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

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Abstract: Discharge of hazardous substances (HSs) in hydrographic basins represent a danger to aquatic biological activity and water supplies and can severely pollute surface water sediments. The increase of pollution in the Danube Basin requires the implementation of systematic monitoring and evaluation of the sediments quality as dictated by the EU Water Framework Directive. For this system development, applicable in mountainous conditions, the Upper Tisa region in the northwest part of Romania on the border with Ukraine, Hungary and Slovakia was selected as a test area. Sampling of overbank (floodplain) sediment, river bottom sediment and suspended sediment was carried out at 10 locations in the test area in order to analyze the concentration and distribution of eight metal(oid)s (Cu, Pb, Zn, Cd, Hg, Ni, Cr and As), in addition to 3 organic components (anthracene, fluoranthene, benzo(e)pyrene) as hazardous substances (HSs). The sediment quality assessment was carried out according to the 2013/39/EU Directive and EU Water Framework Directive standards. Most of the analyzed HS concentrations in river bottom sediment and overbank (floodplain) sediments fall within the limits of environmental quality standards (EQS). As, Cu, Pb, and Zn tend to exceed the EQS at some locations. The highest exceedances were recorded for Pb, for which contents of up to 987 mg/kg were detected. The highest contents were found in the overbank sediments sampled, and the lowest in river bottom sediments, which may indicate historical pollution. Mercury contents in overbank sediment samples exceed all standards, while cadmium content is below the international standards. Anthracene, fluoranthene and benzo(e)pyrene concentrations in overbank and bottom sediments comply with international standards. A few samples in suspended sediments slightly exceed the lowest environmental standard value (i.e., Romanian normal value). HS concentrations remain low in the suspended sediments showing that it is not the main transport route for pollution in this area. HS contents decrease gradually from upstream to downstream due to dilution along the river course. In the last testing point at Someș Aciua, the concentration of metal(oid)s measured in the sediments remain below the EQS limit values, thus there is no risk of transboundary pollution. The main source of metal(oid) contamination is historic base-metal ore mining and the associated mine waste sites in the Baia Mare and other mining areas scattered around the whole region. The main source of the studied organic compounds is the incomplete or low-temperature coal combustion processes that occur in households in rural areas.

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Key words: river sediment, monitoring, heavy metals, organic substances, EQS evaluation, correlation, sources, anthropic activity, geological background**.**

1. INTRODUCTION

This research was carried out in the Lăpus River catchment located in the Upper Tisa area within Danube River Basin (DRB) (Figure 1). The area is characterized by present and past mining activity, intensive industrial and agricultural activities, and a rising degree of urbanization that contributes to the overall sediment pollution. Concentrations of hazardous substances (HSs) due to anthropogenic activity can significantly increase in sediments (Šorša et al., 2019, Dudás et al., 2021).

This research was carried out within the SIMONA project (Sediment-quality Information, Monitoring and Assessment System to support transnational cooperation for joint Danube Basin water management- DTP2-093-2.1) which responded to the current needs for effective monitoring and assessment of sediment quality in surface waters of DRB by providing a ready-to-implement sediment quality information, monitoring and assessment system to support transnational cooperation for joint DRB water management (SIMONA 2018).

Mining was the major industrial activity in the study area, which significantly contributed to the high degree of environmental and human health degradation (Jelea & Jelea, 2007; Bouzekri et al., 2019). Mine waste, including large tailings deposits, can contain large amounts of potentially toxic metal(oid)s even after long periods, which are gradually released into the environment due to weathering and erosion (Perlatti 2021).

Mining is the major source of metal pollution in the environment (Bouzekri et al., 2019). Rodriguez-Hernandez et al., 2021; Burdzieva et al., 2018; Carrizales et al., 2006), including the wide-spread contamination of sediments of surface waters (Schweizer et al., 2018; Gibbs, 1973; Sindern et al., 2016).

Studies on sources of hazardous substances in sediments derived from agriculture and mining waste heaps were carried out in the Upper Tisa area by Maftei et al., (2014, 2018), Jaskuła et al., (2021) and in the Drava River area by Šajn et al., (2011) and Ajn et al., (2022).

Studies of the distribution of potentially toxic elements in river sediment from semi-arid areas by Rodriguez-Hernandez et al., (2021) and Montes-Avila et al., (2019) demonstrated that the high concentration and spatial distribution of potentially toxic metal(oid)s could reveal that mining waste was their main source in the near-site sediments.

Most of the countries in the DRB face serious challenges in implementing HS monitoring in the surface water sediments as required by the EU Water Framework Directive (WFD) and the 2013/39/EU Directive, due to the lack of harmonized international sediment quality monitoring protocols and procedures.

The objective of this research was to provide an assessment of HSs in river bottom sediments, suspended sediments and overbank (floodplain) sediments and compare them in terms of the main sedimentary transport routes in the mountainous conditions prevailing in the Upper Tisa test area where historic ore mining and associated metal industry are the main pollution sources (SIMONA 2018). The sediment quality assessment was carried out in accordance with the 2013/39/EU Directive and the EU Water Framework Directive requirements.

2. SITE DESCRIPTION

The studied Lăpuș River catchment is located in the Upper Tisa area, northwestern Romania, in the border region with Ukraine and Hungary and Slovakia (Figure 1a).

The prevailing relief in the area is mountainous and hilly in character (Posea et al., 1980) (Figure 1b). The nordeastern part is the Volcanic Mountains. In the south and southeast is the Preluca Massif crossed by the Lăpuș River. To the south and southeast of the Preluca Massif are the Boiu limestone plateau and the Breaza peak.

South of the Varatec-Tibleş Mountains is the Lăpuș hills and between the Preluca Massif and the Gutin Mountains are the Copalnic hills. In the western the plain of the Baia Mare Basin is found at the altitude of 200-220m a.s.l.

The 114 km long Lăpuș River springs from the Varatec Mountains where the Baiut mining area is found, and it discharges into the Somes River (Fig. 1b). The Lăpuș Basin covers 1820 km^2 and it has an asymmetric shape being much wider in the northeast with abundant tributaries.

The Preluca massif located in the southern part of the Lăpuș River catchment (Figure 2) consists of mesometamorphic rocks in the amphibolite facies (Kalmár, 1994; Balintoni; 1997), that consists gneiss, micaschists, dolomitic limestones, amphibolites, black quartzites, pegmatite, and manganese carbonates.

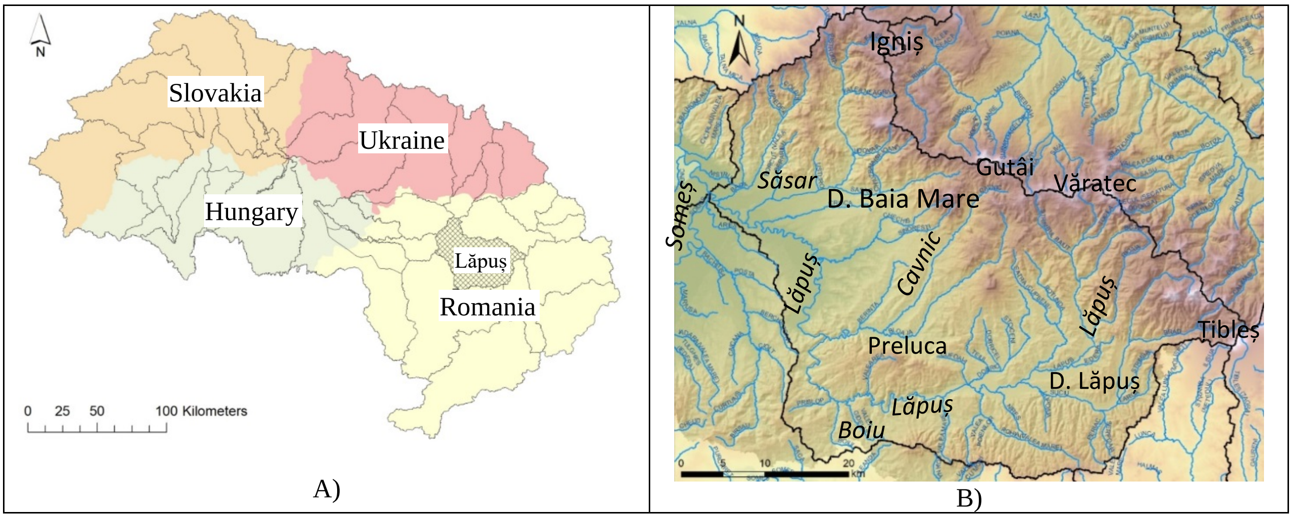

Figure 1. A. the location of the Upper Tisa area. Grey shading: location of the studied Lăpuș River catchment. B. The location of the Lăpuș River catchment within the Upper Tisa area. Black line shows the catchment boundary.

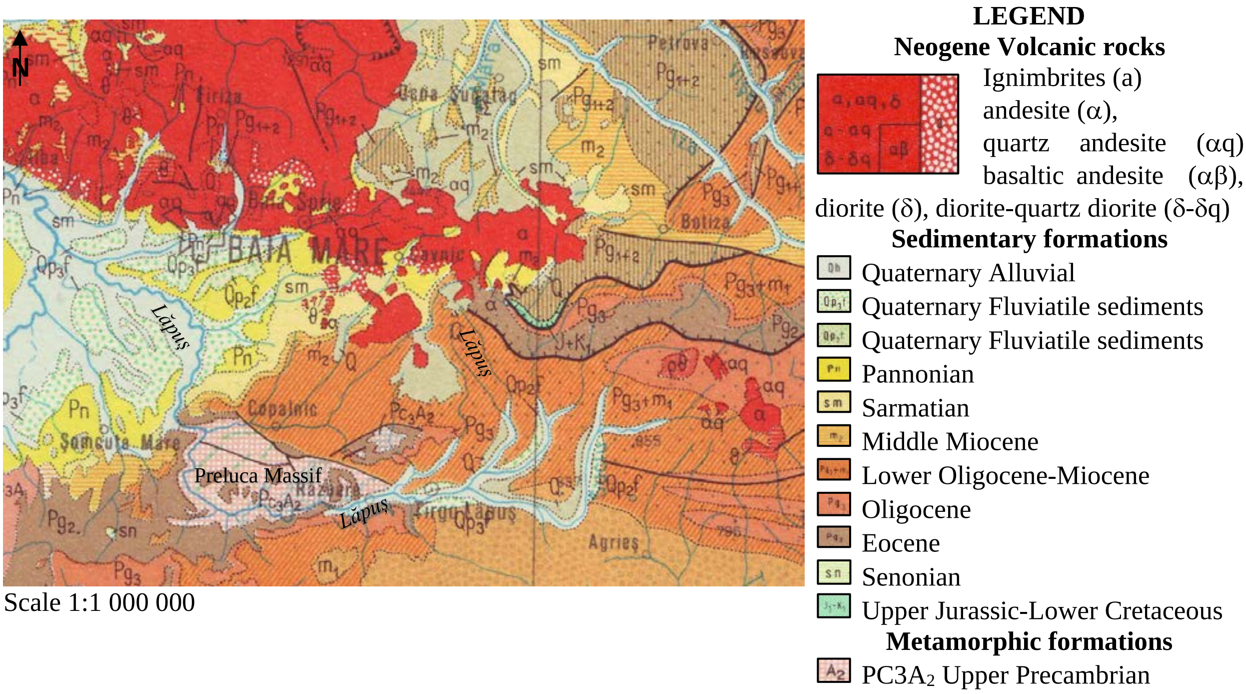

Figure 2. Geological map of the Lăpuș River catchment (after the Geological Map of Romania, 1:1,000,000).

