Carpathian Journal of Earth and Environmental Sciences August 2022, Vol. 17, No. 2, p. 425 – 439; DOI:10.26471/cjees/2022/017/233

ASSESSMENT OF THE QUALITY OF RIVER SEDIMENTS IN BASELINE NATIONAL MONITORING STATIONS OF 12 COUNTRIES IN THE DANUBE RIVER BASIN

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Abstract: Fluvial sediment samples (river bottom sediment, suspended sediment and active floodplain/overbank) were collected in 2 baseline stations of the Transnational Monitoring Network for each of the 12 countries in the Danube Basin Region: Austria, Bosnia and Herzegovina, Bulgaria, Croatia, Czech Republic, Hungary, Republic of Moldavia, Montenegro, Romania, Republic of Serbia, Slovakia and Slovenia, according to a harmonized methodology. The sediment samples were analyzed for selected hazardous substances (HSs): 8 metals, 8 polycyclic aromatic hydrocarbons (PAHs) and 6 pesticides in an accredited laboratory selected as reference laboratory, as well as in national laboratories. Risk ratios were computed in order to compare the results to the Environmental Quality Standards listed in the European Directives, to the national threshold values in the Danube Basin, and to other available international European and American quality standards, and the risk ratios were classified as background, alert and intervention values for readily evaluation. Results show widespread metal(oid) (As, Cd, Cu, Hg, Pb, and Zn) contamination in the Danube Basin, most often associated with historic mining. Concentration values of Ni and Cr exceeding the thresholds are caused by the geological background (ultrabasic and metamorphic rocks in Bosnia and Herzegovina, Republic of Serbia and Romania).

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Concentration values higher than the thresholds for some of the PAHs (e.g. Fluoranthene) and sometimes for Total PAHs were also noted almost in every countries, caused by industrial activities, wastewater discharges or navigation on the Danube River. Pesticides were below the detection limit or below the legislative intervention thresholds at all national baseline sampling sites.

Keywords: monitoring sediment stations, sampling, hazardous substances, environmental quality standards, Danube River Basin.

1. INTRODUCTION

The Danube River Basin (DRB) was subject of many studies aiming at characterisation of its sedimentary processes, geochemical characteristics and status of the waters and the transported sediments. Regional studies were carried out in the Upper Danube River (Pawellek et al., 2001; Hartmann et al., 2007), Lower Danube (Oaie et al., 2005, 2015; Sandru & David, 2011; Duțu et al., 2021), as well as on tributaries where contamination from mining activity and industry was expected (Frančišković-Bilinski, 2008; Damian et al., 2008; Bird et al., 2010; Lučić et al., 2018; Moroșanu et al., 2022), to list just a few.

The "Sediment-quality Information, Monitoring and Assessment System to Support Transnational Cooperation for Joint Danube Basin Water Management" (SIMONA) project was established in 2018 as a joint project of 17 research organisations, 12 associated partners (national and international water and environmental authorities) from 13 countries in the Danube River Basin (DRB) (https://www.interreg-danube.eu/approved-projects/simona). The project aimed at providing harmonised sediment quality monitoring methods (sampling, laboratory analysis, risk evaluation), expert training, case studies and data in accordance with requirements of the European Union's Water Framework Directive (EC, 2000). In this framework, river bottom sediment (BS; 'stream sediment'), suspended sediment (SS; 'suspended particulate matter') and overbank sediment (including 'active floodplain sediment'; FS) samples were collected at 2 critical priority sites in 12 countries (24 sampling sites) yielding altogether 72 sediment samples across almost the whole Danube River Basin. The sediment samples were analysed for selected hazardous substances (HSs): 8 metals, 8 polycyclic aromatic hydrocarbons (PAHs) and 6 pesticides in an accredited laboratory selected as reference laboratory, as well as in national laboratories.

In this way, our study presents the results of the first harmonised sediment quality sampling, laboratory analysis and assessment in the Danube River Basin and provide an overview of the sediment quality status across the whole catchment.

2. STUDY AREA

The study area encompasses 12 countries in the DRB: Austria, Bosnia and Herzegovina, Bulgaria, Croatia, Czech Republic, Hungary, Republic of Moldavia, Montenegro, Romania, Republic of Serbia, Slovakia and Slovenia. The DRB is the most international river basin in the world, as it covers 19 countries (13 part of the Danube Convention, the rest having the areas too small to join).

