3	0.29	14.6	4.04	0.06	4.94	1.73	21.2
SDR08	Taranyi-Rinya	*Bolhás	floodplain sediment 5 cm	FS_SP_TS	56.0	0.32	10.9	5.93	0.14	4.95	4.26	27.7
SDR08	Taranyi-Rinya	*Bolhás	floodplain sediment 40-50 cm	FS_SP_BS	52.0	0.29	13.8	5.46	0.11	5.32	4.49	28.0
SDR09	Almáspatak	Dencsháza	stream sediment 5 cm	BS_CR_TL	2.41	0.74	32.1	12.4	0.3	15.9	8.53	50.6
SDR09	Almáspatak	Dencsháza	stream sediment 5-10 cm	BS_CR_BL	8.85	0.35	29.7	9.74	0.17	14.7	6.72	43.5
SDR09	Almáspatak	Dencsháza	floodplain sediment 5 cm	FS_SP_TS	9.85	0.89	41.6	18	0.83	24.8	12.7	73.2
SDR09	Almáspatak	Dencsháza	floodplain sediment 40-50 cm	FS_SP_BS	14.6	0.85	46	16.7	0.15	29	12.8	59.9

*Bolhás (Somogyszob-Kaszópuszta)

4.2. Evaluation of HSs at the sampling sites

Interpretation of analytical results at the sampling site is observed for the concentration of the selected metal in all sediment samples collected at a given location. Comparison between sampling sites, on the other hand, is based on the sum of the concentrations of the selected metal at each sampling site (Table 1).

4.2.1. Sampling site SDR01

The concentration of As, Cd and Hg is quite the same in the different sediment samples (Table 1; Figure 4). An outstanding high Ni concentration is measured in stream sediment at the 0-5cm depth and in the floodplain sediment sample. The extremely high concentrations of Pb and Zn accumulated in the floodplain sediments. In general, the levels of As, Cr, Cu, Ni, Pb, and Zn are the highest in the floodplain sediments (40-50cm) and in the floodplain sediments (0-5cm), respectively. Sampling site SDR01 had the overall highest Hg concentration of all the 9 sites.

4.2.2. Sampling site SDR02

The content of the metals As, Cd, Hg and Pb is evenly distributed over the different types of samples. Copper, Ni, and Zn concentrations are significantly higher in the uppermost layer of floodplain sediment samples than elsewhere.

Table 2. Summary statistics of metal(oid) concentrations in the studied fluvial sediments.SD: Standard Deviation. Colours from green-yellow-orange-red show increasing metal concentration from the lowest concentration (green) to the highest (red)

Metal(oid)	Summary statistics	Stream (river bottom) sediments		Overbank (Floodplain) sediments	
		stream sediment	stream	floodplain	floodplain
As	Mean	11.6	30.6	15.7	17.5
	Median	10.2	11.4	12.7	9.85
	SD	4.70	57.5	13.9	15.4
	Minimum	6.20	2.41	8.03	7.88
	Maximum	21.3	183	52.0	56.0
	Range	15.1	181	44.0	48.1
Cd	Mean	0.31	0.38	0.40	0.41
	Median	0.31	0.37	0.34	0.33
	SD	0.04	0.15	0.19	0.19
	Minimum	0.26	0.25	0.26	0.28
	Maximum	0.39	0.74	0.85	0.89
	Range	0.13	0.49	0.59	0.61
Cr	Mean	31.1	48.0	37.5	42.6
	Median	23.6	39.1	36.6	33.2
	SD	24.9	31.4	22.4	30.5
	Minimum	9.37	11.4	12.5	10.9
	Maximum	93.4	99.9	84.4	111
	Range	84.0	88.5	71.9	100
Cu	Mean	7.49	12.5	11.1	21.7
	Median	7.22	11.3	10.5	12.1
	SD	3.57	6.69	5.70	29.1
	Minimum	3.55	3.36	3.84	5.45
	Maximum	13.7	25.9	20.1	97.9
	Range	10.2	22.5	16.3	92.5
Hg	Mean	0.22	0.23	0.16	0.28
	Median	0.21	0.25	0.13	0.24
	SD	0.12	0.11	0.09	0.24
	Minimum	0.06	0.09	0.05	0.08
	Maximum	0.37	0.38	0.30	0.83
	Range	0.31	0.29	0.25	0.75
Ni	Mean	11.7	16.2	17.3	17.2
	Median	11.4	15.9	19.1	16.8
	SD	6.13	7.83	9.53	8.88
	Minimum	3.87	3.49	4.83	4.95
	Maximum	23.8	28.1	29.0	29.1
	Range	19.9	24.6	24.2	24.2
Pb	Mean	5.64	7.54	9.52	9.62
	Median	5.77	8.0	7.06	7.19
	SD	3.59	3.91	8.34	6.37
	Minimum	1.33	1.18	1.48	2.62
	Maximum	11.4	12.3	28.3	22.3
	Range	10.1	11.1	26.8	19.7
Zn	Mean	37.8	47.1	48.5	53.1
	Median	35.6	50.6	41.8	45.6
	SD	15.3	16.9	24.0	23.2
	Minimum	19.8	16.5	19.3	25.7
	Maximum	61.8	64.0	92.2	86.5
	Range	42.0	47.5	72.9	60.8