Neogene magmatic rocks appear in the northern part of the study area. These are represented by Pannonian basaltic lava flows (Giuşcă et al., 1973; Borcoş et al., 1973) composed of quartz andesites, dacites, andesites with pyroxenes and amphiboles, pyroxene andesites (Lang et al., 1973) and andesites with biotite. Igneous rocks with a subvolcanic character appear in the eastern part of the area (Pop et al., 1984). According to the mineralogical and chemical composition, the following petrographic types were separated: porphyritic quartz-microdiorites, porphyritic quartz-micromonzodiorites, microgabbros, and tonalites (Pop et al., 1984).

3. MATERIALS AND METHODS

3.1. Sampling methods

The harmonised transnational sediment sampling was carried out according to the SIMONA Sediment Quality Sampling Protocol (Šorša, 2019) and the SIMONA Sediment Quality Sampling Manual (Jordan & Humer, 2021). The applied sampling methods benefit from the methods developed by past pan-European projects: the FOREGS (Forum of European Geological Surveys) Geochemical Baseline Programme (FGBP; Salminen, 2005) and the GEMAS Geochemical Mapping of Agricultural and Grazing land Soil Project (Reimann et al., 2014a; Reimann et al., 2014b), as further developed and adapted to sampling under regular monitoring conditions. Three types of sediments were sampled in this study:

- River bottom sediment (BS), sampled with the vacuum corer or scoop in small rivers (Jordan & Humer, 2021).
- Suspended sediment (SS), sampled by pumping water into a plastic water tank and letting the fine material settle for decanting.
- Overbank (floodplain) sediments (FS), sampled from sampling pits using a soil sampling spade, at two depths levels: 0-5 cm in the topsoil or top layer (FS TS) and 40-50 cm in the bottom layer (FS BS). Sampling at two depths had the objective to identify recent contamination and the earlier contamination, or possibly capture the pre-industrial natural background (Šajn et al., 2011).

The Lăpuș catchment includes the Lăpuș River with 6 sampling points, Cavnic and Săsar tributaries with 2 points and Someș River with 2 points: one upstream and one downstream of the discharge of the Lăpuș River.

River bottom sediment and overbank (floodplain) sediment samples were collected and stored in glass bottles. All the sealed samples were transported and stored dark and cool at a temperature between 2° and 8°C until laboratory analysis. Sample preparation and analysis were carried out at the Balint Analitika Ltd., Hungary, as the project reference laboratory (Čaić et al., 2019). Sample preparation included drying at 40°C until constant weight, followed by dry sieving though a 2mm nylon screen and homogenization before sending the samples to chemical analysis. The samples collected in suspension with the pump and water tank method were separated from the water by settling and decanting, followed by drying at 40°C.

3.2. Analytical methods

In this study, 8 metal(oid)s, 8 polycyclic aromatic hydrocarbons (PAHs) and 6 pesticides as hazardous substances (EQS, 2018) were selected for analysis.

Metal(oid)s (Table 1) were analysed with inductively-coupled plasma mass spectrometry (ICP-MS) after aqua regia extractionand. Organic substances were analysed the GC-MS and HPLC methods as presented by Čaić & Šorša (2019).

Eight metal(oid)s were analyzed: Cu, Pb, Zn, Cd, Hg, Ni, Cr and As, to which 3 organic components were added: anthracene, fluoranthene, benzo (e) pyrene. The analyses were done in the accredited reference laboratory Balint Analitika Ltd. in Budapest, Hungary.

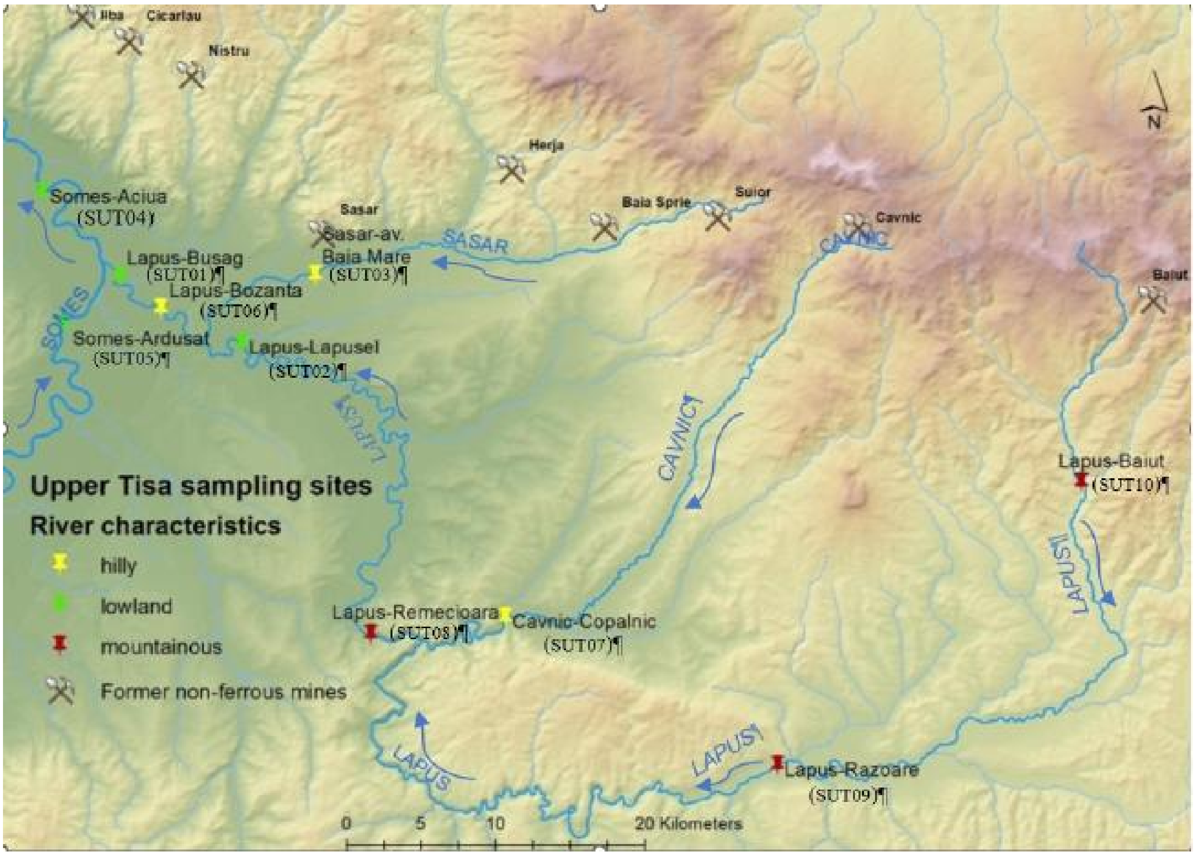

Figure 3. Location and topographic character (mountaneous, hilly, lowland) of sampling sites in the Lăpuș River catchment located in the Upper Tisa area.

4. RESULTS

This study discusses the concentrations of selected metal(oid) and organic hazardous substances in the sediments of the Lăpus River catchment, which is part of the Upper Tisa area (Figure 1; Table 1). International and national environmental standards were used to evaluate the level of contamination of the sediments in the Lăpus River catchment, according to the SIMONA Evaluation Protocol (Dudás et al., 2021).

4.1. Metal(oid)s in sediments

4.1.1. Arsenic

The Elbe upper limit value (Figure 4) is exceeded at the following sampling points: SUT01 Lăpuș Bușag, overbank sediment; SUT03 bottom sediment bottom layer; SUT03 overbank sediment topsoil; SUT06 located on Lăpuș River at Bozânta Mare, bottom sediment top layer and overbank top soil. The Dutch target value is exceeded in all of the collected sediment samples. The Romanian normal value standard is exceeded only in a few samples (Figure 4).

4.1.2. Cadmium

Total cadmium concentrations vary between 0.17 and 0.98 mg/kg. None of the samples exceeds the Romanian normal value (Figure 5).

River bottom sediment is slightly polluted with cadmium. Samples collected in the river bottom sediment top layer (0-5cm depth) exceed the Dutch target value. In all other samples the cadmium contents do not exceed any of the standards (Figure 5).

4.1.3. Copper

The copper contents vary a lot in the range 11.30-292.0 mg/kg. The Elbe River upper limit value is exceeded only at four points: SUT03, SUT06, SUT09 and SUT10 (Figures 3 and 6). At the sampling point SUT10 on the Lăpuș River downstream of Băiuț, the Elbe River upper limit value is exceeded for overbank sediment bottom soil (40-50cm depth), and at sampling point SUT06 Lăpuș Bozânta Mare and SUT09 Lăpuș Răzoare for river bottom sediment top layer. At the SUT03 Săsar River sampling point (Figures 3 and 6), the Cu concentration values are exceeded the Elbe River upper limit value in the overbank sediment top soil.

The Romanian standard alert value for soil is exceeded by several samples. Concentrations in overbank topsoil samples exceed the standard at sampling points SUT01, SUT03, and SUT10 (Figure 3). At point SUT03 copper concentration in river bottom sediment also exceeds the Romanian alert value. The Romanian soil standard value is exceeded at the vast majority of the sampling points (Figure 6).