The DRB has an area of over 800,000 km^2 and the total population reaches 83 million inhabitants http://www.undp-drp.org/drp/danube_population.html. The climate is continental in the Central and Eastern part, while in the West part it feels the influences of the Atlantic climate and in the South-East part, of the Mediterranean climate.

From Austria to Romania and the Republic of Moldavia, the geomorphology in the Danube catchment varies from Alpine/Carpathian Mountains with historic mining since Roman times (some of the mines still being active nowadays and causing, mostly in the past, toxic metals leaching into the Danube via its effluents), to hilly areas with different land cover categories, plains with agricultural fields and the Danube Delta. Industrial activities, sewage discharge from big cities in the catchment (point pollution sources with PAHs emissions) and leaching of fertilizers and pesticides from extensive agriculture in the past (diffuse pollution sources) require periodical evaluation of the quality of water and sediments in the DRB. Another type of pressure on the DRB is the extensive rivers' regulation by construction of water reservoirs, hydroelectric plants and extensive barrage system, affecting the erosion and deposition of sediments by the waters. From each above-mentioned country, 2 baseline stations (Figure 1) were selected, correlated with the water stations already part of the Transnational Monitoring Network (TNMN). Some stations were placed on the Danube River, while others on major tributaries or water bodies having the regime of lakes, connected to the Danube tributaries.

3. METHODS AND DATA

In order to assess the quality of sediments in

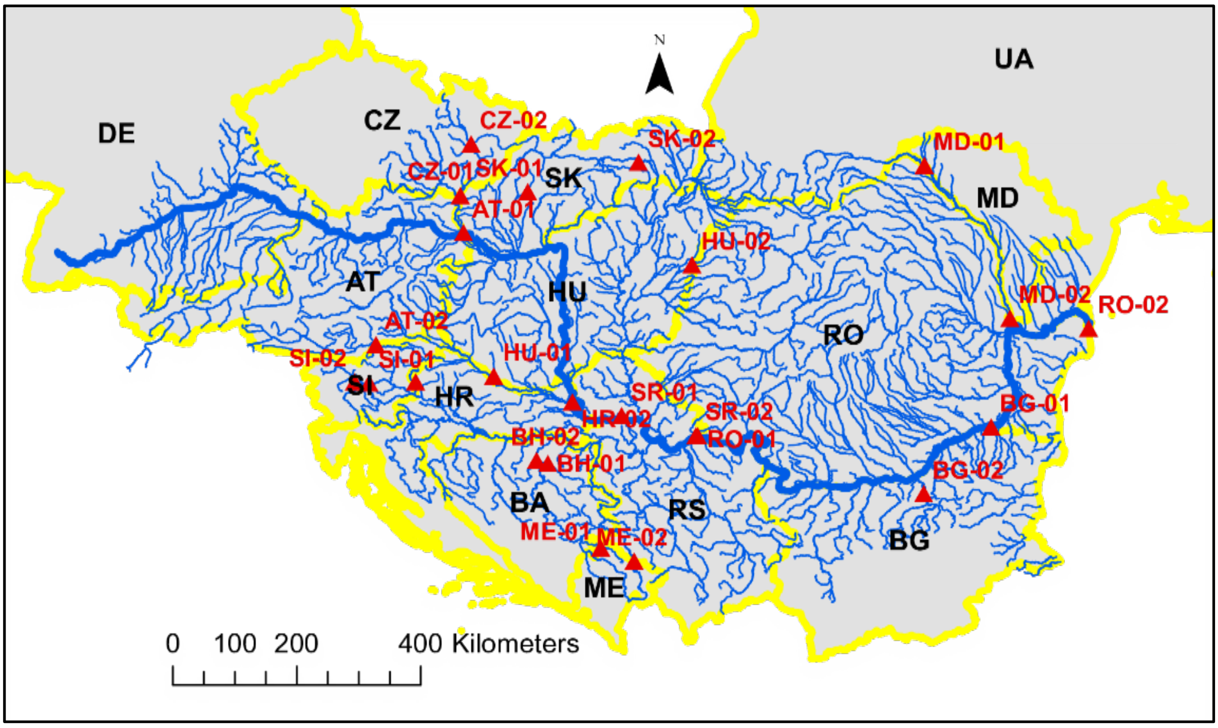

Figure 1. Study area and location of national baseline sampling sites for sediment monitoring (The Danube River Basin – after CCM "Catchment Characterisation and Modelling database of the EC" - De Jager & Jürgen, 2007)

the baseline stations of monitoring network, 3 steps were followed:

