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ASSESSMENT OF RIVER SEDIMENT QUALITY ACCORDING TO THE EU WATER FRAMEWORK DIRECTIVE IN LARGE RIVER FLUVIAL CONDITIONS. A CASE STUDY IN THE LOWER DANUBE RIVER BASIN

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Abstract: Increase of pollution of surface water and water sediments with hazardous substances (HSs) in the Danube River Basin requires implementation of systematic monitoring and evaluation of the sediment quality. The present study is focused on the 'South Danube' Test Area (SDTA) that covers parts of the Lower Danube Basin in Romania, Serbia and Bulgaria. The SD area represents an extended region where Danube reaches its largest widths and depths and where pollution (industrial, mining, agricultural, waste etc.) from tributaries and land is supposed to accumulate in the sediments. Sampling of river bottom sediment (BS), suspended sediment (SS) and overbank (floodplain) sediment at two layers (0-5 cm in the top layer (FS TS) and 40-50 cm in the bottom layer (FS BS)), was carried out at 11 locations in order to analyze the concentration and distribution of 8 metal(oid)s (Cu, Pb, Zn, Cd, Hg, Ni, Cr, As), 6 polycyclic aromatic hydrocarbons (PAHs) and 6 pesticides as hazardous substances. The 2013/39/EU Directive and EU Water Framework Directive standards were used to sediment quality assessment. As a whole, the concentrations of heavy metals in the sediments are comparatively low and are around the normal values for soils. On the other hand, some sampling sites and sediment types have high or very high metal concentrations which exceed intervention levels. Our study well recognizes mining pollution sources in the Danube tributaries Borska Reka, Timok, Ogosta, Malak Iskar and Iskar from past and/or recent mining activity. This pollution is limited to the Danube tributaries and around their confluences into the Danube River. The concentration of heavy metals is strongly diluted in the Danube River and drops around normal values. The studied sediments reveal low concentrations of PAHs. Only fluoranthene content is higher in most of the sediment types and sampling sites on the Danube River, but exceeds the interventional level only at Pristol and at Hârșova. Our results show that the sediments in the Danube River are more polluted with PAHs than its tributaries. The identified organic compounds are assumed to be generated during incomplete or low temperature combustion processes or during road transportation and/or the navigation on the Danube River.

Keywords: monitoring, sampling, hazardous substances, heavy metals, organic substances, geological background, environmental quality standard (EQS), Danube River Basin.

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1. INTRODUCTION

Hazardous Substances (HSs) pollution can cause severe damage to the ecosystems and can have direct effects to the health of the human population. Steady or accidental pollution of surface waters and related biota and river basin sediments may have fast and persistent effect on the ecosystems and should be therefore monitored for HSs following EU directives.

The monitoring of 45 HSs in the surface water sediments of the Danube River Basin (DRB) region following the EU Water Framework Directive (WFD) (EC 2000) and the 2013/39/EU Directive (EC 2013) is partly hampered by the lack of harmonized international sediment quality assessment protocols and procedures.

In order to tackle this gap of the DRB countries and reach a common knowledge and skills of governmental bodies, sectoral agencies, public authorities and academic institution, a joint project of the Danube Transnational Programme (DTP) financing instrument under the European Union Interreg cooperation programme was started in 2018, called SIMONA: **S**ediment-quality **I**nformation, **Mon**itoring and **A**ssessment System to Support Transnational Cooperation for Joint Danube Basin Water Management (https://www.interreg-danube.eu/approved-projects/simona). The SIMONA partnership had 17 full partners (research organizations) and 13 associated partners (government agencies) representing all of the 14 Danube Countries and covering the whole Danube River Basin. The project aimed at delivering a sediment-quality monitoring system for the effective and comparable measurements and assessments of sediment quality in surface waters in the DRB.

In the SIMONA framework, three DRB test areas with distinct characteristics were preselected: Drava, Upper Tisa and Lower Danube (called "South Danube"). The Drava test area is an agricultural plain, where pollution from agricultural lands was expected and assessed (Šorša et al., 2022). The Upper Tisa test area located on the Somes River and its tributaries is a mining region with base metal mines in the NE part of Romania, East Carpathians where past mining activity was shown to be a main source for elevated metal contents (e.g., Pb and Cd content; Damian et al., 2022).

The present study is focused on the "South Danube" (SD) test area (TA) that covers parts of the Lower Danube Basin in Romania, Serbia and Bulgaria. The SD area represents an extended region where Danube reaches its largest widths and depths and where pollution (industrial, mining, agricultural, waste etc.) from tributaries and land is supposed to accumulate in the sediments (Figure 1).

Three types of rivers (fluvial) sediments were object of studies: river bottom sediment (stream sediment), overbank sediment (floodplain sediment), and suspended sediments where available in the quantities sufficient for laboratory analysis. They were chosen, as the monitoring of the HSs in suspended and bottom sediments characterises the routes in large river conditions prevailing in the South Danube test area where historic and present ore mining (Bird et al., 2010a; b) is associated with other industrial and agricultural pollution. Sampling, analytical work and sediment quality assessment was carried out in

Figure 1. Location of the South Danube Test Area

accordance with the 2013/39/EU Directive and the EU Water Framework Directive requirements (EC 2010; EC 2018), following the recommendations of the SIMONA harmonized protocols (Šorša et al., 2019).

2. STUDY AREA

The DRB is the most international river basin in the world, whereas the South Danube Test Area (Figure 1) encompasses 3 countries: Bulgaria (BG), Romania (RO) and Republic of Serbia (RS). The prevailing climate is continental with 17 °C average annual temperature and 600 mm average annual precipitation. The geology of the study area is diverse comprising rocks of different ages (from Precambrian to Neogene), genesis (magmatic, metamorphic and sedimentary) and composition (from basic-ultrabasic to acidic). The geomorphology in the Danube River and its catchments varies from mountainous (Balkan-Carpathian Mountains) to hilly areas with various land cover categories (the Forebalkan) and plain (Danube plain). Historic mining since Roman times is known in the Balkan-Carpathian areas, some of the mines still being active (e.g. Bor, Veliki Krivelj, Majdanpek, Elatsite; Ciobanu et al., 2002; Gallhofer et al., 2015). Of particular importance in the Lower Danube drainage basin are Cu and Cu–Au ore deposits in the Bor mining region of Eastern Serbia and the Panagyurishte metallogenic zone of Central Bulgaria associated with the Apuseni–Banat–Timok–Srednogorie (ABTS) belt (Ciobanu et al. 2002; Gallhofer et al., 2015 - Fig. 2). The latter represents a present day L-shaped structure of Late-Cretaceous calc-alkaline magmatic activity within the Alpine–Carpathian–Balkan–Dinaride orogen of Eastern Europe that it is related to northward subduction of the Vardar Ocean crust beneath the European margin (Gallhofer et al., 2015). The ABTS belt ore deposits are linked with large Miocene base metal deposits in the southern Apuseni Mountains of Romania (Kouzmanov et al. 2005).

The plain areas in the study region are covered with agricultural lands. The Danube plain is among the most fruitful land in Bulgaria and Romania and since ancient time used for corn, cereal crops, vegetables and fruits. In the modern times water of the Danube tributaries and Danube River are used for land amelioration and leaching of fertilizers and pesticides from extensive agriculture in the past (diffuse pollution sources) might be considered a possible source of water and sediment pollution.

The SDTA is also known as industrial region, where big chemical and metallurgical plants are located (e.g. in Svishtov, Giurgiu, Călărași). The Romanian and Bulgarian capitals Bucharest and Sofia and many medium and small cities and villages are located in DRB, too. They are considered potentially influencing the quality of water and sediments due to sewage discharge in the catchments (e.g., point pollution sources with PAHs emissions). Another possible type of pressure on the SDTA is the river regulation by construction of water reservoirs and hydroelectric plants on the Danube River tributaries (e.g. Ogosta Dam; Zhelezov & Benderev, 2021), affecting the erosion and deposition of sediments and the quality of fluvial sediments.

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 et al., 2019) and the SIMONA Sediment Quality Sampling Manual (Jordan & Humer, 2021a). 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; b), as further developed and adapted to sampling under regular monitoring conditions. Three types of sediments were sampled in this study by entities (Table 1) in the 3 countries of DRB:

- river bottom sediment (BS), sampled by a vacuum corer or scoop (Jordan & Humer, 2021 a; b);
- suspended sediment (SS), sampled by a plastic water tank (with or without pumping) and letting the fine material settle for decanting;

Table 1 Entities which performed the sediment sampling

Country	Entity (abbreviation)
Bulgaria (BG)	Geological Institute of the Bulgarian Academy of Sciences (GI-BAS)
Romania (RO)	Geological Institute of Romania (IGR), National Institute for Hydrology and Water Management (INGHA) - subcontracted
Republic of Serbia (RS)	"Jaroslav Černi" Institute (JCI), University of Belgrade - Faculty of Mining and Geology (UB-FMG)

- overbank (floodplain) sediments (FS), sampled from sampling pits using a soil sampling spade and knife, at two levels of depths: 0-5 cm in the topsoil or top layer (FS TS) and 40-50 cm in the bottom soil (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). For the sampling sites in BG only the 0-15 cm and in RS the 0-30 topsoil was sampled using auger sampler.