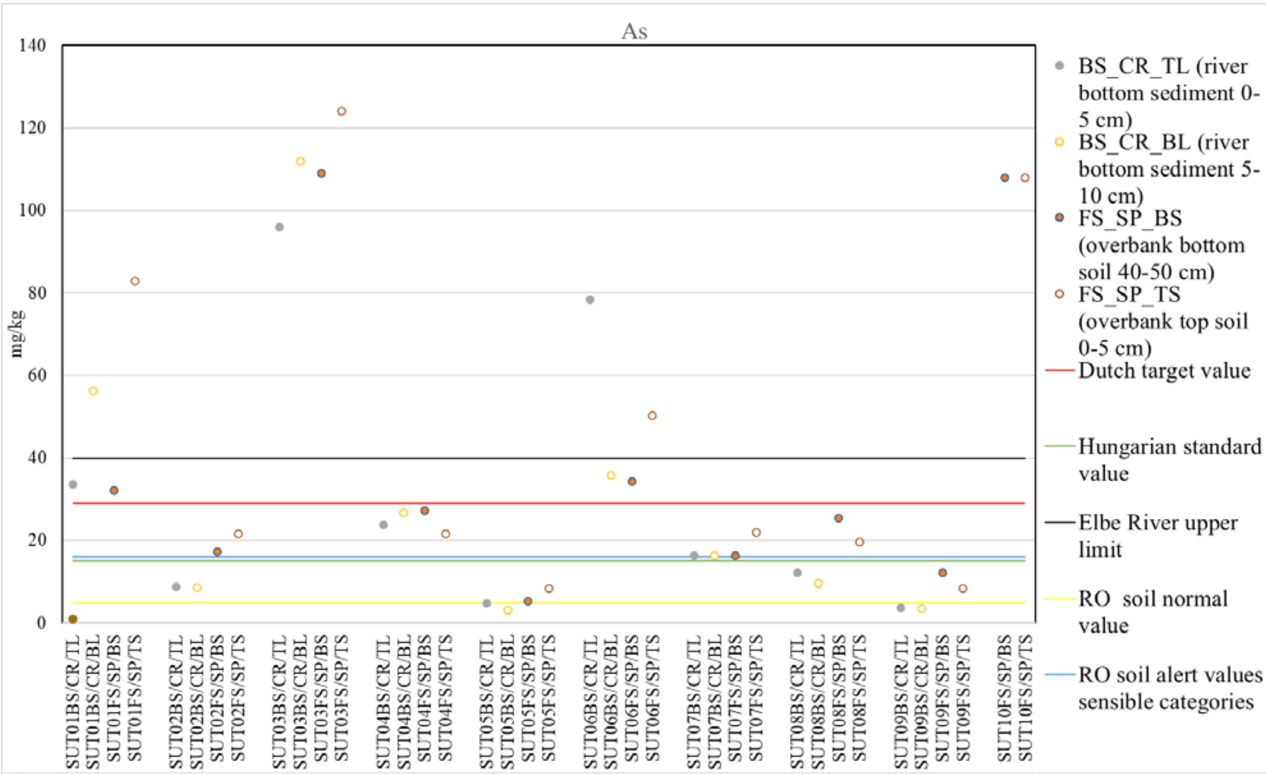

Figure 4. Arsenic concentration in the sediments in comparison with international standards

Table 1. Concentration of metal(oid)s in the sediment samples.

Samples	Sediments	As	Pb	Zn	Cu	Cd	Hg	Cr	Ni
SUT01BS/CR/TL	river bottom sediment 0-5 cm	33.50	97.60	479.00	36.10	0.73	0.09	65.10	7.24
SUT01BS/CR/BL	river bottom sediment 5-10 cm	56.20	178.00	526.00	62.20	0.43	0.37	25.10	9.91
SUT01FS/SP/BS	overbank bottom soil 40-50 cm	32.10	87.30	295.00	28.10	0.80	0.16	11.70	7.86
SUT01FS/SP/TS	overbank top soil 0-5 cm	83.00	354.00	860.00	110.00	0.18	0.33	41.50	27.00
SUT01SS/BR	suspended sediment	0.06	0.32	18.10	0.47	0.04	0.00	0.09	0.09
SUT02BS/CR/TL	river bottom sediment 0-5 cm	8.80	26.70	359.00	22.20	0.30	0.11	22.80	17.50
SUT02BS/CR/BL	river bottom sediment 5-10 cm	8.59	24.60	233.00	31.20	0.26	0.07	30.40	23.40
SUT02FS/SP/BS	overbank bottom soil 40-50 cm	17.20	62.30	583.00	55.70	0.51	0.17	40.40	29.60
SUT02FS/SP/TS	overbank top soil 0-5 cm	21.70	71.30	625.00	69.70	0.77	0.17	60.70	44.50
SUT02SS/BR	suspended sediment	0.01	0.05	0.71	0.05	0.0015	0.00	0.08	0.05
SUT03BS/CR/TL	river bottom sediment 0-5 cm	96.00	987.00	1800.00	292.00	0.46	0.30	60.80	30.30
SUT03BS/CR/BL	river bottom sediment 5-10 cm	112.00	476.00	1280.00	153.00	0.37	0.33	35.00	22.70
SUT03FS/SP/BS	overbank bottom soil 40-50 cm	109.00	287.00	2170.00	219.00	0.49	0.35	37.00	24.30
SUT03FS/SP/TS	overbank top soil 0-5 cm	124.00	448.00	1430.00	158.00	0.98	0.33	33.50	17.20
SUT03SS/BR	suspended sediment	0.18	1.22	4.09	0.82	0.025	0.00	0.07	0.04
SUT04BS/CR/TL	river bottom sediment 0-5 cm	23.80	96.70	597.00	67.10	0.82	0.44	63.30	43.30
SUT04BS/CR/BL	river bottom sediment 5-10 cm	26.70	101.00	504.00	62.70	0.42	0.33	64.40	43.10
SUT04FS/SP/BS	overbank bottom soil 40-50 cm	27.20	64.50	371.00	47.70	0.90	0.32	48.30	28.00
SUT04FS/SP/TS	overbank top soil 0-5 cm	21.70	56.50	281.00	49.10	0.88	0.39	73.00	48.60
SUT04SS/BR	suspended sediment	0.02	0.07	1.14	0.05	0.03	0.00	0.09	0.05
SUT05BS/CR/TL	river bottom sediment 0-5 cm	4.81	13.40	72.00	15.70	0.78	0.23	39.50	23.20
SUT05BS/CR/BL	river bottom sediment 5-10 cm	3.20	10.20	53.40	11.30	0.72	0.27	47.70	17.10
SUT05FS/SP/BS	overbank bottom soil 40-50 cm	5.32	14.10	68.00	15.80	0.75	0.42	34.60	19.10
SUT05FS/SP/TS	overbank top soil 0-5 cm	8.43	16.80	94.90	20.90	0.84	0.34	58.00	36.10
SUT05SS/BR	suspended sediment	0.01	0.03	0.18	0.05	0.0015	0.00	0.07	0.04
SUT06BS/CR/TL	river bottom sediment 0-5 cm	78.30	503.00	1390.00	191.00	0.62	0.59	26.70	19.80
SUT06BS/CR/BL	river bottom sediment 5-10 cm	35.80	127.00	666.00	82.50	0.65	0.38	18.70	11.50
SUT06FS/SP/BS	overbank bottom soil 40-50 cm	34.40	85.40	609.00	55.10	0.92	0.46	21.60	12.80
SUT06FS/SP/TS	overbank top soil 0-5 cm	50.20	220.00	647.00	89.40	0.59	0.37	42.10	26.80
SUT06SS/BR	suspended sediment	0.12	0.63	16.80	0.75	0.05	0.00	0.10	0.20
SUT07BS/CR/TL	river bottom sediment 0-5 cm	16.30	123.00	1110.00	82.20	0.72	0.23	22.40	18.10
SUT07BS/CR/BL	river bottom sediment 5-10 cm	16.30	143.00	1010.00	49.50	0.60	0.27	25.20	19.50
SUT07FS/SP/BS	overbank bottom soil 40-50 cm	16.30	134.00	975.00	65.80	0.31	0.26	30.50	19.60
SUT07FS/SP/TS	overbank top soil 0-5 cm	21.90	120.00	804.00	77.10	0.70	0.36	42.30	27.70
SUT07SS/BR	suspended sediment	0.02	0.15	14.00	0.18	0.06	0.0025	0.13	0.08
SUT08BS/CR/TL	river bottom sediment 0-5 cm	12.20	80.90	621.00	40.80	0.94	0.03	34.50	23.00
SUT08BS/CR/BL	river bottom sediment 5-10 cm	9.68	55.20	509.00	36.10	0.98	0.32	34.10	19.00
SUT08FS/SP/BS	overbank bottom soil 40-50 cm	25.40	168.00	766.00	75.00	0.90	0.10	44.90	26.20
SUT08FS/SP/TS	overbank top soil 0-5 cm	19.70	106.00	528.00	67.30	0.25	0.14	49.30	25.50
SUT08SS/BR	suspended sediment	0.04	0.16	10.00	0.54	0.02	0.0025	0.12	0.08
SUT09BS/CR/TL	river bottom sediment 0-5 cm	3.74	10.00	139.00	175.00	0.91	0.03	24.50	14.40
SUT09BS/CR/BL	river bottom sediment 5-10 cm	3.46	12.40	123.00	15.90	0.84	0.03	21.90	14.80
SUT09FS/SP/BS	overbank bottom soil 40-50 cm	12.10	26.40	280.00	66.40	0.36	0.07	60.40	27.30
SUT09FS/SP/TS	overbank top soil 0-5 cm	8.35	20.90	162.00	29.30	0.95	0.07	48.10	27.50
SUT09SS/BR	suspended sediment	0.10	0.10	9.61	0.80	0.02	0.0025	0.13	0.17
SUT10FS/SP/BS	overbank bottom soil 40-50 cm	108.00	306.00	732.00	175.00	0.25	0.58	73.30	40.10
SUT10FS/SP/TS	overbank top soil 0-5 cm	108.00	353.00	367.00	151.00	0.94	0.38	61.00	33.90
SUT10SS/BR	suspended sediment	0.35	0.21	9.47	2.32	0.02	0.0025	0.09	0.06
Dutch_target value		29	85	140	36	0.8	0.3	100	35
Hungarian limit value		15	100	200	75	1	0.5	75	40
Elbe River upper limit value		40	53	800	160	2.3	0.47	640	3
Romania soil normal value		5	20	100	20	1.05	0.1	30	20

The Dutch target value is exceeded by the samples discussed so far, in addition to the following samples: SUT04, SUT06, SUT07, SUT08, SUT09, in overbank bottom soil samples; SUT04, SUT02, SUT08 overbank top soil samples; SUT04, SUT01, SUT07 river bottom sediment bottom layer; and SUT04, SUT01, SUT07 in river bottom sediment top layer (Figure 6).