- Selection of the 2 baseline stations in each country, following the criteria listed in subchapter 3.1;
- Sampling the sediments according to an especially developed protocol: SIMONA Sediment Quality Sampling Protocol (Šorša, 2019) and the SIMONA Sediment Quality Sampling Manual (Jordan et al., 2021);
- Analysing the set of hazardous substances (HSs) selected in the SIMONA Quality Laboratory Protocol (Čaić et al., 2019).

3.1. Selection of national baseline stations

For the selection of 2 representative sampling points for the DRB baseline network, the criteria listed in the following standards and documents were analysed:

- ISO 5667 – 12:2017
- ISO 5667 – 17:2008
- Guidance Document No. 25 (EC, 2010)
- TNMN monitoring sites criteria (ICPDR, 2019)
- SIMONA Sediment Quality Sampling Protocol (Šorša, 2019).

Many of the criteria in the above documents are overlapping, therefore weights were given to them and finally the selection of the 2 national baseline stations in each country took into account:

- Presence of Transnational Monitoring Network (TNMN) water quality monitoring point;
- Existent sediment/water monitoring sites;
- The transnational character of the water body;
- Having tributaries of different sizes in the network, including the Danube;
- Different geological background;
- Known impact of diverse pollution sources;
- Good infrastructure and access to the sampling point.

The selected 24 sediment sampling baseline stations are shown in Figure 1 and their exact coordinates, river name and neighbour locality name, in Table 1. The selection of the baseline stations was done in consultation with the national Water Authorities in each of the participating 12 DRB countries. The baseline stations refer to the monitoring stations (part of a network) where the baseline for different contaminants is determined. The baseline represents the actual concentration of hazardous substances in a given environment at a given time (Albanese et al., 2007). The presence of TNMN monitoring points was a leading priority because: 1) these water quality monitoring points are already located at priority sites of international significance supervised by the International Commission for the Protection of the Danube River (ICPDR), and 2) the evaluation of sediment quality has to be done with respect to the observed water

Table 1 Selected baseline stations for sediment monitoring in 12 countries of the Danube River Basin

Country (Code)	Station Code	River name	Site name	WGS Lat (N)	WGS Long (E)
Austria (AT)	AT-01	Danube	Hainburg	48°9'51.64"	16°59'33.38"
	AT-02	Drau	Lavamünd	46°38'26.37"	14°56'38.28"
Bosnia and Herzegovina (BH)	BH-01	Spreca	Karanovak (Gracanica)	44°41'46.00"	18°16'25.00"
	BH-02	Bosna	Rudanka	44°45'47.06"	18° 3'0.45"E
Bulgaria (BG)	BG-01	Danube	Silistra, right bank	44°7'27.78"	27°16'0.534"
	BG-02	Yantra	Karantsi	43°23'12.98"	25°40'5.23"
Croatia (HR)	HR-01	Sutla	Kumrovec	46°3'33.44"	15°42'53.75"
	HR-02	Drava	Aljmaš	45°32'40.70"	18°54'38.59"
Czech Republic (CZ)	CZ-01	Morava	Lanžhot	48°42'27.41"	16°59'47.95"
	CZ-02	Bečva	Troubky	49°26'5.20"	17°20'27.93"
Hungary (HU)	HU-01	Babócsai-Rinya	Babócsa	46° 2'34.09"	17°21'8.46"
	HU-02	Berretyó	Pocsaj	47°16'42.68"	21°47'50.39"
Republic of Moldavia (MD)	MD-01	Prut	Costești Stînca	48° 1'55.60"	27° 6'32.13"
	MD-02	Beleu Lake	Slobozia Mare	45°35'22.47"	28° 8'18.90"
Montenegro (ME)	ME-01	Ćehotina	Gradac	43°23'23.26"	19° 9'3.95"
	ME-02	Lim	Dobrakovo	43°8'12.83N	19°46'35.09"
Romania (RO)	RO-01	Danube	Bazias	44°48'49.60"	21°22'48.76"
	RO-02	Danube	Sulina	45°9'30.86"	29°40'19.45"
Republic of Serbia (SR)	SR-01	Danube	Novi Sad	45°15'30.8"	19°53'16.4"
	SR-02	Danube	Ram	44°49'10.7"	21°20'22.5"
Slovakia (SK)	SK-01	Nitra	Chalmová	48°39'27.08"	18°28'41.81"
	SK-02	Hnilec	Jaklovce (Ružín reservoir tributary)	48°52'12.52"	20°58'35.54"
Slovenia (SI)	SI-01	Sava	Jevnica, Kersniške Poljane	46°05'18.6"	14°44'54.6"
	SI-02	Sava	Medno	46°07'14.4"	14°26'29.8"