Eleven sampling sites (Figure 1) were selected in the South Danube test area following as much as possible the criteria prescribed in the standards ISO 5667-12:2017 and ISO 5667-17:2008, recommendations in the Guidance Document No. 25 (EC, 2010), and the accumulated knowledge and experience of the Trans-national Monitoring Network (TNMN) in the Danube River Basin. The main applied site selection criteria were the following: (a) trans-national character of the sampled water body; (b) different hydromorphology and size (medium or large) of the represented catchment, including the Lower Danube River section as well; (c) existing sediment or water monitoring sites; (d) covering areas with various geology; (e) representing diverse pol-lution sources; (f) good infrastructure for site access.

The sampling sites with coordinates and sample types are presented in Table 2. They include 5 samples at tributaries: Borska Reka River – RS; the transboundary section of Timok River – BG/RS; Iskar River, upstream to the confluence with Danube – BG; Malak Iskar River, tributary of Iskar River, – BG; and Ogosta River at Mizia – BG. The sampling point of the Ogosta River is assumed to represent the potential pollution from the past mining activities in the area. Two RO sampling points are at the lower Jiu River and Lower Olt River. Finally, three transnational sampling points are located on the Danube River: near Pristol (RO), near Svishtov- Zimnicea (BG-RO) and near Oltenita (RO) (Figure 1; Table 1). In addition, a station at Hârșova was added in order to check the 'good status' of water body in this part of the Danube Basin.

As a result of a pre-sampling survey, three preselected sampling sites were relocated either due to the presence of industrial plant or waste, or due to dangerous sampling conditions (the new coordinates listed in Table 2).

Transverse profiles were sampled at 3 sampling points (Pristol, Svishtov-Zimnicea and Oltenița; Figure 1), with 3 verticals: Left (50 m from the left Danube bank, Centre (in the middle of the river) and Right (50 m from the right bank). For suspended sediments, at each vertical, water was pumped from 3 depths in to a 90L plastic tank (Vîjdea et al., 2022).

All types of sediment samples (bottom sediment, overbank (floodplain) sediment, suspended sediment) were collected as composite samples. A composite sample of bottom sediment
consists of three sub-samples collected at approximately equal intervals (50 m) along a 150 m section of river. For overbank (floodplain) sediment sampling, three 50 cm deep holes were dug along the 150 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.

Field documentation included field photographs and completion of the standard SIMONA Sampling Protocol field sheets.

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

Table 2 South Danube Test Area sampling sites

No.	Name of the river	Name of the site	WGS Long	WGS Lat	Suspended sediment	Bottom sediment	Floodplain sediment	Responsible for sampling
1.	Borska Reka	Rgotina	44.03049	22.21088	no	yes	yes	JCI-UB/ GI-BAS
2.	Timok	Timok at Bregovo	44.10397	22.57042	no	yes	yes	JCI-UB/ GI-BAS
3.	Ogosta	Ogosta before Danube at Mizia	43.691609	23.826234	no	yes	yes	GI-BAS
4.	Malak Iskar	Malak Iskar near Roman	43.135981	23.926079	no	yes	yes	GI-BAS
5.	Iskar	Iskar before Danube at Baykal	43.703047	24.456328	no	yes	yes	GI-BAS
6.	Danube	Danube at Svishtov - Zimnicea	43.620321	25.360049	yes	yes	yes	GI-BAS/ IGR
7.	Danube	Danube at Pristol	44.2132	22.682069	yes	yes	yes	IGR
8.	Jiu	Zaval, downstream of bridge	43.841761	23.844953	yes	yes	yes	IGR
9.	Olt	Islaz, upstream Danube confluence	43.717558	24.792675	yes	yes	yes	IGR
10.	Danube	Oltenița (upstream confluence Argeș)	44.054251	26.605097	yes	yes	yes	IGR
11.	Danube	Hârșova	44.68058	27.95259	yes	yes	yes	IGR

Table 3. Concentration (mg/kg) of hazardous substances in the sediment samples from SDTA; n.d. - not detected.

Sample ID	Sample type	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Anthra-cene	Fluoran-thene	Benzo(a) pyrene	Benzo(b+k)fluor-anthene	Benzo (g,h,i) perylene	Indeno (1,2,3) pyrene
Detection limit		0.005	0.003	0.03	0.1	0.005	0.005	0.005	0.1	0.001	0.001	0.001	0.001	0.001	0.001
SDTA-BR/BS	bottom sediment	875	10.9	57.4	6890	0.16	31.9	402	3130	0.001	0.012	0.004	0.008	0.004	0.004
SDTA-BR/FS	floodplain sediment 0-30 cm	186	0.28	74	1280	0.35	6.63	156	532	0.002	0.019	0.008	0.015	0.006	0.005
SDTA-TI/BS	bottom sediment	146	4.01	20.45	2560	0.247	64.6	114	221.75	n.d.	0.004	0.001	0.003	0.002	0.002
SDTA-TI/FS	floodplain sediment 0-30 cm	64.1	0.23	20	329	0.23	5.73	46.8	71.4	n.d.	0.003	0.001	0.004	0.002	0.002
RO/PR/BS	bottom sediment	79.75	29.35	61.35	1890	0.145	105.4	56.55	496	0.265	0.31	0.206	0.125	0.028	0.017
RO/PR/FS/TS	floodplain sediment 5 cm	7.3	0.17	96	12.9	0.04	38.6	10.8	53.6	0.001	0.005	0.001	0.003	0.001	0.001
RO/PR/FS/BS	floodplain sediment 40-50cm	8	0.18	60.6	29.4	0.003	21.4	9.44	51.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
RO/PR/SS	suspended sediment	53.57	7.83	60.2	887.9	0.23	86.9	57.7	474.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
RO/ZV/FS/TS	floodplain sediment 5 cm	5.26	0.21	60.1	26.3	0.55	30	10.4	45.5	0.023	0.053	0.023	0.025	0.052	0.019
RO/ZV/FS/BS	floodplain sediment 40-50cm	5.33	0.23	55.4	29.8	0.57	30	10.5	47	0.021	0.05	0.021	0.022	0.046	0.017
RO/ZV/SS	suspended sediment	7.82	0.4	53.5	61.4	0.299	53	20.4	111	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BG/OG/BS	bottom sediment	20.8	0.39	20.8	12	0.02	11.8	37.1	80.1	n.d.	n.d.	n.d.	n.d.	0.001	n.d.
BG/OG/FS/TS	floodplain sediment 0-15 cm	75.3	0.47	28.9	22.8	0.03	15.6	69.2	102	0.001	0.003	0.001	0.005	0.003	0.002
BG/MI/BS	bottom sediment	5.27	0.2	22.7	71.1	0.04	21.6	11.8	63.6	n.d.	0.001	n.d.	0.001	0.001	n.d.
BG/MI/FS/FS	floodplain sediment 0-15 cm	7.64	0.27	31.3	120	0.04	24.7	13.7	76.9	n.d.	0.002	0.001	0.004	0.004	0.002
BG/IS/BS	bottom sediment	9.46	0.34	50.3	37.1	0.05	33.2	19.9	82.7	n.d.	0.001	n.d.	0.001	0.001	n.d.
BG/IS/FS/TS	floodplain sediment 0-15 cm	9.5	0.6	37.4	62.4	0.03	19.1	24.8	99.9	0.002	0.019	0.012	0.025	0.011	0.012
RO/IS2/FS/TS	floodplain sediment 5 cm	6.73	0.25	61.1	19.7	0.07	32.1	12.9	52.8	0.014	0.105	0.041	0.076	0.024	0.022
RO/IS2/FS/BS	floodplain sediment 40-50cm	7.3	0.37	64.2	30.5	0.12	38.2	17.2	72.2	0.003	0.022	0.008	0.015	0.01	0.006
BG/SV/BS	bottom sediment	6.58	1.35	55.7	31.2	0.13	35.2	20.6	117	0.004	0.035	0.016	0.031	0.014	0.014
BG/SV/FS/TS	floodplain sediment 0-15 cm	9.68	0.5	48	45.8	0.09	33.6	20	99.4	0.007	0.099	0.029	0.062	0.024	0.027
BG/SV/SS	suspended sediment	n.d.	n.d.	0.12	n.d.	n.d.	0.09	0.06	n.d.	n.d.	0.073	0.021	0.086	0.033	0.014
RO/SV-ZM/BS	bottom sediment	4.94	0.113	34.57	3.39	0.07	25.5	10	36.6	0.005	n.d.	n.d.	n.d.	n.d.	n.d.
RO/ZM/FS/TS	floodplain sediment 5 cm	8.49	0.3	65.9	23.3	0.16	37.4	17.9	59.2	0.003	0.025	0.009	0.016	0.016	0.008
RO/ZM/FS/BS	floodplain sediment 40-50cm	12.9	0.24	64	29.2	0.25	38.4	15.3	59.7	0.012	0.098	0.04	0.06	0.049	0.025
RO/SV-ZM/SS	suspended sediment	16.63	0.752	61.03	62.65	0.159	57.5	34.9	154.8	n.d.	0.045	0.022	n.d.	0.0265	0.195
RO/OT/FS/TS	floodplain sediment 5 cm	7.92	0.4	74.9	29.8	0.05	39	18.4	78.8	0.002	0.018	0.008	0.019	0.008	0.006
RO/OT/FS/BS	floodplain sediment 40-50cm	6.48	0.27	59.4	26.3	0.06	32.4	14.2	60	0.003	0.015	0.006	0.015	0.006	0.005
RO/OT/SS	suspended sediment	14.3	0.675	44.1	57.75	0.127	45.5	30.8	145.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
RO/CL/FS/TS	floodplain sediment 5 cm	4.78	0.13	40.2	10.9	0.003	21.7	8.14	36.2	n.d.	0.002	0.001	0.002	0.001	0.001
RO/CL/FS/BS	floodplain sediment 40-50cm	5.37	0.19	54.3	18.3	0.003	32.5	12.8	51.9	0.002	0.012	0.005	0.009	0.004	0.003
RO/HR/BS	bottom sediment	30.8	1.65	77	150	0.646	58.8	67.1	178	0.106	0.012	n.d.	n.d.	0.01	n.d.
RO/HR/FS/TS	floodplain sediment 5 cm	7.24	0.4	37.35	44.65	0.11	42.6	23.4	86.4	0.01	0.28	0.129	0.263	0.111	0.094
RO/HR/FS/BS	floodplain sediment 40-50cm	6.625	0.4	31.2	31.1	0.86	34.15	21	72.6	0.043	0.02	0.016	0.023	0.016	0.014
RO/HR/SS	suspended sediment	17.57	0.9	61	79.03	0.171	65.1	55	225.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