4.1.4. Mercury

Mercury contents are low, in general. All samples have values below the Romanian soil alert value. The Hungarian standard is exceeded only by a few samples (Figure 7): site SUT06 bottom sediment top layer and site SUT10 overbank sediment bottom soil.

It seems that elevated mercury concentrations are found in the overbank sediments and less in river bottom sediments. There are very few samples that do not exceed at least one of the environmental standard values of mercury (Figure 7).

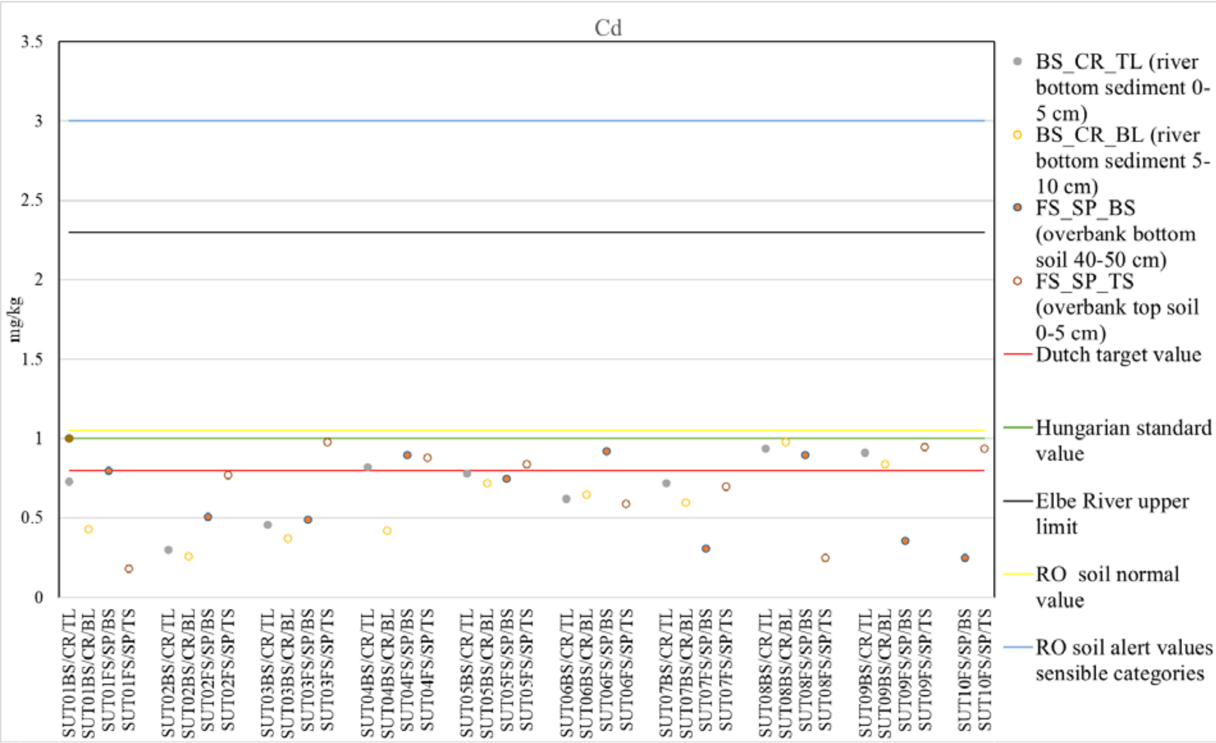

Figure 5. Cadmium concentration in the sediments in comparison with international standards

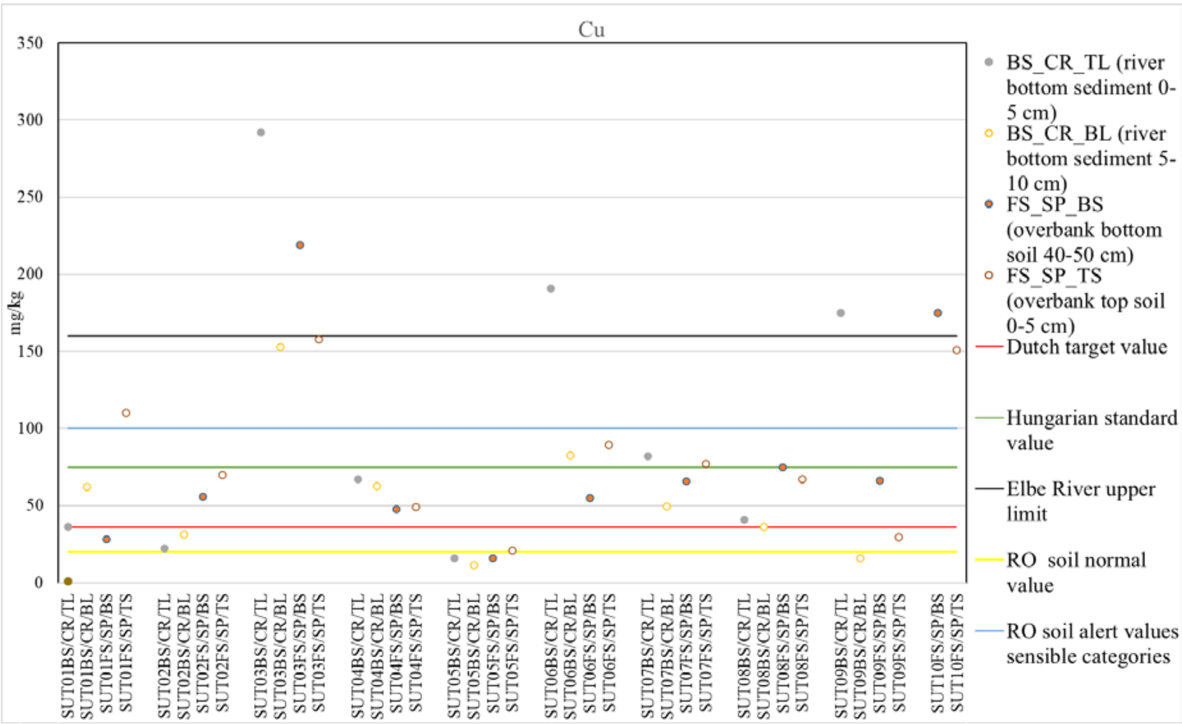

Figure 6. Copper concentration in the sediments in comparison with international standards

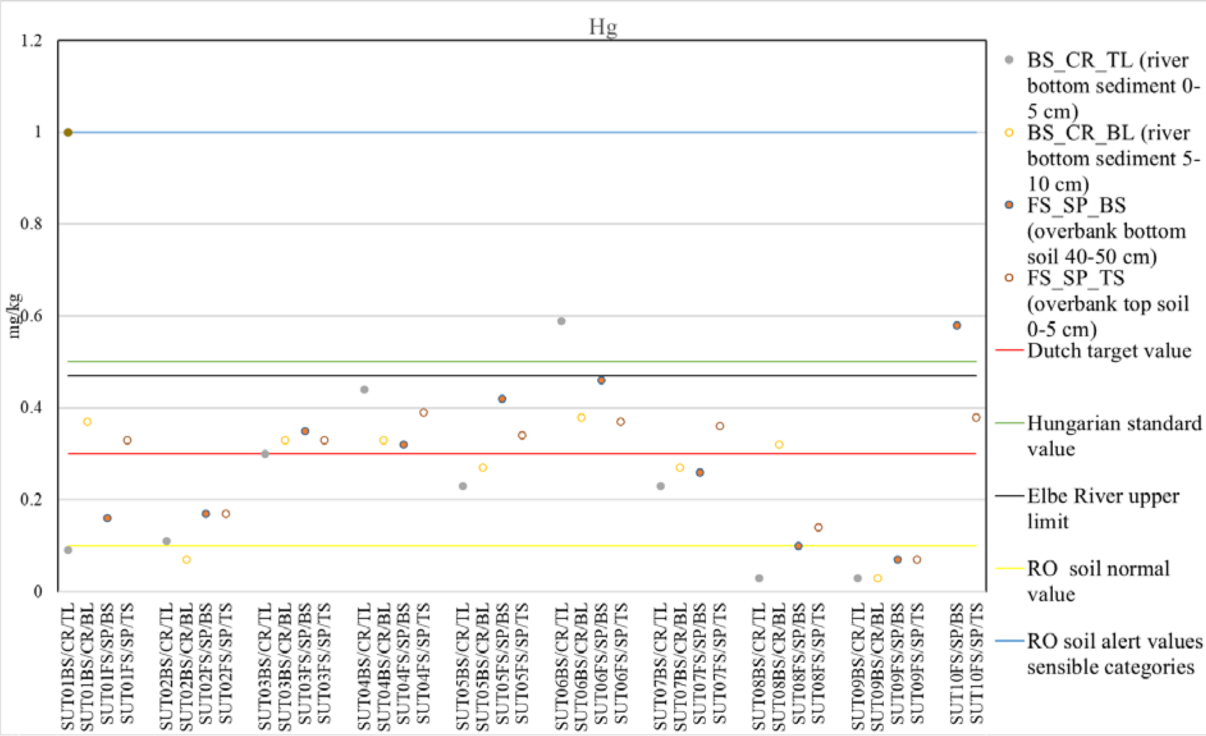

Figure 7. Mercury concentration in the sediments in comparison with international standards