4.2.3. Sampling site SDR03

The far outstanding 97.9 mg/kg concentration measured in the floodplain sediment top layer sample seems to be a measurement error (Table 1; Figure 4). For all the other elements this site has elevated concentrations but for As. The measured concentration of As, Cd, Cr, Hg, and Pb is uniform in the different sediment types.

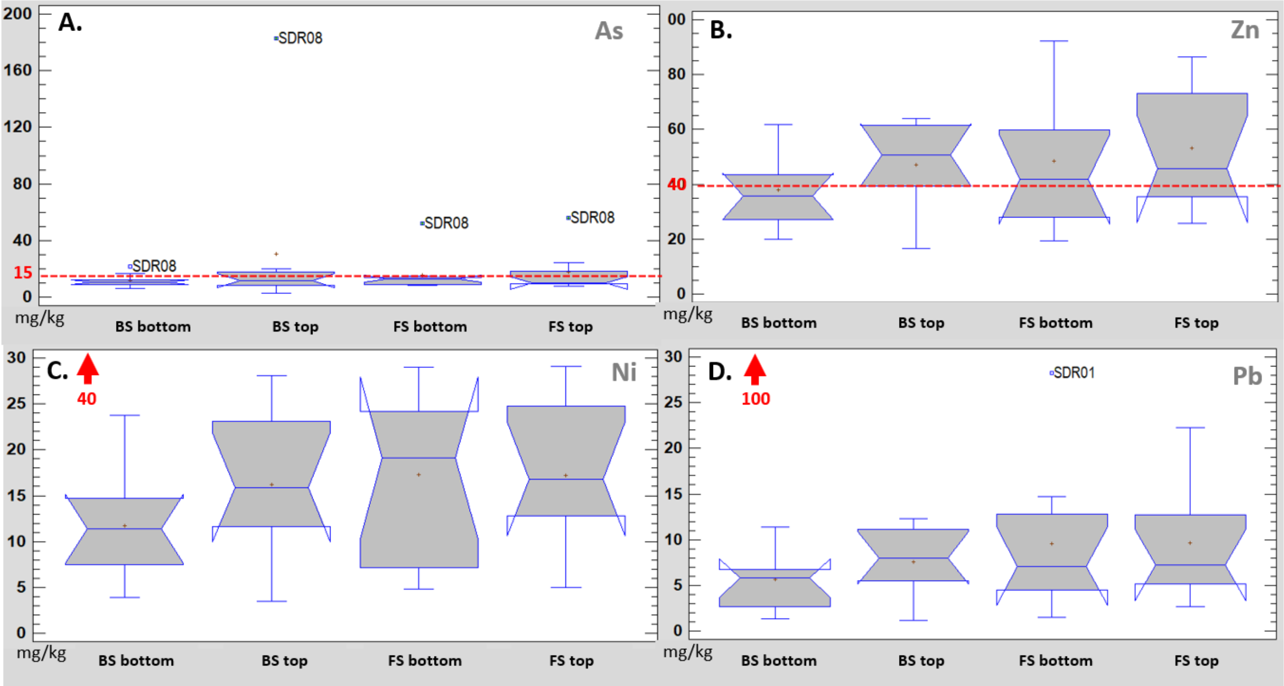

Figure 2. Box-Whiskers plots for metal(oid) hazardous substance concentrations in the studied fluvial sediments. Notches indicate the 95% confidence interval of the median. A. Arsenic. B. Zinc. C. Nickel. D. Lead. BS bottom and BS top indicate bottom layer (5-10cm) and top layer (0-5cm) stream sediment (river bottom sediment); FS bottom and FS top indicate bottom soil (40-50cm) and top soil (0-5cm) overbank (floodplain) sediment. Dashed red line and figure indicate the Hungarian limit value (Decree 6/2009 (2009).