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 2 mm nylon screen and homogenization before sending the samples to chemical analysis. The samples collected in suspension by the 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, 6 polycyclic aromatic hydrocarbons (PAHs) and 6 pesticides as hazardous substances (ICPDR, 2003; EC, 2018) were selected for analysis. The analyses were done in the accredited reference laboratory Balint Analitika Ltd. in Budapest, Hungary. Metal(oid)s were analysed with inductively-coupled plasma mass spectrometry (ICP-MS) after aqua regia digestion. Organic substances were analysed following the GC-MS and HPLC (gas chromatography-mass spectroscopy and high performance liquid chromatography) methods (Čaić et al., 2019).

4. RESULTS

The concentrations of selected metal(oid) and organic hazardous substances in the sediments of South Danube Test Area (SDTA) (Table 3) are compared with international and national environmental standards (Figures 2–15) to evaluate the level of contamination of the sediments in the SDTA, according to the SIMONA Evaluation Protocol (Dudás et al., 2021). The data are compared to the following EQS values: Dutch target values for soils, Elbe lower and upper limit values for sediments, Romanian maximum allowable, alert and intervention threshold values for sensitive and less sensitive soils (Order nr. 756/03.11.1997, updated 28.11.2011), Bulgarian normal and intervention threshold values for sensitive and less sensitive soils (Ordinance no. 3 of August 1, 2008).

4.1. Metal(oid)s in the sediments

4.1.1. Arsenic

The arsenic concentrations in the studied sediment samples vary between 0.02 and 875 mg/kg. Most of the concentrations are below or around the Bulgarian soil normal (10 mg/kg) and Romanian alert (15 mg/kg) values (Figure 2). The highest arsenic concentrations detected are at Borska Reka (875 mg/kg for bottom sediments and 186 mg/kg for floodplain sediments), at Timok (146 mg/kg for bottom sediments and 64.1 mg/kg for floodplain sediments), at Pristol (79.75 mg/kg for bottom sediments and 53.57 mg/kg for suspended sediments), at Ogosta (20.8 mg/kg for bottom sediments and 75.3 mg/kg for floodplain sediments) and at Hârșova (30.8 mg/kg for bottom sediments). The pollution of Danube River at Pristol is a result of recent mining activity in the Bor region in Serbia and the polluted Danube tributaries Borska Reka and Timok Rivers (Nikolic et al., 2011; Adamovic et al., 2022). The pollution is confined to the Danube right bank in bottom and suspended sediments, while arsenic concentrations are low in the Pristol floodplain sediments (Figure 2). The pollution of floodplain sediments of Ogosta River is a result of past mining activity in the Chiprovtsi region (Kotsev et al., 2006; Mladenova et al., 2008), however, the bottom sediments have lower arsenic concentration

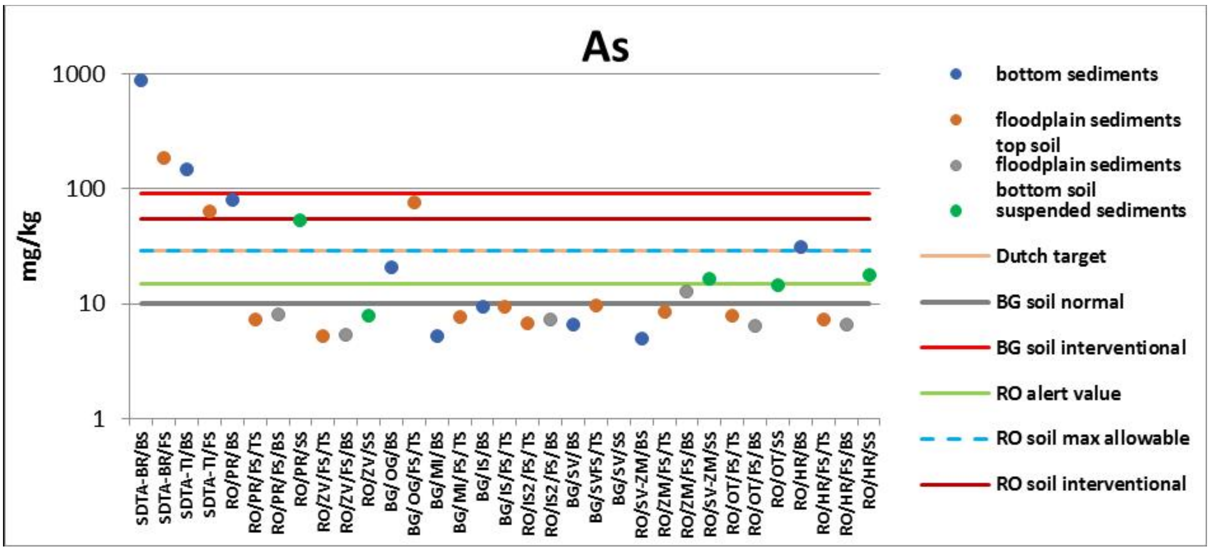

Figure 2. Arsenic concentration in the studied sediments in comparison with international and national standards

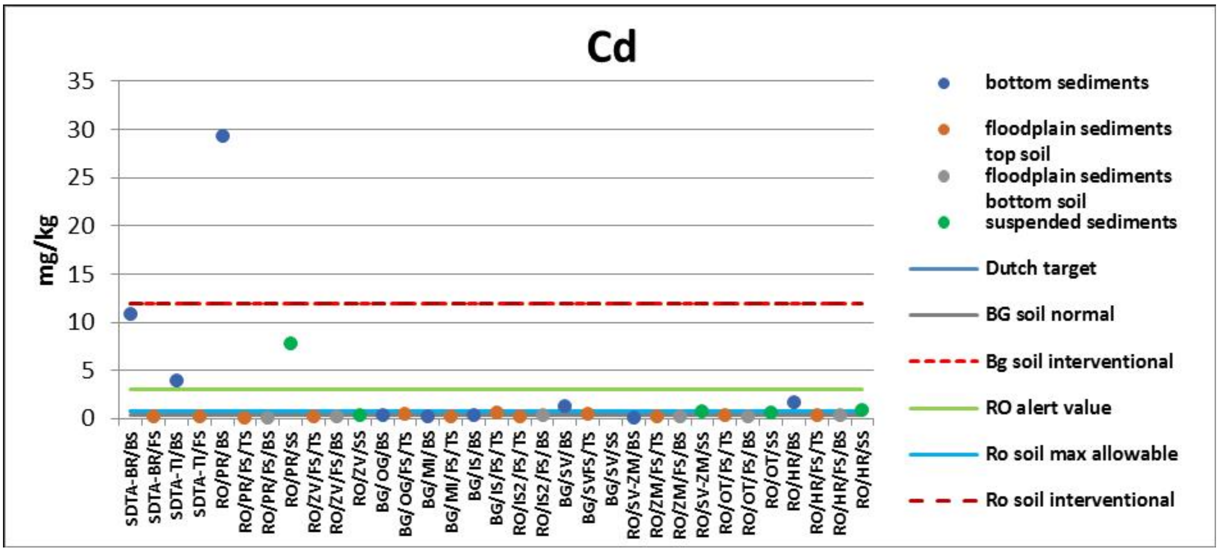

Figure 3. Cadmium concentration in the studied sediments in comparison with international and national standards

at this site. The polluted bottom sediments at Hârşova maybe a result of industrial activity, but As concentrations in floodplain and suspended sediments at Hârşova are low because the location of the sample is around 1 km downstream the Carsinav dockyard of the city, presently with a reduced activity.

4.1.2. Cadmium

Only one sample of bottom sediments at Pristol exceeded (29.35 mg/kg) all EQS limits for cadmium (Figure 3). The Cd content in Borska Reka bottom sediments (10.9 mg/kg) and in Pristol suspended sediments (7.83 mg/kg) is also high but do not exceed interventional levels (12 mg/kg). Cadmium contents slightly higher than the normal BG and RO soil levels are observed in bottom sediments at Svishtov (1.35 mg/kg) and Hârşova (1.65 mg/kg). All other concentrations are around normal values for Cd in soils. The cadmium pollution of bottom and suspended sediments at Pristol is considered the result of recent activity at the Bor mining region in Serbia (Nikolic et al., 2011), but Cd concentration in Pristol floodplain sediments and in other samples downstream the Danube River are low.