quality which data is readily provided by the long-term TNMN monitoring network (http://icpdr.org/main/publications/tnmn-yearbooks). In the stations of this network, continuous monitoring of the hydrologic regime (water level and flow) is carried out twice a day, while priority substances listed in Annex 1 of Directive 2008/105/EC, modified by the Directive 2013/39/EC in the water are measured 12 times per year. Metals (Cd Ni, Hg and Pb) in suspensions are measured 4 times per year (surveillance monitoring program) and some PAHs and pesticides are measured in river bottom sediments and in biota once per year (Project of Updated National Management Plan, 2021).

3.2. Sampling sediments in the national baseline stations

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 et al., 2021). The applied sampling methods are benefit from the methods developed by past pan-European projects: the FOREGS (Forum of European Geological Surveys) Geochemical Baseline Programme (FGBP; Salminen, 2005 Ed.) and the GEMAS Geochemical Mapping of Agricultural and Grazing land Soil Project (Reimann et al., 2014a Eds.; Reimann et al., 2014b Eds.), as further developed and adapted to sampling under regular monitoring conditions. Three types of sediments were sampled by entities in the 12 countries of DRB (Table 2):

- River bottom sediment (BS), sampled with the vacuum corer or scoop in small rivers (Jordan et al., 2021). For Danube in Romania, a Van Venn grabber was used from the boat.
- Suspended sediments (SS), sampled by pumping water in plastic water tanks and letting the fine material settle. Where available, a centrifuge was additionally used (Czech Republic) or a sedimentation box (Austria).
- Overbank (floodplain) sediments (FS), sampled 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).

Table 2 Entities which performed the sediment sampling

Country	Entity (abbreviation)
Austria	Austrian Institute of Technology GmbH (AIT), Environment Agency Austria (UBA), and Geological Survey of Austria (GBA)
Bosnia and Herzegovina	Geological Survey of the Federation of Bosnia and Herzegovina (FZZG), Vode Srpske
Bulgaria	Geological Institute of the Bulgarian Academy of Sciences (GI-BAS)
Croatia	Croatian Geological Survey (HGI-CGS)
Czech Republic	Czech hydro-meteorological institute (CHMI)
Hungary	Hungarian University of Agriculture and Life Sciences (MATE)
Republic of Moldavia	Institute of Chemistry (ICHEM)
Montenegro	Geological Survey of Montenegro (GSM)
Romania	Geological Institute of Romania (IGR), National Institute for Hydrology and Water Management (INGHA) - subcontracted
Republic of Serbia	“Jaroslav Černi” Institute (JCI)
Slovakia	State Geological Institute of Dionýz Štúr (SGIDS)
Slovenia	Geological Survey of Slovenia (GEOZS)

Table 3. Analysed substances

Category	Substance
Metals	Arsenic
	Cadmium
	Chromium
	Copper
	Mercury
	Lead
	Nickel
	Zinc
Polycyclic aromatic hydrocarbons (PAHs)	Anthracene
	Benzo(a)pyrene
	Benzo(b)fluoranthene
	Benzo(k)fluoranthene
	Benzo(g,h,i)perylene
	Fluoranthene
	Indeno(1,2,3-cd)pyrene Total PAHs*
Organochlorine pesticides	Dicofol
	Heptachlor
	Heptachlor epoxide
	Hexachlorobenzene
	Hexachloro cyclohexane
	Quinoxyfen

* Total PAHs (Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k) fluoranthene, Benzo(g,h,i)perylene, Indeno(1,2,3-cd)pyrene)

In Romania transverse profiles were done for the 2 sampling stations, with 3 verticals: Left (50 m away from the left Danube bank, Centre (in the middle of the river) and Right (50 m away from the right bank). For suspended sediments, at each vertical, water was pumped from 3 depths.