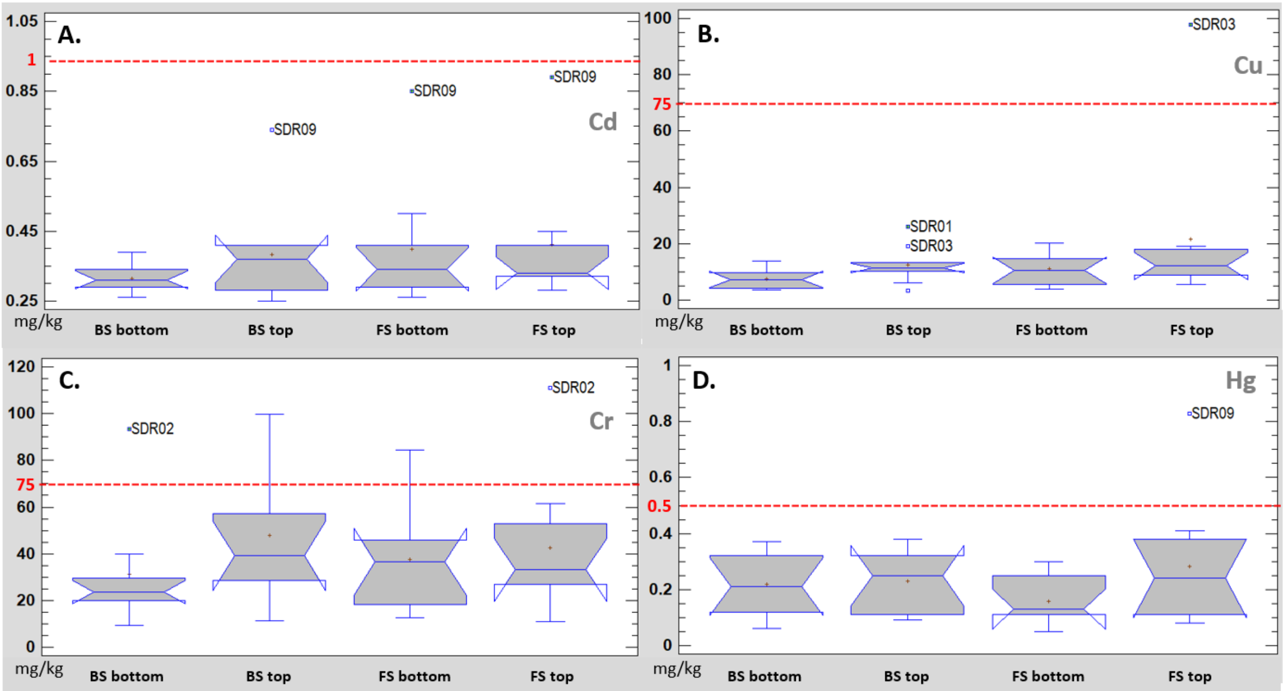

Figure 3. Box-Whiskers plots for metal(oid) hazardous substance concentrations in the studied fluvial sediments. Notches indicate the 95% confidence interval of the median. A. Cadmium. B. Copper. C. Chromium. D. Mercury. BS bottom and BS top indicate bottom layer (5-10cm) and top layer (0-5cm) stream sediment (river bottom sediment); FS bottom and FS top indicate bottom soil (40-50cm) and top soil (0-5cm) overbank (floodplain) sediment. Dashed red line and figure indicate the Hungarian limit value (Decree 6/2009 (2009).

4.2.4. Sampling site SDR04

The content of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn is fairly evenly distributed across the different sample types. Ni (188 mg/kg) is most elevated at site SDR04 as compared to the other sampling sites. The content of all other investigated metal(oid)s is also elevated.

4.2.5. Sampling site SDR05

The magnitude of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn contents is similar for the different sample types, and Hg content in floodplain sediment. The very low Pb content (1.68 mg/kg) is measured in the floodplain sediments at a depth of 40-50 cm. In general, this site has the lowest metal(oid) concentrations among others.