4.1.3. Chromium

Our results show that chromium concentrations (Figure 4) are below or around the Bulgarian soil normal value (65 mg/kg) and below the Dutch target and Romanian alert values (100 mg/kg). The highest concentrations are detected in Borska Reka floodplain sediments (74 mg/kg), in Pristol floodplain sediments (94 mg/kg), Oltenita floodplain sediments (74.9 mg/kg) and Hârşova bottom sediments (77 mg/kg). It can be concluded that chromium content in the sediments is low and does not indicate any pollution source.

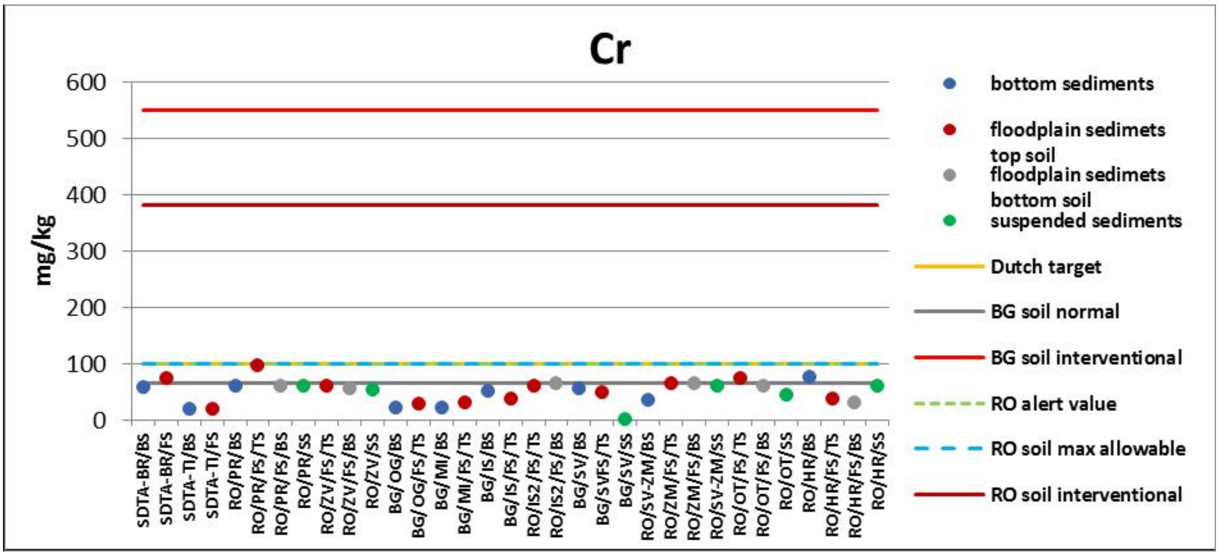

Figure 4. Chromium concentration in the studied sediments in comparison with international and national standards

4.1.4. Copper

The highest copper concentrations in the studied sediments are measured in Borska Reka bottom (6890 mg/kg) and floodplain (1280 mg/kg) sediments, in Timok bottom (2560 mg/kg) and floodplain (329 mg/kg) sediments, in Pristol bottom (1890 mg/kg) and suspended (887.9 mg/kg) sediments (Figure 5), which are a result of the recent copper mining at the Bor region in Serbia and high copper concentrations in the Danube tributaries Borska Reka and Timok Rivers (Nikolic et al., 2011; Adamovic et al., 2022). On the other hand, copper contents in the Pristol floodplain sediments, both topsoil FS TS (12.9 mg/kg) and bottom soil FS BS (29.4 mg/kg) are below the normal values for soils (34-36 mg/kg). Relatively high copper content is measured in Malak Iskar bottom (71.1 mg/kg) and floodplain (120 mg/kg) sediments which is the result of present copper mining in the Elatsite mine in the Etropole region (Bird et al., 2010 a). The contamination is lower in the bottom sediments due to the wastewater treatment measures taken during last 15 years (Gartsiyanova, 2016) and as a consequence the copper contents downstream the Iskar River are lower – 37.1 mg/kg in the bottom and 62.4 mg/kg in the floodplain sediments. Most of the sediments in the Romanian tributaries and downstream the Danube River have copper concentrations below or around the normal values. Comparatively high Cu contents are found in suspended sediments at Zaval (61.4 mg/kg), Svishtov-Zimnicea (62.65 mg/kg), Oltenita (57.75 mg/kg) and Hârșova (79.03 mg/kg) which are still below the Romanian alert value (100 mg/kg) only in the Hârșova bottom sediments are detected somewhat elevated copper concentrations (150 mg/kg), which are most probably a result of industrial activities in the region (Carsinac dockyard) and natural geological background (geothermal water occurs as hot springs and was also found in wells, the chloro-sodic and

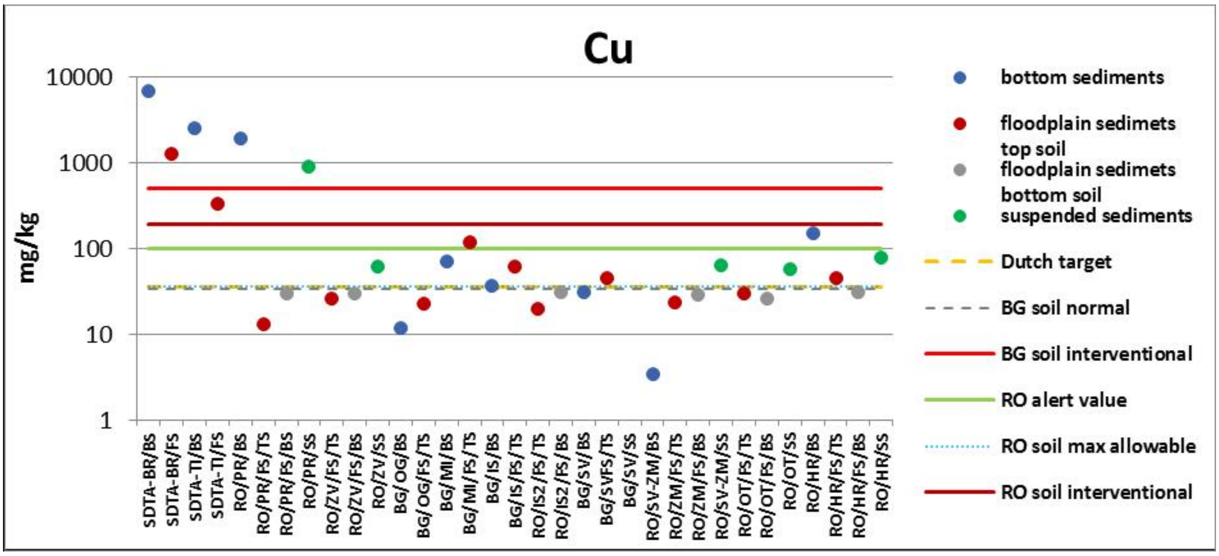

Figure 5. Copper concentration in the studied sediments in comparison with international and national standards

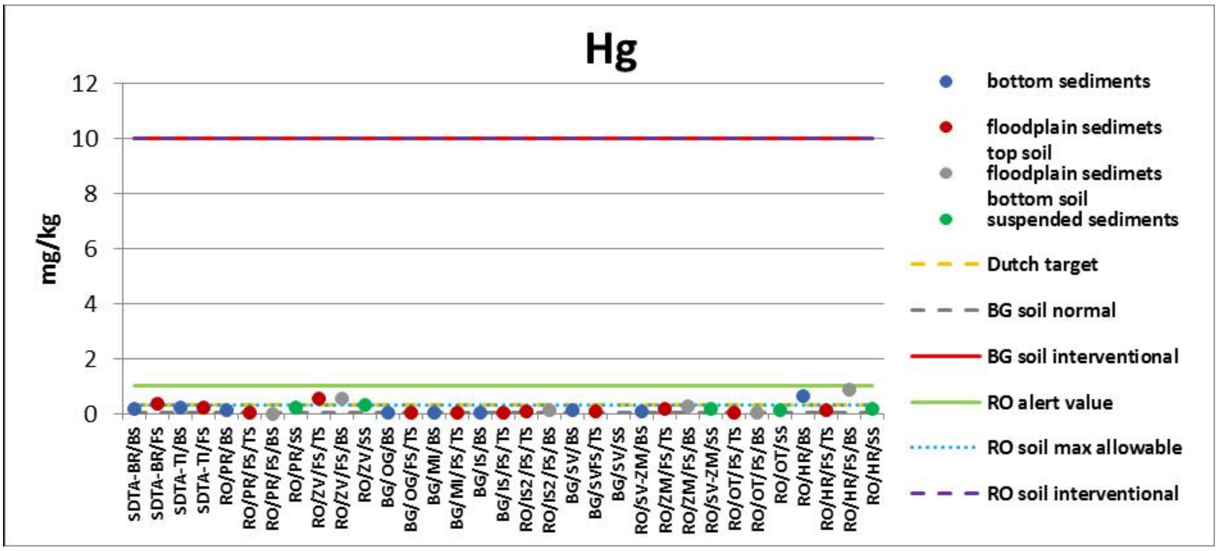

Figure 6. Mercury concentration in the studied sediments in comparison with international and national standards

sulphurous hypo-thermal water being circulated (Perşa & Baltres, 2019) on Hârşova – Taşaul Fault.

4.1.5. Mercury

The studied sediments from SDTA have comparatively low concentrations of mercury which are around the normal values for soils (Figure 6). Slightly elevated contents are measured in Zaval floodplain topsoil FS TS (0.55 mg/kg) and bottom soil FS BS (0.57 mg/kg) sediments and in Hârşova bottom BS (0.646 mg/kg) and floodplain bottom soil FS BS (0.86 mg/kg) sediments, but they are below the Romanian alert value for soils.