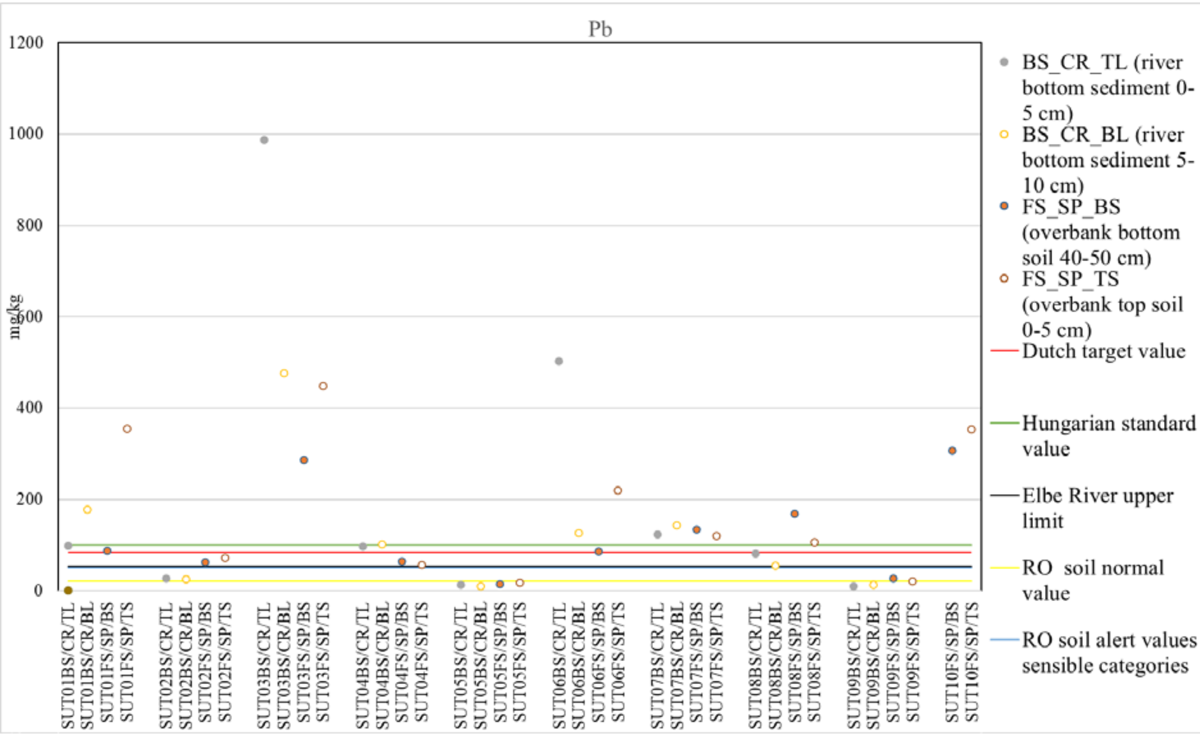

Figure 8. Lead concentration in the sediments in comparison with international standards

4.1.5. Lead

Lead exceeds all standards discussed apart from sites SUT05 Someș Ardusat and SUT09 Lăpuș Răzoare (Figure 8).

4.1.6. Zinc

The results of the analysis of Zn in the studied sediments indicate a large variation between 53.4-2170 mg/kg. The measured values only partially exceed all international reference values and especially the Elbe River upper limit value (Figure 9). Only at a single sampling location, SUT03 on Săsar River. all the sediment samples exceed the international and national environmental limit values. The Elbe River upper limit value (Figure 9) is exceeded at the following locations: SUT01 Lăpuș Bușag in overbank top soil; SUT06

Lăpuș Bozânta Mare in bottom sediment top layer; SUT07 Cavnic Copalnic in overbank sediment top and bottom soils, and in river bottom sediment top and bottom layers.

Most of the samples are projected between the Elbe River upper limit value and the Romanian normal value, indicating moderate Zn pollution levels (Figure 9). Contents that do not exceed any standard are found in all samples at the SUT05 Someș Ardusat site, and the bottom sediment bottom layer sample collected at the SUT09 Lăpuș Razoare site (Figure 9).

4.1.7. Nickel

Most samples are projected between the Hungarian standard limit at the top and the Elbe River upper limit value indicating low pollution (Figure 10).

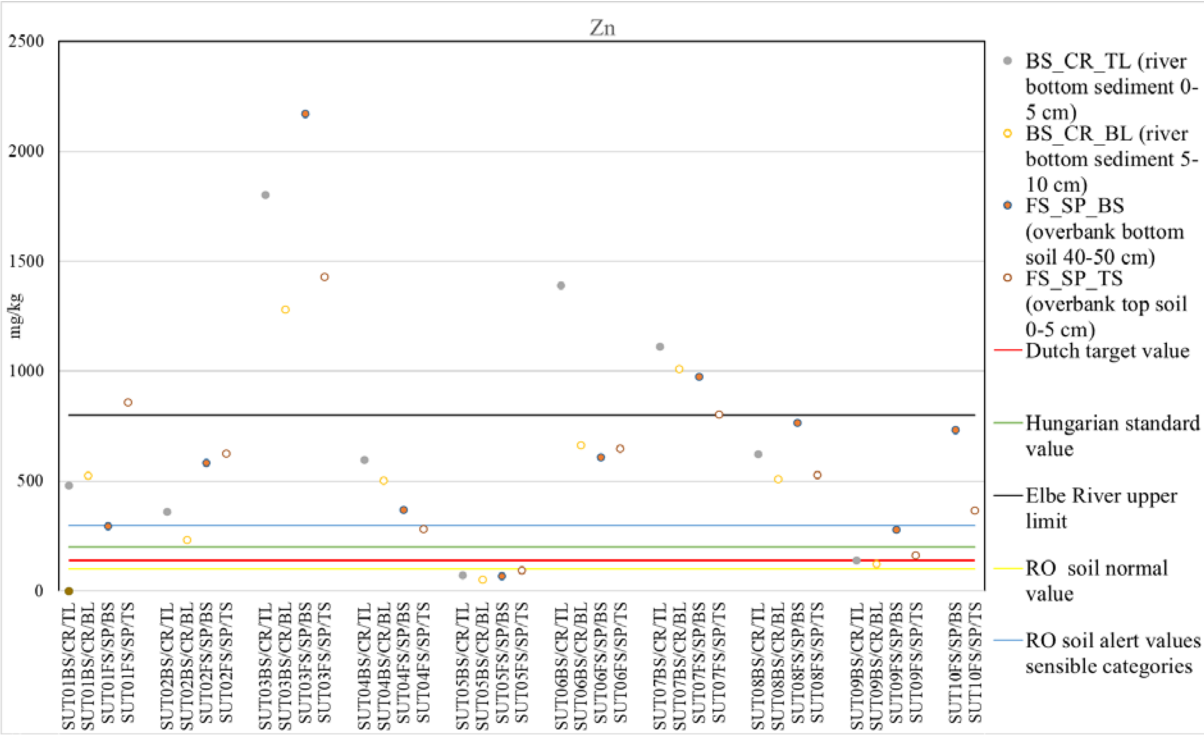

Figure 9. Zinc concentration in the sediments in comparison with international standards

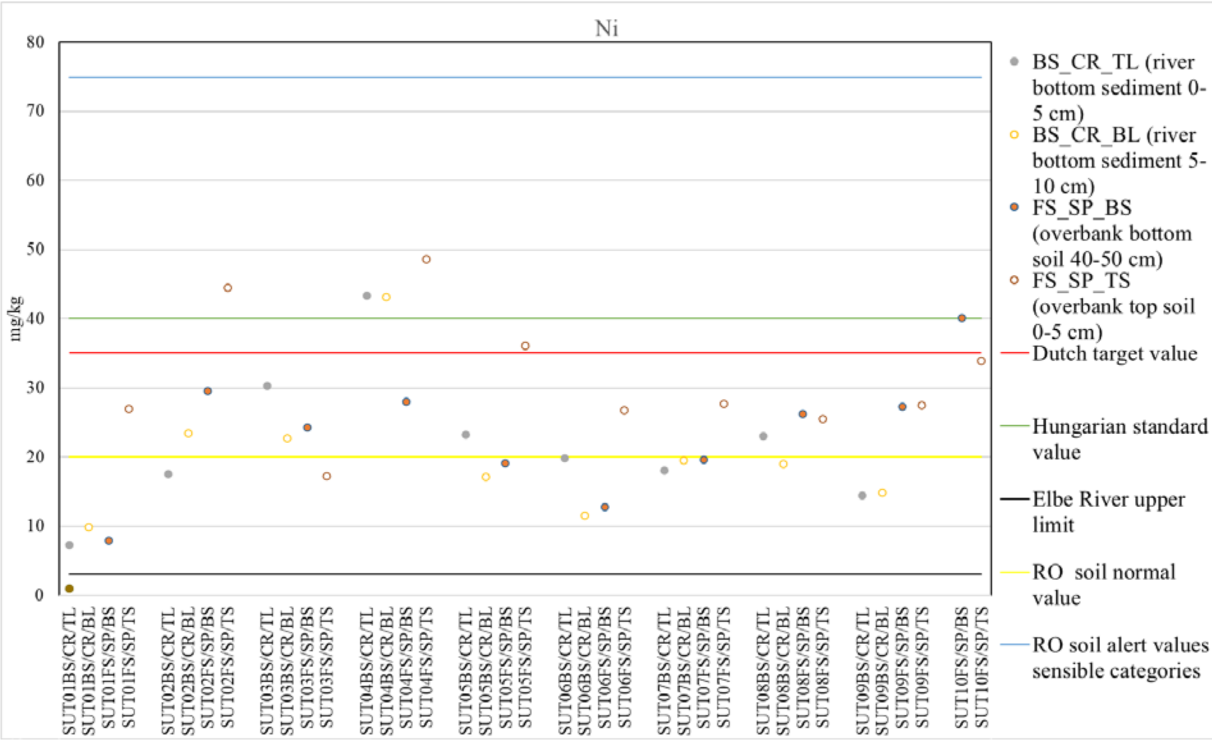

Figure 10. Nickel concentration in the sediments in comparison with international standards

Exceedance of the maximum standard value (Hungarian environmental limit) is found only in a few samples from the locations SUT04 Someș Aciua, SUT02 Lăpuș Lapușel and SUT10 Lăpuș Băiuț. Since these sites with high Ni contents are located downstream in the Lăpuș River catchment, it suggests that nickel has a source other than the Baia Mare mining area, where nickel does not accumulate in the ore (Mariaș et al., 2015; Buzatu et al., 2015; Damian et al., 2021).