3.3. Analyses of sediments

From the list of priority substances (PS) in the field of water policy (EC, 2013) and the list of River Basin Specific Pollutants for the Danube River Basin (ICPDR, 2003) 22 substances were selected (Table 3) to be analysed in accredited laboratories according to the specific analytical standards (Čaić et al., 2019).

Laboratory analyses of the sediment samples (grain size < 2mm), including sample preparation, were carried out in the selected accredited reference laboratory Balint Analitika Ltd. from Budapest, Hungary. After being analysed in the reference laboratory, the samples were split and sent to the participating national laboratories in each of the 12 countries for parallel analyses (Table 4).

Table 4. Selected national laboratories

Country	**Selected National Laboratory**
Austria	Laboratory of the Geological Survey of Austria (only metals)
Bosnia and Herzegovina	Laboratory of the Federal Institute of Agropedology
Bulgaria	Regional Laboratory Stara Zagora (RLSZ) of the Executive Environmental Agency (ExEA) at the Ministry of Environment and Water.
Croatia	BIOINSTITUT Ltd. Health and Veterinary Services, in Čakovec
Czech Republic	Laboratory of the State Geological Institute of Dionýz Štúr in Spišská Nová Ves
Hungary	Laboratory of the Department of Environment, Nature Conservation and Waste Management, Hajdú - Bihar County Government Office
Republic of Moldavia	Laboratory of the Institute of Chemistry in Chişinău
Montenegro	Centre for Ecotoxicological Research (CETI) in Podgorica
Romania	ALS Life Sciences S.R.L. in Ploieşti
Republic of Serbia	Laboratory of JCWI
Slovakia	Laboratory of the State Geological Institute of Dionýz Štúr in Spišská Nová Ves
Slovenia	National Laboratory of Health, Environment and Food (NLZOH) in Maribor

4. RESULTS AND DISCUSSIONS

The HSs concentrations in the river bottom sediment, suspended sediment and overbank (floodplain) sediments measured both by SIMONA reference laboratory and by the national laboratories were compared to the relevant environmental threshold values. The risk ratios (R) were obtained by dividing the measured HS concentration (C) with the Quality Standards (QS):

$$R = \frac{C}{QS} \quad (1)$$

The evaluation of results was based on SIMONA Evaluation Protocol (Dudás et al., 2021) and on a developed Excel tool that calculated the risk ratios of each HS in the studied three sediment matrices – equation 1). The evaluation was performed for bottom and suspended sediments using the European Union Environmental Quality Standards (EQS) for benthic organisms in freshwater, bottom sediments and suspended sediments referred herein as "EQS dossiers" (EC, 2013; EC, 2018). Other standards used for bottom sediment assessment were found in the following documents:

- Republic of Serbia - Official Gazette, No. 50/2012 (bottom sediment quality targets concentration);
- United States – Environmental Protection Agency (US-EPA), where ratio R is concentration C divided by TEC (Threshold Effect Concentration) - a value below which adverse effects are not expected to occur; (Ingersoll et al., 2000);
- Elbe basin (lower threshold in bottom sediments - IKSE/ICPER 2018);
- Rhine basin (intervention threshold for "poor quality" bottom sediments - ICPR, 2009).

For floodplain sediments the risk ratios R were computed taking into account the thresholds values in soils given in the following legislations:

- Republic of Serbia - Official Gazette No. 30/2018 and 64/2019;
- Bulgaria (Ordinance no. 3 of August 1, 2008 on the levels of maximum allowable concentration of harmful substances in soils);
- Romania (Order no. 756/03.11.1997, updated 28.11.2011);
- Hungary (Law 6/2009);
- Dutch pollution list (target values in soils).