4.1.6. Nickel

Most of the samples have nickel concentrations below or around normal values for soils (Figure 7). The highest contents which exceed the Romanian alert value for soils are detected again in the Pristol bottom (105.4 mg/kg) and suspended (86.9 mg/kg) sediments. Nickel concentrations slightly exceed the normal values in some of the sediment samples: Timok floodplain sediments (64.6 mg/kg), Zaval suspended sediments (53 mg/kg), Svishtov-Zimnicea suspended sediments (57.5 mg/kg), Hârşova bottom (58.8 mg/kg) and suspended (65.1 mg/kg) sediments.

4.1.7. Lead

The studied sediments have comparatively low concentrations of lead – below or around the normal values for soils (Figure 8). The highest lead concentrations are detected in Borska Reka bottom (402 mg/kg) and floodplain (156 mg/kg) sediments and in Timok bottom sediments (114 mg/kg) which are below the Bulgarian (500 mg/kg) and Romanian (530 mg/kg) intervention values. Some samples have higher lead content between 50 mg/kg (Romanian alert value) and 85 mg/kg (Dutch target value and Romanian

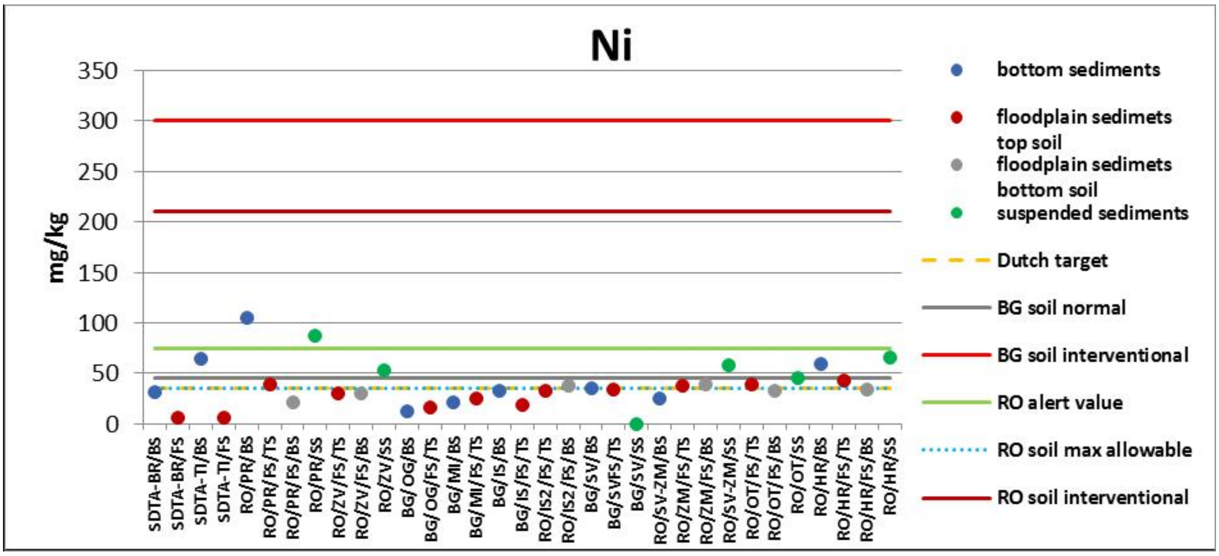

Figure 7. Nickel concentration in the studied sediments in comparison with international and national standards

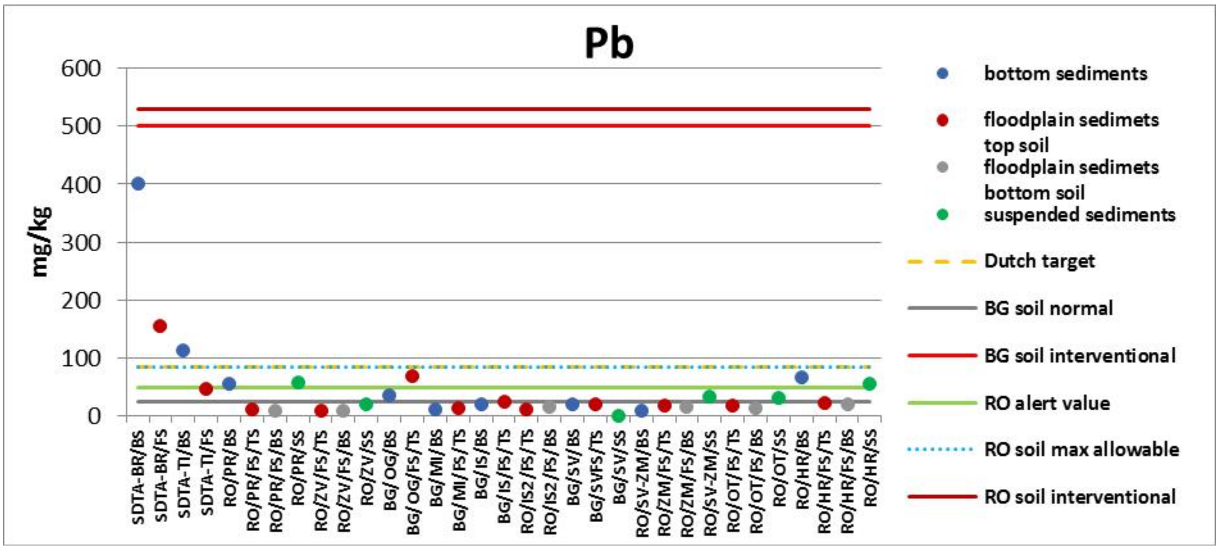

Figure 8. Lead concentration in the studied sediments in comparison with international and national standards

maximum allowable value): Pristol bottom (56.55 mg/kg) and suspended (57.7 mg/kg) sediments, Ogosta floodplain topsoil sediments (69.2 mg/kg), Hârşova bottom (67.1 mg/kg) and suspended (55 mg/kg) sediments.

4.1.8. Zinc

The highest zinc concentrations are detected in Borska Reka bottom (3130 mg/kg) and floodplain (532 mg/kg) sediments, and in Pristol bottom (495 mg/kg) and suspended (474.7 mg/kg) sediments (Figure 9) and are the result of recent mining activity at the Bor region in Serbia and polluted Danube tributaries Borska Reka and Timok Rivers (Nikolic et al., 2011). Most of the other samples have zinc concentrations below or around the Bulgarian normal values for soils (88 mg/kg). Some samples have values close to the Dutch target value and Romanian maximum allowable value (140 mg/kg): Zaval suspended sediments (111 mg/kg), Ogosta floodplain sediments (102 mg/kg), Iskar floodplain sediments (99.9 mg/kg), Svishtov bottom (117 mg/kg), floodplain (99.4 mg/kg) and suspended (154.8 mg/kg) sediments, Oltenita suspended (145.5 mg/kg), Hârşova bottom (178 mg/kg) and suspended (225.3 mg/kg) sediments.

4.2. Organic components/ Polycyclic aromatic hydrocarbons (PAH)

4.2.1. Anthracene

Most of the studied sediment samples have low anthracene concentrations – around the Bulgarian normal values for soils (0.005 mg/kg) and below the Elbe lower limit (0.03 mg/kg) and Romanian normal values for soils (0.05 mg/kg), some of them being below the detection limit of 0.001 mg/kg (Figure 10). The highest anthracene concentrations are measured in Pristol bottom sediments (0.265 mg/kg) and in

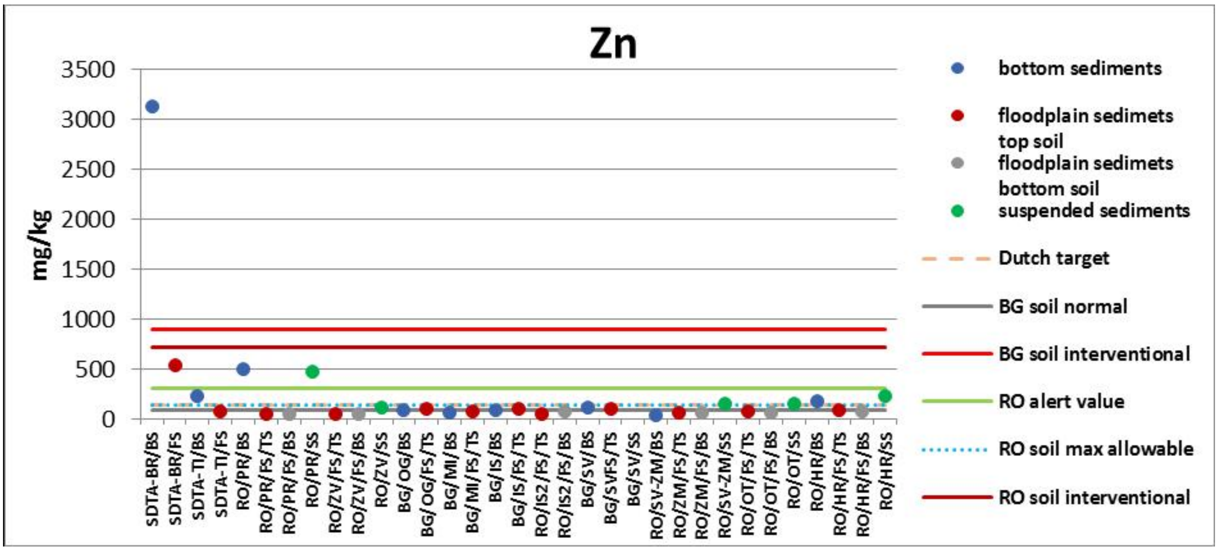

Figure 9. Zinc concentration in the studied sediments in comparison with international and national standards