4.1.8. Chromium

Chromium contents do not exceed even the highest Hungarian limit value, neither the Romanian soil alert value (Table 1). Most of the sediment samples have Cr concentrations below the Romanian soil normal value. In general, chromium contents are very low and do not indicate any pollution source.

4.2. Metal(oid)s in suspended sediments

The concentrations of metal(oid)s do not exceed the Romanian water standard for suspended sediment <63 micron and the Romanian soil normal standard value (Table 1). Transport of large amount of metal-polluted suspended sediment occur during flood events (Beuselinck et al., 2002). The suspended sediment studied in the Lăpus River catchment have low concentrations for all of the studied metal(oid)s showing that suspended sediment is not a major transport route for these elements, at least in the base flow conditions prevailing during the sampling campaign.

4.3. Organic components

The organic components analyzed in overbank and bottom sediments are anthracene, fluoranthene, and benzo(e)pyrene. For the most part, the results obtained show concentration values below the international and national standards considered in this study.

Fluoranthene contents are below the Romanian normal value. The Romanian normal value is exceeded only at three locations: SUT03 Săsar River, SUT01 Lăpuș Bușag and site SUT08 Lăpuș Remecioara (Table 2).

Benzo(e)pyrene is present in most of the sediment samples but in concentrations below the Romanian normal value. The This environmental standard is exceeded only at the following locations: SUT03 Săsar River and SUT10 Lăpuș Băiuț (Table 2).

Fluoranthene and Benzo(e)pyrene are present in all suspended sediment samples but its concentrations are extremely small and exceed slightly only the lowest standard, the Romanian normal value.

5. DISCUSSION

5.1. Assessment of heavy metals

Most of the analytical results of As, Cd, Cu, Pb, Hg, Zn, Ni, Cr (Figures 4-10, Table 1) fall between the Elbe River upper limit value and the Romanian standard value indicating an incipient pollution of the sediments in the Lăpus River catchment.

The highest exceedances of the standards for As are in the overbank areas indicating a historical pollution due to the uninterrupted mining activity for five centuries. Arsenic has been used for the production of pesticides in agriculture (Čaić Janković & Šorša, 2019). The Lăpuș River catchment area is a rural area with organic farming that does not use chemicals and pesticides, thus, agriculture is not a major source of As pollution.

In general, the cadmium contents are very low in the studied sediments and exceed the Dutch target value, mainly in the overbank sediments. The contents of Cd are higher in the river bottom sediment samples than in the overbank samples due to the high mobility of cadmium (Mao et al., 2020). Also, no obvious correlation of the Cd contents exists between bottom sediments and overbank sediments at the same sites. The Cd concentration in the studied bottom sediments is much lower than in the overbank areas, which may indicate a decrease of pollution in recent decades. Some of the bottom sediments with high Cd content could be the result of overbank erosion in periods of flooding or of mining accidents (Jelea et al., 2007).

The copper concentrations vary a lot in the range 11.30-292.0 mg/kg. The Elbe River upper limit value is exceeded in two samples only. Copper concentrations fall between the highest Elbe River upper limit and the lowest Romanian normal value indicating low sediment pollution. Very few samples have contents below the Romanian standard value.

Mercury belongs to the most toxic elements that can accumulate in soil and river sediment in abandoned mining areas that contain large amounts of cinnabar (Andráš et al., 2015; Baptista-Salazar et al., 2019; Rauf et al., 2020). Mercury readily accumulates in the ecosystems in the Upper Tisa area (Andráš 2022). Mercury has high contents mostly in the overbank sediment samples and lower concentrations in the river bottom sediment samples. This may indicate historical rather than recent pollution. The main sources of Hg are the mercury minerals, especially cinnabar (Damian & Damian 2004) from

Table 2. The organic components analyzed in sediments from Lăpuș River catchment

Samples	Sediments	PAH_Anthracene			PAH_Fluoranthene			PAH_Benzo(e)pyrene		
		Value mg/kg	Elbe River upper limit	RO soil normal value	Value mg/kg	Elbe River upper limit	RO soil normal value	Value mg/kg	Elbe River upper limit	RO soil normal value
SUT01BS/CR/TL	river bottom sediment 0-5 cm	*n.d.*	*n.d.*	*n.d.*	0.002	0.18	0.02	0.001	0.6	0.02
SUT01BS/CR/BL	river bottom sediment 5-10 cm	*n.d.*	*n.d.*	*n.d.*	0.001	0.18	0.02	0.001	0.6	0.02
SUT01FS/SP/BS	overbank bottom soil 40-50 cm	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
SUT01FS/SP/TS	overbank top soil 0-5 cm	0.001	0.31	0.05	0.010	0.18	0.02	0.003	0.6	0.02
SUT01SS/BR	suspended sediment	*n.d.*	*n.d.*	*n.d.*	0.070	0.18	0.02	0.069	0.6	0.02
SUT02BS/CR/TL	river bottom sediment 0-5 cm	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
SUT02BS/CR/BL	river bottom sediment 5-10 cm	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.001	0.6	0.02
SUT02FS/SP/BS	overbank bottom soil 40-50 cm	*n.d.*	*n.d.*	*n.d.*	0.001	0.18	0.02	0.001	0.6	0.02
SUT02FS/SP/TS	overbank top soil 0-5 cm	*n.d.*	*n.d.*	*n.d.*	0.002	0.18	0.02	0.001	0.6	0.02
SUT02SS/BR	suspended sediment	*n.d.*	*n.d.*	*n.d.*	0.066	0.18	0.02	0.038	0.6	0.02
SUT03BS/CR/TL	river bottom sediment 0-5 cm	*n.d.*	*n.d.*	*n.d.*	0.003	0.18	0.02	0.005	0.6	0.02
SUT03BS/CR/BL	river bottom sediment 5-10 cm	0.003	0.31	0.05	0.026	0.18	0.02	0.028	0.6	0.02
SUT03FS/SP/BS	overbank bottom soil 40-50 cm	0.001	0.31	0.05	0.023	0.18	0.02	0.008	0.6	0.02
SUT03FS/SP/TS	overbank top soil 0-5 cm	0.002	0.31	0.05	0.030	0.18	0.02	0.018	0.6	0.02
SUT03SS/BR	suspended sediment	*n.d.*	*n.d.*	*n.d.*	0.059	0.18	0.02	0.064	0.6	0.02
SUT04BS/CR/TL	river bottom sediment 0-5 cm	0.001	0.31	0.05	0.015	0.18	0.02	0.005	0.6	0.02
SUT04BS/CR/BL	river bottom sediment 5-10 cm	0.001	0.31	0.05	0.014	0.18	0.02	0.010	0.6	0.02
SUT04FS/SP/BS	overbank bottom soil 40-50 cm	0.001	0.31	0.05	0.006	0.18	0.02	0.004	0.6	0.02
SUT04FS/SP/TS	overbank top soil 0-5 cm	*n.d.*	*n.d.*	*n.d.*	0.003	0.18	0.02	0.001	0.6	0.02
SUT04SS/BR	suspended sediment	*n.d.*	*n.d.*	*n.d.*	0.035	0.18	0.02	0.037	0.6	0.02
SUT05BS/CR/TL	river bottom sediment 0-5 cm	*n.d.*	*n.d.*	*n.d.*	0.003	0.18	0.02	0.001	0.6	0.02
SUT05BS/CR/BL	river bottom sediment 5-10 cm	*n.d.*	*n.d.*	*n.d.*	0.001	0.18	0.02	0.001	0.6	0.02
SUT05FS/SP/BS	overbank bottom soil 40-50 cm	*n.d.*	*n.d.*	*n.d.*	0.001	0.18	0.02	*n.d.*	*n.d.*	*n.d.*
SUT05FS/SP/TS	overbank top soil 0-5 cm	*n.d.*	*n.d.*	*n.d.*	0.003	0.18	0.02	0.001	0.6	0.02
SUT05SS/BR	suspended sediment	*n.d.*	*n.d.*	*n.d.*	0.027	0.18	0.02	0.026	0.6	0.02
SUT06BS/CR/TL	river bottom sediment 0-5 cm	0.001	0.31	0.05	0.014	0.18	0.02	0.004	0.6	0.02
SUT06BS/CR/BL	river bottom sediment 5-10 cm	0.001	0.31	0.05	0.004	0.18	0.02	0.006	0.6	0.02
SUT06FS/SP/BS	overbank bottom soil 40-50 cm	*n.d.*	*n.d.*	*n.d.*	0.002	0.18	0.02	0.001	0.6	0.02
SUT06FS/SP/TS	overbank top soil 0-5 cm	0.001	0.31	0.05	0.011	0.18	0.02	0.005	0.6	0.02
SUT06SS/BR	suspended sediment	*n.d.*	*n.d.*	*n.d.*	0.077	0.18	0.02	0.066	0.6	0.02
SUT07BS/CR/TL	river bottom sediment 0-5 cm	*n.d.*	*n.d.*	*n.d.*	0.005	0.18	0.02	0.001	0.6	0.02
SUT07BS/CR/BL	river bottom sediment 5-10 cm	0.001	0.31	0.05	0.004	0.18	0.02	0.006	0.6	0.02
SUT07FS/SP/BS	overbank bottom soil 40-50 cm	*n.d.*	*n.d.*	*n.d.*	0.002	0.18	0.02	0.001	0.6	0.02
SUT07FS/SP/TS	overbank top soil 0-5 cm	0.002	0.31	0.05	0.008	0.18	0.02	0.002	0.6	0.02
SUT07SS/BR	suspended sediment	0.067	0.31	0.05	0.693	0.18	0.02	0.817	0.6	0.02
SUT08BS/CR/TL	river bottom sediment 0-5 cm	*n.d.*	*n.d.*	*n.d.*	0.001	0.18	0.02	*n.d.*	*n.d.*	*n.d.*
SUT08BS/CR/BL	river bottom sediment 5-10 cm	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
SUT08FS/SP/BS	overbank bottom soil 40-50 cm	0.003	0.31	0.05	0.022	0.18	0.02	0.007	0.6	0.02
SUT08FS/SP/TS	overbank top soil 0-5 cm	0.001	0.31	0.05	0.004	0.18	0.02	0.003	0.6	0.02
SUT08SS/BR	suspended sediment	0.079	0.31	0.05	0.588	0.18	0.02	0.865	0.6	0.02
SUT09BS/CR/TL	river bottom sediment 0-5 cm	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.002	0.6	0.02
SUT09BS/CR/BL	river bottom sediment 5-10 cm	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.004	0.6	0.02
SUT09FS/SP/BS	overbank bottom soil 40-50 cm	*n.d.*	*n.d.*	*n.d.*	0.002	0.18	0.02	0.001	0.6	0.02
SUT09FS/SP/TS	overbank top soil 0-5 cm	*n.d.*	*n.d.*	*n.d.*	0.002	0.18	0.02	0.002	0.6	0.02
SUT09SS/BR	suspended sediment	0.048	0.31	0.05	0.360	0.18	0.02	0.387	0.6	0.02
SUT10FS/SP/BS	overbank bottom soil 40-50 cm	0.003	0.31	0.05	0.016	0.18	0.02	0.016	0.6	0.02
SUT10FS/SP/TS	overbank top soil 0-5 cm	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.18	0.02	0.003	0.6	0.02
SUT10SS/BR	suspended sediment	*n.d.*	*n.d.*	*n.d.*	0.030	0.18	0.02	0.040	0.6	0.02