The results are assessed per category of HSs (metal(oid)s, PAHs and organochlorine pesticides). Only analyses showing values of risk ratios R > 1 are presented and discussed. Tables are shown for Mercury, Lead and Anthracene.

4.1. Metals

4.1.1. Arsenic

There are no thresholds for As specified in EQS dossiers, neither for the Danube nor for the Rhine river basin. Values of R > 1 are found in 14 analyses in: Austria, Hungary and Slovakia.

In Austria: 2 analyses at station 02, in floodplain sediments FS (both in top layer TS and bottom layer BS measured in the reference laboratory).

In Hungary: 1 analysis at station 01 in FS TS (reference laboratory).

In Slovakia: 11 analyses, at both stations (01 and 02), in bottom sediments BS, as well as in floodplain sediments FS (in TS and BS), measured in the reference and national laboratory. The highest values of R are found in bottom sediments at station 01 (10.66 and 11.95 national and reference laboratory, after US-EPA TEC criterion; respectively 13.22 and 14.81 after Elba lower limit criterion). After Serbian target in bottom sediments, R values for station 01 BS are of an order of magnitude smaller (3.60 and 4.03). Mining activity and ore exploitation and processing are the sources of arsenic in surface and groundwater and associated river bottom sediments and soils in Slovakia (Fľaková et al., 2017).

4.1.2. Cadmium

There are no thresholds for Cd specified in EQS dossiers. Values R > 1 are found only at station 02 of Austria, in bottom sediments BS measured in the national laboratory and at the same station in floodplain sediments (both TS and BS, measured in national and reference laboratory – 4 analyses). The highest values were found for AT 02 FS BS (R = 8.33, for the national laboratory result, R = 9.05 for the reference laboratory result), after the Bulgarian maximum level of Cd in soils.

4.1.3. Chromium

There are no thresholds for Cr specified in EQS dossiers, neither for the Danube nor for the Rhine River basin. Values of R > 1 occur in: Bosnia and Herzegovina, Romania, and Slovakia.

In Bosnia and Herzegovina: in 12 analyses, at both stations (01 and 02) in bottom sediments BS and floodplain sediments FS (both TS and BS, measured in the national, as well as in the reference laboratory). The highest values for R in bottom sediments BS occur at station 01 (reference laboratory: 7.81 and 13.04 after US – EPA TEC and Elbe lower limit, but 3.39 after the Serbian legislation for sediments).

In Romania: at station 01, on the right side of the Danube transverse profile (reference laboratory).

In Slovakia: in station 02 in FS TS measured in the national laboratory, with values of R around 1 (1.25, respectively 1.08 after the Bulgarian and Hungarian legislation).

4.1.4. Copper

There are no thresholds for Cu specified in EQS dossiers. All the other standards for bottom sediments and soils showed that values R > 1 were found in Bulgaria and Slovakia.

In Bulgaria: only at station 01 in FS BS (national laboratory), the range of R values being between 1.21 and 2.63.

In Slovakia: at station 02, in bottom sediments BS and floodplain sediments (TS and BS), measured both in national and reference laboratory (6 analyses). There is a tight range of R values for bottom sediments BS after the Serbian legislation and US-EPA TEC (between 10.56 and 13.42). Elbe lower limit standard is stricter for Cu, the R values being 27.14 (national laboratory) and 30.29 (reference laboratory).

4.1.5. Mercury

There are no thresholds for Hg specified in EQS dossiers, but in all the other standards these exist. Values of R > 1 are found in: Austria, Bosnia and Herzegovina and Slovakia (Table 5 and Table 6).

In Austria: R > 1 at station 01 in floodplain sediments (FS BS in the reference laboratory).

In Bosnia and Herzegovina: 4 analyses at station 01, in bottom sediments (reference laboratory) and floodplain sediments FS (BS in the national and reference laboratory and TS in the reference laboratory).