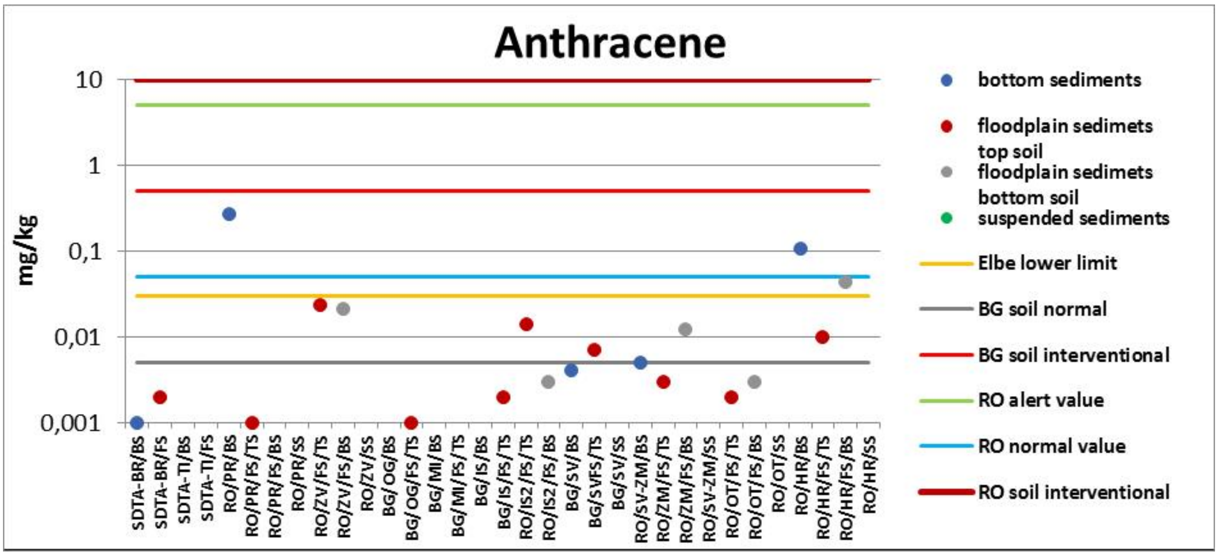

Figure 10. Anthracene concentration in the studied sediments in comparison with international and national standards

Hârşova bottom (0.106 mg/kg) and floodplain bottom soil (0.043 mg/kg) sediments.

4.2.2. Fluoranthene

The studied sediments samples show significant variety of fluoranthene concentrations (Figure 11), ranging from below or around the detection limit of 0.001 mg/kg, to concentrations around the Bulgarian (0.015 mg/kg) and Romanian (0.02 mg/kg) normal values for soils, up to concentrations exceeding the Bulgarian soil intervention threshold (0.1 mg/kg) and Elbe upper limit values for sediments (0.18 mg/kg) in Pristol floodplain bottom soil FS BS (0.31 mg/kg) and in Hârşova floodplain topsoil FS TS (0.28 mg/kg) sediments. Relatively high fluoranthene contents are detected in the Zaval floodplain topsoil FS TS (0.053 mg/kg), and in the bottom soil FS BS (0.05 mg/kg) sediment samples, in the Islaz floodplain topsoil sediments FS TS (0.105 mg/kg), in the Svishtov floodplain topsoil FS TS (0.099 mg/kg) and suspended (0.073 mg/kg) sediments, and in the Zimnicea floodplain bottom soil FS BS (0.098 mg/kg) and suspended (0.045 mg/kg) sediments.

4.2.3. Benzo(a)pyrene

Most of the samples have benzo(a)pyrene concentrations below or around normal values for soils (Figure 12). Concentrations which exceed the Bulgarian soil intervention threshold (0.1 mg/kg) are detected in Pristol bottom BS (0.206 mg/kg) and in Hârşova floodplain topsoil FS TS (0.129 mg/kg) sediments. Comparatively high benzo(a)pyrene contents are detected in Islaz floodplain topsoil FS TS (0.041 mg/kg), Svishtov floodplain topsoil FS TS (0.029 mg/kg) and Hârşova floodplain bottom soil FS BS (0.04 mg/kg) sediments.

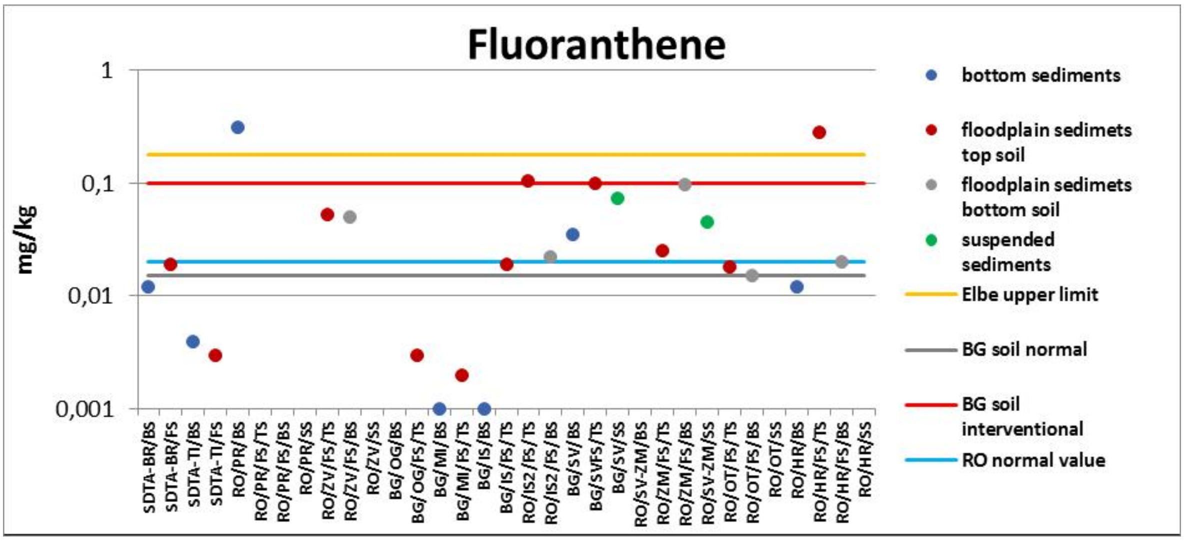

Figure 11. Fluoranthene concentration in the studied sediments in comparison with international and national standards

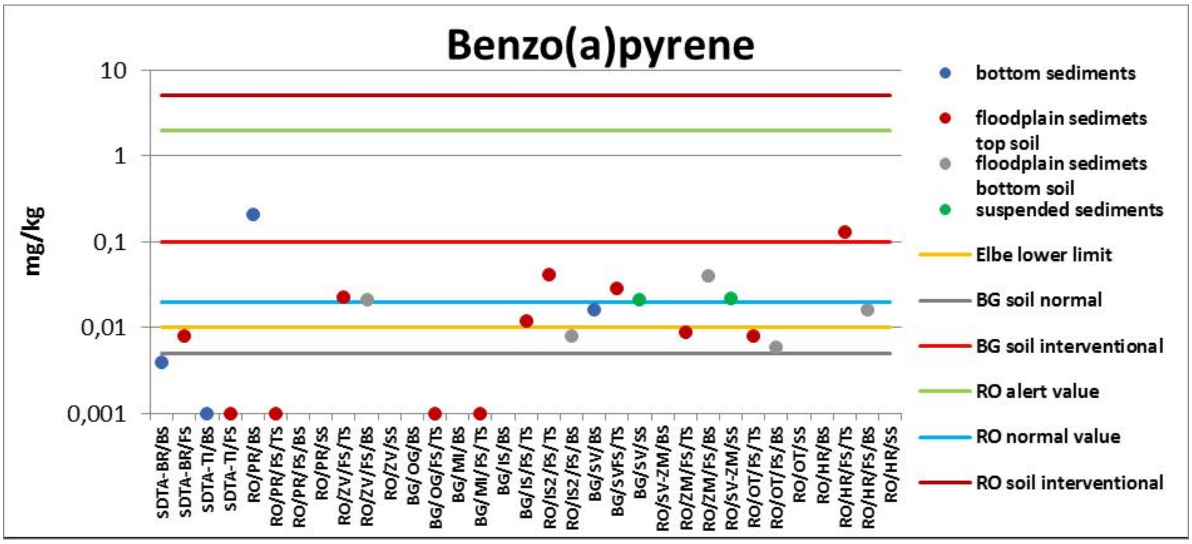

Figure 12. Benzo(a)pyrene concentration in the studied sediments in comparison with international and national standards

4.2.4.Benzo(b+k)fluoranthene

The studied sediments have benzo(b+k)fluoranthene concentrations below or around the Romanian normal values (0.02 mg/kg) for soils (Figure 13). Relatively high concentrations (but still below the Romanian alert value of 2 mg/kg) are detected in Islaz floodplain topsoil sediments FS TS (0.076 mg/kg), Svishtov floodplain topsoil FS TS (0.062 mg/kg) and suspended (0.086 mg/kg) sediments, Zimnicea floodplain bottom soil FS BS (0.06 mg/kg) and Hârşova floodplain topsoil FS TS (0.263 mg/kg) sediments.