4.2.6. Sampling site SDR06

The concentration of As is moderate and uniform in all samples. The content of Cd, Cr, Cu, Hg, Ni, Pb, and Zn is lower in stream sediments than in other type of sediment, but an anomalous value (99.9 mg/kg) is recorded for Hg in stream sediment collected with a vacuum core.

4.2.7. Sampling site SDR07

The concentration of As is moderate and that of Cd, Cr, Cu, Hg, Ni, Pb, and Zn is low. On this basis, the sediments of this site seems to be the cleans.

4.2.8. Sampling site SDR08

Anomalous high concentration value in is measured for As in the stream sediment 0-5cm depth

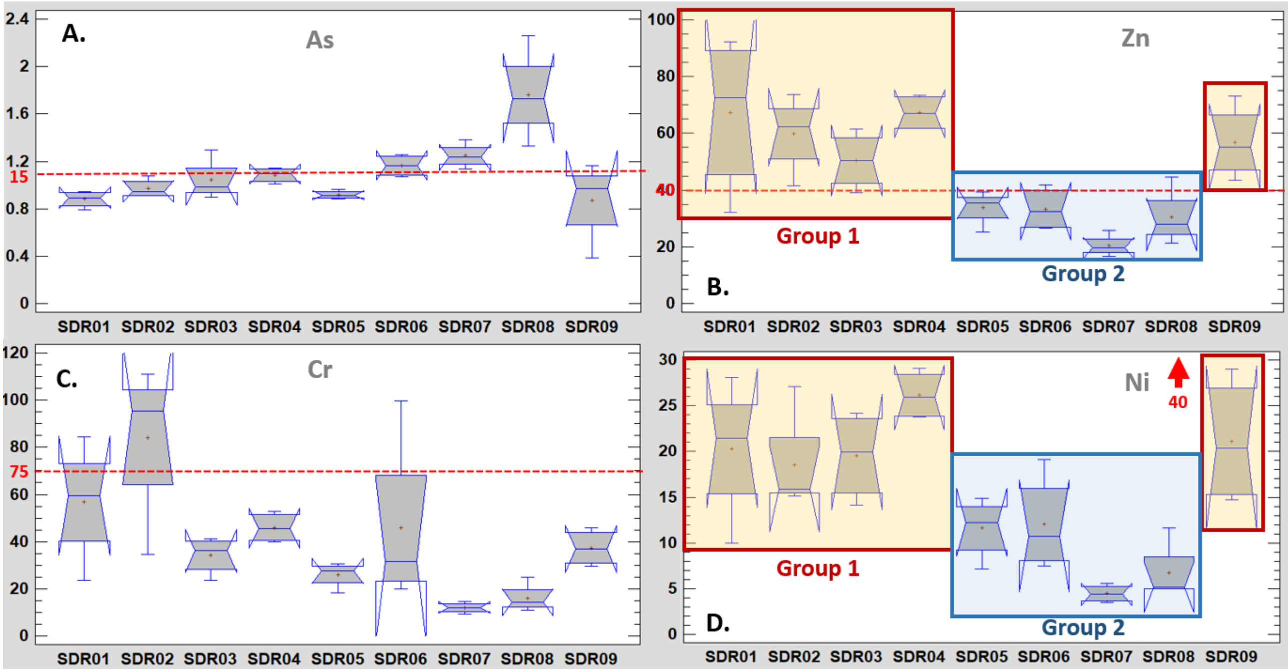

Figure 4. Box-Whiskers plots for metal(oid) hazardous substance concentrations according to the sampled monitoring sites. A. Arsenic. B. Zinc. C. Chromium. D. Nickel. Dashed red line and figure indicates the Hungarian limit value (Decree 6/2009 (2009). Red rectangles show Group 1 sites; Blue rectangle shows Group 2 sites. Note that Cu, Cd and Pb have patterns very similar to that of Zn and Ni. Concentrations are given in mg/kg. Compare to Figure 1. See text for details.