In Slovakia: at both stations in bottom sediments, both in the national and reference laboratory (Table 5). R values at station 01 are of an order of magnitude higher than in station 02. The floodplain sediments in both stations (8 analyses – Table 6) present also values of R > 1 at the two sampling depths (TS and BS), measured in both national and reference laboratory. The Bulgarian threshold for normal values of Hg in soils is stricter, allowing ten times less Hg than the Serbian and Dutch standards. Mercury content in floodplain sediments surpassing all these thresholds, including the soil limits in Slovakia (0.15 mg/kg d.w. – Act no.220/2004 for sandy and loam – sandy soil type, lower limit, pH dependent), is in accordance with other researches in Slovakia in regions with past mining activity, which found soil, groundwater, surface water and some plants strongly polluted by mercury (Andráš et al., 2022; Dadová et al., 2014).

4.1.6. Nickel

There are thresholds for Ni specified in EQS dossiers and in all listed standards. Values of R > 1 are found in: Bosnia and Herzegovina, Bulgaria, Czech Republic, Romania, and Republic of Serbia.

In Bosnia and Herzegovina – at both stations, in all types of sediments (suspended, bottom,

Table 5. Risk ratio R for Hg in bottom sediments BS and suspended sediments SS

Sample Code	Lab. Type	BS-EQS benthic	BS-EQS sed.	BS-R. Serbia Target sed.	BS-US EPA lower limit	BS-Elbe Lower limit	BS-Rhine (poor)	SS-EQS
SBA01/BS	Ref.	n.d.	n.d.	1.6	2.67	3.20	< 1	n.r.
SK01 BS	Ref.	n.d.	n.d.	25.87	43.11	51.73	3.88	n.r.
SK01 BS	Nat.	n.d.	n.d.	26.67	44.44	53.33	4.00	n.r.
SK02 BS	Nat.	n.d.	n.d.	2.93	4.89	5.87	< 1	n.r.
SK02 BS	Ref.	n.d.	n.d.	3.67	6.11	7.33	< 1	n.r.

n.r. – not relevant; n.d. – not determined due to lack of limit value;

Table 6. Risk ratio R for Hg in floodplain sediments FS

Sample Code	Lab. Type	FS-R. Serbia Max con.	FS-Bulgaria normal value	FS-Romania Alert values sensible categories	FS-Hungary Legislation	FS-Dutch Target value
AT01 FS1 BS	Ref.	3.53	35.33	1.06	2.12	3.53
SBA01 FSSP/BS	Nat.	2.09	20.90	< 1	1.25	2.09
SBA01 FSSP/BS	Ref.	5.20	52.00	1.56	3.12	5.20
SBA01 FSSP/TS	Ref.	2.37	23.67	< 1	1.42	2.37
SK01 FS BS	Nat.	7.03	70.33	2.11	4.22	7.03
SK01 FS BS	Ref.	8.33	83.33	2.50	5.00	8.33
SK01 FS TS	Nat.	3.77	37.67	1.13	2.26	3.77
SK01 FS TS	Ref.	4.00	40.00	1.20	2.40	4.00
SK02 FS BS	Ref.	5.50	55.00	1.65	3.30	5.50
SK02 FS BS	Nat.	13.80	138.00	4.14	8.28	13.80
SK02 FS TS	Ref.	4.10	41.00	1.23	2.46	4.10
SK02 FS TS	Nat.	6.13	61.33	1.84	3.68	6.13

floodplain TS and BS), measured both in the national and reference laboratory (14 analyses).

In Bulgaria: at station 01, in suspended sediments SS (reference laboratory) and in floodplain sediments FS (in TS measured in the national laboratory).

In Czech Republic: in suspended sediments SS, at both sampling stations.

In Romania: at station 01, in suspended sediments SS in the middle of the Danube profile (national laboratory) and in bottom sediments BS in the right part of the transverse Danube profile (both laboratories). Ni at station 02 occurs only in floodplain sediments (TS and BS measured in the national laboratory), the values of R being small (between 1.23 and 1.04).

In Republic of Serbia: at station 02, in bottom sediments BS measured in both laboratories.

The presence of higher values for R was interpreted as being due to the geological background (ultrabasic and metamorphic rocks in Bosnia and Herzegovina, Republic of Serbia and Romania). High values of Ni in soils were mentioned in the Balkan Peninsula in GEMAS pan-European study (Jordan et al., 2018).

4.1.7. Lead

Like for Ni, there are thresholds for Pb specified in EQS dossiers and in all listed standards. Values of R > 1 are found in: Austria, Bosnia and Herzegovina, Bulgaria, Czech Republic, Croatia, Hungary, Romania, Slovakia and Republic of Serbia (Tables 7 and 8).