4.2.5. Benzo(g,h,i)perylene

The concentrations of benzo(g,h,i)perylene in the studied sediments are around the Bulgarian (0.004 mg/kg) and Romanian (0.02 mg/kg) normal values for soils (Figure 14). The samples with elevated concentrations are Zaval floodplain topsoil FS TS (0.052 mg/kg) and bottom soil FS BS (0.046 mg/kg) sediments and Zimnicea floodplain bottom soil FS BS (0.049 mg/kg), while the only sample which exceeds the Bulgarian soil intervention threshold (0.1 mg/kg) is the Hârşova floodplain topsoil FS TS sediments (0.111 mg/kg).

4.2.6. Indeno(1,2,3-cd)pyrene

The studied sediments have low concentrations of indeno(1,2,3-cd)pyrene, around the Bulgarian (0.011 mg/kg) normal values for soils (Figure 15). Only the Hârşova floodplain topsoil sediment samples have relatively high concentration (0.094 mg/kg), but it does not exceed the Bulgarian soil intervention threshold (0.2 mg/kg).

4.2.7. Other organic components

The studied sediments were also analysed for 6 pesticides: Dicofol, Heptachlor, Heptachlor epoxide,

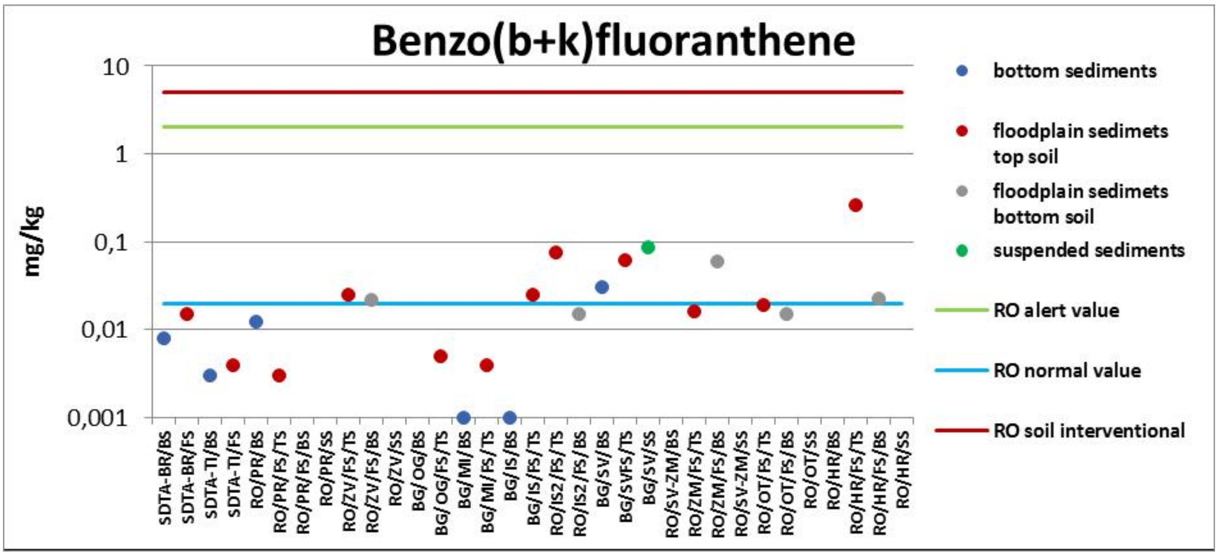

Figure 13. Benzo(b+k)fluoranthene concentration in the studied sediments in comparison with national standards

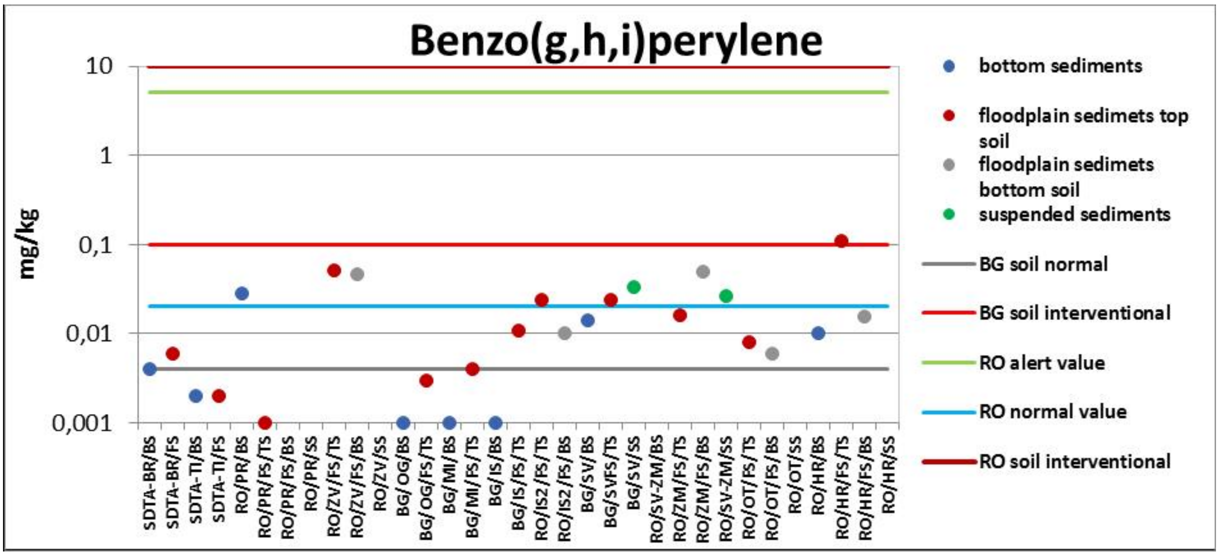

Figure 14. Benzo(g,h,i)perylene concentration in the studied sediments in comparison with national standards

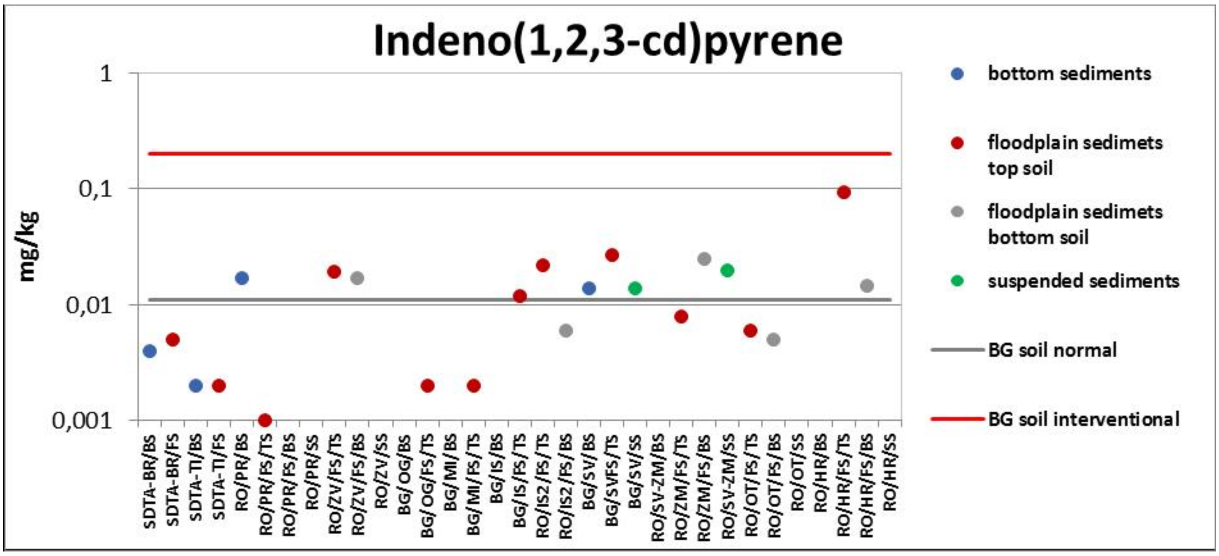

Figure 15. Indeno(1,2,3-cd)pyrene concentration in the studied sediments in comparison with national standards

Hexachlorobenzene, Hexachloro cyclohexane and Quinoxyfen. The concentrations of these hazardous substances are very low and measured below the limit of detection (0.005 mg/kg) in all samples.

5. DISCUSSION

The study of the selected sediment sample sites in the South Danube Test Area allows us to make an assessment of the river sediment quality and the main possible sources of contamination of the Lower Danube River basin. As a whole, the concentrations of heavy metals in the sediments are low, in general, and are around the normal values for soils. On the other hand, some sampling sites and sediment types have high or very high metal concentrations which exceed interventional levels. The latter concerns Borska Reka, Timok and Pristol sampling sites. The bottom and floodplain sediments in these sites and Pristol suspended sediments have very high concentrations of As, Cd, Cu, Zn – close or above the Bulgarian and Romanian soil intervention values, whereas Ni and Pb contents in the same samples exceed the normal sediment and soil values, too. As pointed out above, the monitoring of the HSs in suspended and bottom sediments characterises the baseline concentration values and current contamination. Consequently, the pollution of Danube River at the three sites is attributed to the recent mining activity in the Late Cretaceous Cu porphyry and epithermal ore deposits at the Bor mining district in Serbia (Ciobanu et al., 2002) (Figure 1) . Pollution with heavy metals in that region of intensive mining activity is reported also for soils (Nikolic et al., 2011), surface waters (Korac & Kamberovic, 2006; Brankov et al., 2012) and groundwaters (Adamovic et al., 2022). The highest heavy metal pollution was recorded in the Borska Reka River (Brankov et al., 2012). Borska Reka is a tributary of the Timok River which flows into the Danube River near Pristol (Figure 1). Our results show that the pollution is concentrated around the Danube right bank in the bottom and suspended sediments and the concentrations of heavy metals in the Pristol floodplain both topsoil and bottom soil sediments are below or around the normal values for soils. The concentrations of heavy metals decrease after the confluence with the Danube River, however, the effect of the Timok River pollution on the sediment quality status should be studied further and monitored at higher frequency (similar to water quality monitoring).