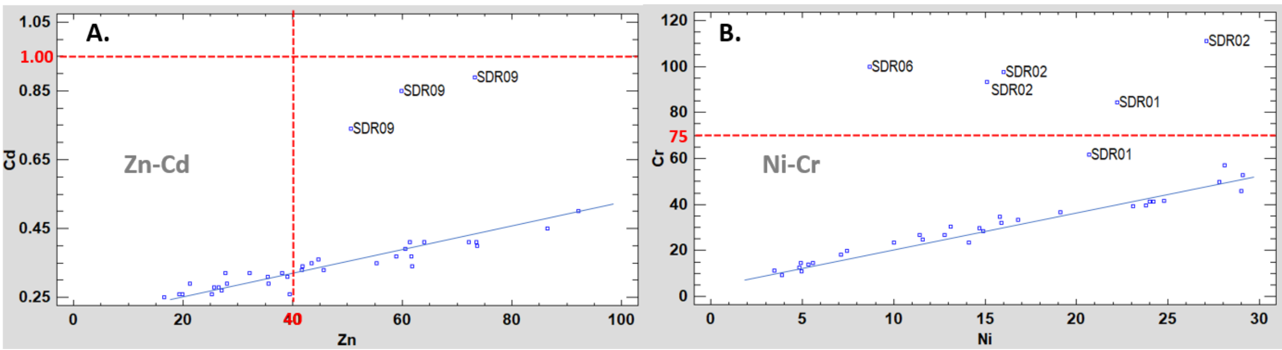

Figure 5. Biplots between metal(oid) hazardous substance concentrations measured in the sediments. A. Biplot for Zn-Cd. Note the bivariate outliers for site SDR09. B. Biplot for Ni-Cr. Dashed red line and figure indicates the Hungarian limit value (Decree 6/2009 (2009). Concentrations are given in mg/kg. Note the bivariate outliers for sites SDR01, SDR02, and SDR06. See text for details.

(183 mg/kg) (Table 1; Figure 4). The amount of As in all sediment samples at site SDR08 is the highest among all the sampling sites. The concentration values for the other studied metals are low.

4.2.9. Sampling site SDR09

This site has outstanding high Cd concentrations (still below the environmental standards) and, apart from As, it has elevated concentrations for all the studied metals (Figure 4). An anomalously high value for Hg is observed in floodplain sediment top layer (0.83 mg/kg). The highest Cd concentrations are found in all sediment types at site SDR09.

In addition to the above, an interesting pattern emerges in the multiple box plot in Figure 4 for Zn, Ni (and for Cu, Cd and Pb, not shown in the figure): there are two distinct groups of sites having high overall concentrations (Group 1: SDR01, SDR02, SDR03, SDR04 and SDR09) and low concentrations (Group 2: SDR05, SDR06 and SDR 07, and SDR08) (See Figures 4B and 4D). According to the Man-Whitney test, there is a statistically significant difference between the medians of the sites between the two groups at the 95% confidence level.

When plotting the group in the map, the groups tend to have a distinct spatial pattern whereas Group 2 sites with the lower concentrations align up along a line in the west parallel to the Drava River course, while Group 1 sites with the lower metal concentrations have a similar arrangement but located in the eastern part of the study area (Figure 1). This pattern may need further investigation to be explained. The concentration distributions of As, Cu, Cr and Hg, however, do not show similar grouping or spatial pattern (Figure 4).

Finally, an interesting and efficient way of identifying anthropogenic pollution is offered by plotting chemical elements against each other which have similar geochemistry under natural conditions. For example, since Zn and Cd have very similar chemical and geochemical behaviour, their plot shown in Figure 5A immediately reveals the site

SDR09 sediment samples as bivariate outliers having Cd concentrations far above those expected from the natural Zn-Cd relationship. Similarly, the Ni-Cr biplot shown in Figure 5B identifies sites SDR01 and SDR02, and site SDR06, as bivariate outliers having disproportionally high Cr content, which strongly suggests human contamination of sediments at these sites.

5. CONCLUSIONS

In general, there is no significant differences in metal(oid) HS concentrations among the various sediment types, should it be stream sediment (river bottom sediment) or floodplain sediment (overbank sediment), and top layer or deeper bottom layer sediment horizons. This suggests that the large lowland Drava River fluvial system is an extensive single fluvial system with homogeneous distribution of sediments and the associated contaminants. In terms of sediment quality monitoring design, the experienced homogeneity has important implications and it suggests that the various sediment types carry the same information therefore it is sufficient to monitor the easiest-to-collect one. Specifically, the studied sediments in the tributaries of the Drava River do not seem to be contaminated with metal(oid) hazardous substances but at certain sites concentrations are elevated above the environmental limit values. Important exceptions are As and Zn, and Cr to a lesser extent, having wide-spread pollution levels in the study area. From a methodological point of view, the proper use of data analysis techniques, together with the appropriate geochemical considerations, enabled the identification of sites with anthropogenic pollution and the recognition of regional pattern in HSs distribution.

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