n.d. – not determined

the upper parts of the mineralized veins. Until the beginning of the 20th century, gold was processed using Hg (Bodiu et al., 1969; Beregic et al., 1985). Lead generally has concentrations that exceed all environmental standards which indicate widespread historical and recent pollution in the studied area. Sediments are the ultimate receptors of heavy metals (Luo et al., 2021). The high contents may also be due to the fact that lead forms poorly soluble compounds and persists in sediments for a long time (Pueyo et al., 2004) and can be transported and accumulated in the bottom sediments (Bouzekri et al., 2019). Galena (PbS), the main lead mineral, has high density, it tends to accumulate close to its source.

Zinc has high contents at Săsar River downstream of the Baia Mare because it collects all the streams in the mining and metallurgical area. High Zn contents exceeding the Elbe River upper limit value.

5.2. Evaluation of pollution along the river courses

The possible sources of contamination for the Upper Tisa sampling sites are presented along the water courses from upstream to downstream, also considering the tributaries. In this way, the spatial distribution of the selected HS concentrations and possible sources of contamination can be identified.

The sampling point SUT10 Lăpuş Băiuţ is located in the upstream area of the Lăpuş River (Figure 11). Arsenic and lead, partially copper, and mercury exceed the EQS limits. Concentrations of all the other elements analyzed Cd, Zn Ni, and Cr fall between the Elbe River upper limit value, the Ducth target value, the Hungarian limit value and the Romanian soil normal value. The source of these metal(oid)s in sediments is the mining activity. The Ni and Cr concentrations tend to be low in most of the samples.

At the next sampling point SUT09 Lăpuş Răzoare located downstream of the SUT10 Lăpuş Baiuţ point, the lower contents of heavy metals compared to the previous point are readily explainable by simple dilution caused by the tributaries of the Cisma River and the Suciu River discharging into the Lăpuş River which carry large quantities of unpolluted sediments from the mountain areas (Figures 3 and 11).

The sampling point SUT07 Cavnic Copalnic is located on the Cavnic River which is a tributary of the Lăpuş River downstream of the test point SUT09 Lăpuş Razoare and before the SUT08 Lăpuş Remecioara sampling point (Figure 11). Most prominently, the Pb and Zn contents exceed all of the EQS limits, and the other metal(oid)s also have high concentration values in the sediments. The source of metals is the mining activity in the Cavnic mining area located upstream of the sampling point (Figure 3).

The SUT08 Lăpuş Remecioara sampling point is located after the confluence of the Lăpuş River and the Cavnic River (Figure 11). Heavy metal contents are slightly higher than at the previous sampling points, because of the contribution of polluted sediments in the Cavnic River.

The SUT02 Lăpuş Lăpuşel sampling point is located downstream of Lăpuş Remecioara sampling site and before the discharge location of the Săsar River into the Lăpus River. The contents of metal(oid)s fall within the limits of EQS standard.

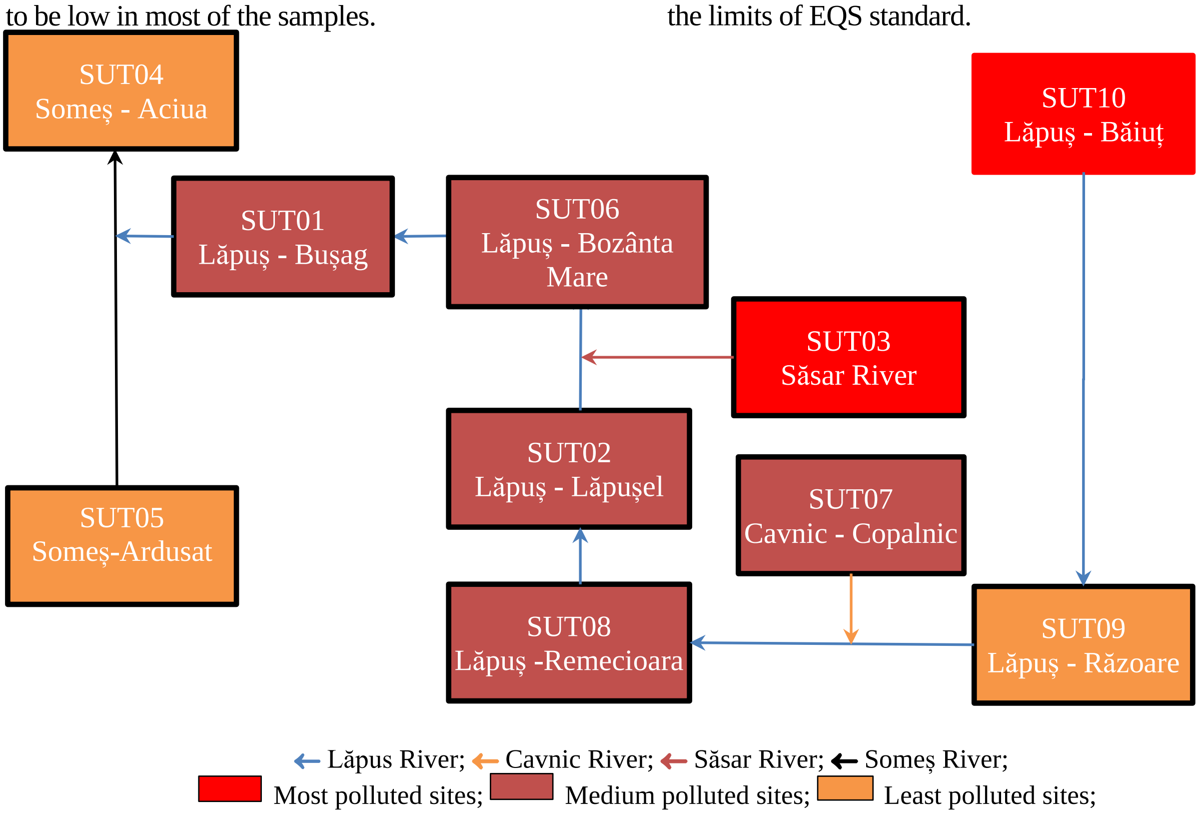

Figure 11. Upper Tisa sampling sites presented schematically from upstream to downstream

The Săsar River collects sediments from the Baia Mare mining area. At this sampling point the heavy metal concentrations exceed all limits for As, Cu, Pb, and Zn. The other components, Hg, and Ni are below the Elbe River upper limit value. The high values of heavy metals are due to the industrial activity of mining and metallurgy in Baia Mare.

The sampling site SUT06 Lăpus, Bozânta Mare is on the Lăpuș River downstream of the confluence with the Săsar River. The contents of heavy metals are higher than in the previous point SUT02 on the same Lăpuș River.

The sampling point SUT01 Lăpuș Bușag is located after the confluence with the Baița River, a tributary of the Lăpuș River, but before the confluence with the Someș River. The content of As, Pb, Zn is high mostly exceeding the limits of EQS standards. At this sampling point the Lăpus River collects all the sediments from the entire basin that covers most of the Baia Mare mining area, which explains the high Pb contents.

The contents of the studied metal(oid)s in all samples at the SUT05 Someș Ardusat site do not exceed the EQS limits, because the point is located on the Someș River before the confluence with the heavily polluted Lăpuș River.

The SUT04 Someș Aciua site lies the furthest downstream after the confluence of the Someș River and the Lăpus Rivers. EQS standards for heavy metals are not exceeded at this location. This is explained by the dilution of the heavily polluted Lăpuș River sediments with the high quantities of the much less polluted Someș River sediments.

Large amounts of mercury bound to organic matter in soils can reach river sediment (Baptista-Salazar & Biester 2019) which can explain the presence of Hg in quantities identical in the Someş River to those in the Săsar River and in the Lăpuş River. All metal(oid)s contents of the suspended sediment have concentrations below the EQS values including the Romanian soil standard limits.

Organic HS components have low concentration values in sediments at all sampling points and exceed occasionally only the Romanian standard value.

5.3. Correlation analysis of hazardous substances

The correlations among the studied metal(oid)s in the overbank sediments are presented in Tables 3-4. Significant positive correlations (higher than 0.75) are between Cu-Pb, Pb-Zn, Pb-As, Cu-As, and Zn-Cu indicating the same source (Suresh et al., 2011) from the base metal ore deposits from the Baia Mare mining area (Buzatu et al., 2015; Cook & Damian, 1997; Damian, 2000, 2003; Damian et al., 2008, 2020, 2021; Damian & Damian 2004; Mariaş 2005). The Cu-Zn correlation in the overbank bottom soil (40-50 cm) samples is less than in the overbank topsoil (0-5 cm). There is a moderate positive correlation between Zn and As which suggests their different sources and behavior in the studied sediments. The strong correlations of As-Pb and Cu-As indicate that the main source of As is mining activity (Bouzekri et al., 2019). Mercury in the overbank sediments has moderate correlation with As and moderate with Cu and Pb and no correlation with Zn and Cd. For Hg there could be several sources. Until the twentieth century, gold was extracted with mercury to obtain an amalgam (Beregic et al., 1985). We consider that through this mining operation method there were losses of Hg that were deposited in relatively old sediments currently located in the river overbank area. In base metal ore deposits, Cd is included in sphalerite (ZnS) (Buzatu et al., 2015, Damian et al., 2021) and should correlate with Zn. Cadmium could also have a source other than the base metal ore deposits in the Baia Mare area. A source of Cd could be the processing of ore concentrates in metallurgical plants. Cr and Ni have a strong positive correlation between them, but they have low correlations or no correlation with the other metals. The source of Ni and Cr is different from the other metals.