The second site with expected and reported pollution is the Ogosta sampling site (Site 3 in Figure 1). It was selected because of known pollution from past mining activity in the Chiprovtsi region. Agricultural pollution was also suspected but not found as all analysed pesticide concentrations were below the limit of detection. At the Ogosta site, the heavy metal content (Cu, Pb, Hg, Zn, Cd, Cr, Ni, As) is higher in floodplain sediments than in bottom sediments which suggests that their source is historical rather than current contamination. The most prominent contaminant at this site is arsenic concentration which exceeds the EQS limits both for bottom and floodplain sediments. This is in agreement with previous studies concerning As contamination of soils and river sediments around the Ogosta basin (Vesselinov et al., 1996; Kotsev et al., 2006; Mladenova et al., 2008; Bird et al., 2010a; Jordanova et al., 2013). Arsenic, Cd, Pb and Zn contents are higher than the normal content of trace elements in soils. The content of all metals is lower than the maximum (allowable) content in soils with regard to the Bulgarian Soil Standards (AQUA-ENV Consortium, 2017).

Both Iskar River sampling sites (the Malak Iskar site at the town of Roman, and the Iskar River site at Gigen, 5 km upstream from the confluence with the Danube River) were selected because of reported former pollution (Bird et al., 2010 a; Gartsiyanova, 2016) from recent (Elatsite copper mine) and past mining and processing activities (Cholakova, 2004; 2006; Parvanov et al., 2008), whereas agriculture pollution was less expected at this site. At the Malak Iskar site, the bottom soil and topsoil floodplain sediment analyses revealed Cu content exceeding some of EQS limits but still below the Bulgarian and Romanian soil interventional values. Among the other metals, the content of Cd, Cr and Zn in floodplain sediments is slightly higher than in bottom sediments but is below or around the normal values for soils. The data suggest improvement of the quality of river sediments from past (floodplain sediment) to present day (bottom sediment) that may also result from the new water purification plant at the Elatsite mine.

The Iskar sampling site is situated on the Iskar River, between the villages Baykal and Gigen, 5 km before the confluence with the Danube (Figure 1). Previous studies documented significant past industrial and mining pollution in the middle course of the Iskar River between Sofia and the Eliseina smelting plant, in addition to possible agricultural pollution in the Lower Iskar River (Cholakova, 2004; 2006; Parvanov et al., 2008). Our results show that heavy metal contents both in the bottom and top floodplain sediments before the confluence with the Danube River are low and close to the normal soil values for most analysed elements, only the contents of Cu, Cd, Ni, Pb and Zn remaining slightly elevated. Compared with the data for the Malak Iskar site, all metal(oid) concentrations are lower and close to the EU good quality status, consequently, we should not consider contamination or pollution of the Danube River at this confluence.

Two sampling sites are situated in the Danube tributaries Jiu River (at Zaval) and Olt River (at Islaz) before the confluence with the Danube River in Romania. The results show that heavy metal contents both in the bottom and floodplain sediments before the confluence with the Danube River are comparatively low and are below the normal values for soils. Only the concentration of Hg in Zaval floodplain topsoil and bottom soil depth levels are higher than the normal values, but still do not exceed the Romanian alert values. Probably this is a result of mining and incineration of coal, as in the Jiu River hydrographic basin there are the most important lignite reserves of Romania. Here, in Gorj county, there are 13 active exploitation licenses out of a total of 18 licenses, corresponding to an estimated figure of coal reserves and resources of 2.446 billion tonnes, 252.5 million tonnes being commercially exploited (Dorin et al., 2014). Medical and other waste, probably mainly from Craiova, the Gorj county seat (Barbu, 2008), is, together with mining activity, another source for higher Hg concentrations. The contents of Cu, Ni and Zn in suspended sediment samples from the Zaval sampling site exceed some normal soil values but are still below the interventional threshold. All results for heavy metals from the Islaz sampling site are below the normal values for soils.

The water quality of the Danube at the Svishtov sampling site is monitored by the Bulgarian Water Authority and is also a part of the Danube Basin Trans-national Monitoring Network (TNMN). Possible pollution from industrial and agricultural activity is expected in this region but also the influence of the tributaries (e.g., the Ogosta and Iskar rivers) could be assumed. In addition to bottom soil and topsoil floodplain sediments, suspended sediment samples were also collected at the Svishtov-Zimnicea sample site. The heavy metal content, both in bottom and floodplain sediments, is low, and only the content of Cr, Cu and Zn is slightly higher than the normal values for soils. In the suspended sediments, a bit higher than average content for As, Cd, Cu, Ni and Zn were found but still below the Romanian alert values, except for As which slightly exceeds this limit. Long distance transport of As due to current (Timok River) and past (Ogosta River) mining activities might be assumed as possible sources, although the content of the studied chemical elements is significantly lower than the Romanian and Bulgarian soil intervention values.

Results show that heavy metal concentrations in all the studied sediment types (river bottom, floodplain and suspended sediment) are below or close to the normal values for soils at the Oltenita sampling site located on the Danube River (Figure 1). Only the concentrations of As, Cu and Zn in suspended sediments are slightly elevated above the average, but are still below the the Romanian alert and interventional threshold. As a whole, the river Danube sediments at Oltenita have low heavy metal content.

The last sampling site at the Danube River is at Hârșova (Figure 1). The results show different concentrations of heavy metals in different sediment types. The floodplain sediments (both topsoil and bottom soil) have low heavy metal content, below or around the normal values for soils. On the other hand, the bottom and suspended sediments have elevated heavy metal contents which do not exceed the interventional levels. The observed concentration distribution of the studied metal(oid)s may be a result of the slow current of the Danube River near the Hârșova sampling site. The flow rate of the Danube River on the transverse profiles at Pristol, Svistov-Zimnicea and Oltenita was over 6000 m^3/s, while at

Hârşova the flow rate was only around 2200 m^3/s, according to the Field Observation Sheets (Šorša et al., 2019) of the campaign.

The studied sediments from the SDTA reveal low concentrations of hazardous organic components (polycyclic aromatic hydrocarbons (PAHs)). Only fluoranthene content is elevated in most of the sediment types and sampling sites on the Danube River, and only accidently exceeds the intervention levels. The most polluted are the Pristol bottom sediments for anthracene, fluoranthene and benzo(a)pyrene, and the Hârşova floodplain sediments for all the measured PAHs. Our results show that the sediments in the Danube River are more polluted with PAHs than its tributaries. The identified organic compounds are assumed to be generated during incomplete or low temperature combustion processes occurring in households (mainly in rural areas) or during road transportation in urban areas and/or the navigation on the Danube River.

6. CONCLUSIONS

Our assessment of sediment quality in the Lower Danube River Basin test area, carried out in accordance with the 2013/39/EU Directive and the EU water Framework Directive reveals a generally low danger to the aquatic biological activity and water supplies in this region.

In the test area, an exception is well recognized at the mining pollution sources in the Danube tributaries Borska Reka, Timok, Ogosta, Malak Iskar/Iskar from past and/or recent mining activities. However, this pollution is limited to the Danube tributaries and around their confluences into the Danube River. The concentration of heavy metals is strongly diluted in the Danube River where they reach concentration values close to the normal values for soils. As pointed out by previous studies (e.g., Bird et al., 2010 a; b), despite the presence of mining, metallurgy, in addition to other industrial and municipal sources within the Danube drainage basin which often lead to extensive contamination of the related catchments, river waters downstream the tributaries and in the Danube River itself, generally drop below the EU target values. The study of ICPDR (ICPDR, 2008) shows relatively low concentrations of heavy metals in the Danube water and sediments, in general, and the limit values are exceeded only around the confluences of some rivers like river Timok.

In some regions of known metal(loid) pollution, tendencies of water and sediment quality status improvement can be recognized as a result of mine closures (Ogosta site), or due to the improved purification of mining waste waters (Malak Iskar). The floodplain (overbank) sediments at these regions still should be considered possible sources of contamination during floods and be monitored regularly. The most dangerous sites with HSs discharge like the tributaries Borska Reka and Timok, in addition to the confluence of the latter with the Danube at Pristol require more frequent monitoring and measures to reduce pollution.

Data from the SDTA sites also show that the concentrations of individual PAHs in the Danube River sediments are below the EQS limits, but the sum of the concentrations of PAHs slightly exceeds the limits. Our results indicate increased PAHs concentrations in some Danube sampling sites which shall be monitored with higher frequency in the future.

Although the DRB countries have their specific geology, landscape, industry and agriculture, unified EQS should help the better and comparable quality assessment of river sediments. This, together with the new sampling, laboratory and evaluation protocols will harmonize sediment quality monitoring in the Danube countries.

Acknowledgements

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