In the river bottom sediment, the correlations are similar to the overbank sediment samples. Among Cu, Pb, Zn, and As there are the same strong correlations (Tables 5 and 6) which indicate the ore mining in the Baia Mare area as their main source (Buzatu et al. 2015; Cook & Damian, 1997; Damian, 2000, 2003;

Table 3. Pearson's linear correlation coefficients between the studied metal(oid)s for the overbank sediment top soil (0-5cm depth) samples

	As	**Pb**	**Zn**	**Cu**	**Cd**	**Hg**	**Cr**	**Ni**
As	1							
Pb	0.980	1						
Zn	0.654	0.736	1					
Cu	0.957	0.956	0.721	1				
Cd	0.073	-0.092	-0.163	0.005	1			
Hg	0.440	0.434	0.212	0.405	0.109	1		
Cr	-0.390	-0.519	-0.715	-0.405	0.294	0.062	1	
Ni	-0.454	-0.552	-0.592	-0.449	0.237	0.100	0.933	1

Table 4. Pearson's linear correlation coefficients between the studied metal(oid)s for the overbank sediment bottom soil (40-50cm depth) samples

	As	**Pb**	**Zn**	**Cu**	**Cd**	**Hg**	**Cr**	**Ni**
As	1							
Pb	0.920	1						
Zn	0.700	0.754	1					
Cu	0.932	0.912	0.835	1				
Cd	-0.360	-0.398	-0.303	-0.508	1			
Hg	0.551	0.424	0.145	0.373	-0.090	1		
Cr	0.335	0.336	-0.004	0.438	-0.517	0.163	1	
Ni	0.409	0.441	0.147	0.516	-0.521	0.195	0.940	1

Table 5. Pearson's linear correlation coefficients between the studied metal(oid)s for the river bottom sediment top layer (0-5 cm depth) samples

	As	**Pb**	**Zn**	**Cu**	**Cd**	**Hg**	**Cr**	**Ni**
As	1							
Pb	0.951	1						
Zn	0.886	0.894	1					
Cu	0.786	0.850	0.729	1				
Cd	-0.427	-0.448	-0.389	-0.211	1			
Hg	0.615	0.480	0.563	0.373	-0.209	1		
Cr	0.367	0.324	0.162	0.091	0.050	0.155	1	
Ni	0.203	0.276	0.252	0.170	0.044	0.522	0.392	1

Table 6. Pearson's linear correlation coefficients between the studied metal(oid)s for the river bottom sediment bottom layer (5-10 cm depth) samples

	As	**Pb**	**Zn**	**Cu**	**Cd**	**Hg**	**Cr**	**Ni**
As	1							
Pb	0.971	1						
Zn	0.759	0.869	1					
Cu	0.949	0.955	0.855	1				
Cd	-0.487	-0.433	-0.290	-0.459	1			
Hg	0.492	0.468	0.527	0.533	-0.032	1		
Cr	-0.047	-0.054	-0.147	-0.029	-0.184	0.199	1	
Ni	0.001	0.042	0.082	0.121	-0.358	0.013	0.835	1

Damian et al., 2008, 2020, 2021; Damian & Damian 2004; Mariaş 2005). Mercury has moderate and low correlations with the other base metals, indicating a slight change in source (Li et al., 2022). In the last century, gold extraction has not used Hg, but gold was extracted with cyanide (Bodiu et al., 1969; Beregic et al., 1985). In this situation, the source of mercury was mainly the mining operations. Mercury occurs in the form of mineral cinnabar (HgS) in the ore deposits in this area and was present in the upper part of the deposits (Damian & Damian 2004). At the end of the 20th century, the ores in the Baia Mare mining area were extracted from great depths where the Hg contents were low, which explains the changes in the source of this metal.

There is a strong correlation between Ni-Cr in river bottom sediment but with a slightly lower value indicating that in recent sediments there could be source another than in overbank sediments. The source of Ni and Cr seem to be the geological background. In northern part of the Lăpuș River catchment, basaltic lava flows are extended. In the Săsar River catchment, there are large amounts of magnetite and titanomagnetite in sediments. Electronic microprobe analysis of these minerals indicates Cr_2O_3 = 0.003-0.086% and NiO = 0.13-0.024% contents, which explains the Cr and Ni contents in the sediments in the overbank and river bottom sediments. Other studies on stream sediments near ore deposits indicated that Cr and Ni are of natural origin (Li et al., 2017).

The association of seven heavy metals and As in the analyzed fluvial sediments indicates a mixed metal pollution (Zhou et al., 2020). Resongles et al., (2014) demonstrated that ancient mining activity still contributes to heavy metal enrichment in sediments in Gardon River, Southern France. Rieuwerts et al., (2014) also showed that the Tamar Valley located in southwest England remains extremely polluted by the historical mining and processing of ores. The metal contents of the old overbank sediment in the Lăpuș River catchment are higher than those in the river bottom sediments. In the Baia Mare area, there is a mining waste heap since the

Middle Ages. According to these data and those presented by Resongles et al., (2014) and Rieuwerts et al., (2014), the old mining activity can contribute to the enrichment of heavy metals in the recent sediments in the Lăpuș River catchment.

Studies carried out in other areas on river sediments (Maftei et al., 2018) indicated that the source of metals such as Mg, Ti, Ni, and Cr is mainly geogenic, and anthropogenic input was detected only near abandoned mining sites.

The analyzed organic components (anthracene, fluoranthene, benzo (e) pyrene) in overbank sediments have low values and are below the international and national standards. The presence of these components may be due to the mining activity in the Baia Mare area and the widespread use of wood as a fuel for heating homes. Organic matter in the sediment is known to play an important role in the adsorption and retention of heavy metals (Sabo et al., 2013).

Anthracene has been found in the environment in surface water and drinking water, exhaust emissions, cigarette smoke, smoked foods and edible aquatic organisms (Faust 1991). Anthracene was detected at the single SUT01 Lăpuș Bușag location in overbank sediment and could come from exhaust emissions because this sampling site is close to transport routes.

Fluoranthene occurs in small amounts in overbank sediment. Also, all the suspended sediment samples contained some fluoranthene but the contents barely exceed the Romanian standard value. Fluoranthene is produced as a result of incomplete combustion of solid fuels. Charcoal production by incomplete combustion method in this area can be another source of fluoranthene.

Benzo(e)pyrene is present in all samples collected from suspended sediment and from samples collected from overbank sediment and river bottom sediment from all locations. The contents are very small and barely exceed the Romanian standard value. This organic compound is generated during incomplete low temperature combustion processes that take place in households (mainly in rural areas) or during road transport in urban areas, or where rivers flow near national high ways.

6. CONCLUSIONS

For the evaluation of the sediment quality in accordance with the 2013/39/EU Directive and the EU water Framework Directive 10 sampling points were selected, 8 of them in Lăpuș River catchment and two in the Someș River. The Lăpuș River is a tributary of the Someș River.

Most of the HSs analyzed (As, Cd, Cu, Pb, Hg, Zn, Ni, Cr and organic substances) from river and overbank sediments fall within the limits of environmental quality standards. Only As, Cu, Pb, Zn in overbank sediment samples and, to a smaller extent from river sediments, exceed the international and national standards. Of these, Pb exceeds international standards the most frequently.

Mercury has excess concentration in three overbank sediment samples. Ni is exceeded in the sediments taken from the Someș River and Cr has contents that do not exceed the Romanian standard. In suspended sediments, the contents do not exceed any limit.

The organic components in overbank and river bottom sediments, anthracene, fluoranthene, benzo(e)pyrene, have low values and are below the international and national standards. In many samples, the contents were below the detection limit. Higher contents of organic substances (fluoranthene and benzo (e) pyrene) are found in suspended sediments, but only slightly exceed the Romanian standard value.

The most polluted sites are SUT03 Sasar River and SUT10 Lăpuș Băiuț, while the least polluted are SUT05 Someș Ardusat and SUT09 Lăpuș Razoare. A decrease of heavy metal concentrations can be observed from SUT10 Lăpuş Băiuț, to SUT04 Someș Aciua. The significant variations of heavy metal concentrations are related to the sources of pollution at different locations and the discharge of unpolluted river sediment from the tributaries. At the SUT04 Someș Aciua location the environmental limits for heavy metals are not exceeded.

At SUT05 Someș Ardusat the contents for heavy metals in all samples for this location do not exceed the EQS limits because the point is placed on the Somes River upstream of the confluence with the Lapuş River polluted by ore mining.

Since in Someş River, after diluting the sediments from the Lapuş River tributary, the HS contents do not exceed the EQS limits and the suspended sediment contents are very small, thus, there is no possibility of transborder pollution. The transport of sediments from river bottom sediments can only be carried out at high river flows and only over short distances.

The main source of HSs is mainly the anthropic activity of ore mining and processing of base-metal ores from the Baia Mare mining area. Zinc frequently forms soluble compounds that can be leached from the surface of the sediments by rainfall or floods, which explains the lower contents in the upper part of the overbank sediments. The HS contents in the old overbank sediments are higher than those in the river bottom sediments may be due to historic industrial activity. Until the beginning of the 20th century, tailings from processing stations were discharged directly into the rivers and accumulated in the overbank sediments (Beregic et al., 1985). In the Baia Mare area, there is a mining waste heap from the Middle Ages which could be another source of pollution. Thus, the old mining activity can contribute to the enrichment of current sediments with heavy metals.

For Hg there are several sources such as the ore deposits and other human activity. Gold extraction was done with mercury to obtain a mercury amalgam in the Middle Ages until the end of the 20th century. The extraction method caused losses of Hg that was deposited in relatively old sediments currently located in the overbank. Cadmium would have another source than the deposits of non-ferrous ores in the Baia Mare area and could also come from metallurgical plants.

Chromium and Ni have a different source from the other HSs. The source for Ni and Cr is mainly the geological background.

The identified organic compounds are generated during incomplete or low temperature combustion processes occurring in households (mainly in rural areas) or during road transportation in urban areas or where the rivers flow near heavy traffic national and express roads. The presence of these components cannot be associated with the mining activity in the Baia Mare area because the mines were closed in 2006.

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