In Austria: at station 01 in suspended sediments SS sampled with the barrel (reference laboratory) and the sedimentation box (national laboratory). At station 02, R > 1 occurs in bottom sediments BS sampled at both locations (AT02 BS 01 and AT02 BS 02 – Table 7), in suspended sediments SS sampled with the barrel and the sedimentation box, as well as in floodplain sediments FS (both in FS and BS, measured in both laboratories – Table 8).

Table 7. Risk ratio R for Pb in bottom sediments BS and suspended sediments SS

Sample Code	Lab. Type	BS-EQS benthic	BS-EQS sed.	BS-R. Serbia Target sed.	BS-US EPA lower limit	BS-Elbe Lower limit	BS-Rhine (poor)	SS-EQS
AT01 SS BARREL	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	1.71
AT01 SS BOX	Nat.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	1.11
AT02 BS 01	Nat.	1.07	< 1	< 1	1.22	1.75	< 1	n.r.
AT02 BS 02	Ref.	1.83	< 1	< 1	2.09	3.00	< 1	n.r.
AT02 BS 02	Nat.	1.96	< 1	< 1	2.25	3.22	< 1	n.r.
AT02 SS BARREL	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	2.99
AT02 SS BOX	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	1.28
AT02 SS BOX	Nat.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	1.40
BG/01/SS/R	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	1.71
BG-01-SS	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	2.60
CZ-01-SS	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	1.56
CZ-02-SS	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	1.55
CZ-02-SS centrif	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	1.07
HR01 SS	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	3.73
HR02 SS	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	2.16
HU-02_SS	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	1.17
RO-01 BS-R	Ref.	1.06	< 1	< 1	1.22	1.74	< 1	n.r.
RO-01 BS-R	Nat.	1.25	< 1	< 1	1.43	2.05	< 1	n.r.
RO-01-SS-C	Nat.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	2.09
RO-01-SS-R	Nat.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	1.59
RO-02-SS-C	Nat.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	1.01
RO-02-SS-L	Nat.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	1.09
RO-02-SS-R	Nat.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	1.08
SBA02 SS/BR	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	2.03
SK02 BS	Ref.	1.8	< 1	< 1	2.06	2.95	< 1	n.r.
SK02 BS	Nat.	2.00	< 1	< 1	2.30	3.29	< 1	n.r.
SK02 SS	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	2.20
SR-02 BS	Nat.	1.08	< 1	< 1	1.23	1.77	< 1	n.r.

n.r. – not relevant; n.d. – not determined due to lack of limit value;

In Bosnia and Herzegovina, Bulgaria, Czech Republic, Croatia and Hungary R > 1 occurs only in suspended sediments measured in the reference laboratory, the values ranging from 1.17 in Hungary at station 02 up to 3.73 in Croatia at station 01.

In Romania: at station 01 in bottom sediments in the right part of the transverse profile on the Danube, as well as in suspended sediments from the centre and right part. At station 02 it occurs only in suspended sediments, on all three points of the profile (left, centre and right).

In Slovakia: at station 02 in all types of sediments (bottom, suspended, floodplain at both depth levels TS and BS).

In Republic of Serbia at station 02 in bottom sediments (national laboratory), with small R values (1.08 - 1.77).

There are 20 analyses which highlighted R > 1 in suspended sediments (out of 35 analyses presented in Tables 7 and 8), a fact which proves the affinity of Pb for suspended fine material in the water.

4.1.8. Zinc

There are no thresholds for Zn specified in EQS dossiers, but they exist in all the other listed standards. Values of R > 1 are found in: Austria, Croatia and Slovakia.

In Austria: at station 02, in bottom sediments BS sampled at both locations, as well as in floodplain sediments (both TS and BS), measured in the national and reference laboratory (8 analyses).

In Croatia – at station 01 in floodplain sediments (TS in the national laboratory).

In Slovakia: at station 02 in floodplain sediments (both TS and BS), measured in the national and reference laboratory (4 analyses).

4.2. Polycyclic aromatic hydrocarbons

PAHs listed in Table 2 were assessed, as well as Total PAHs (EEA 33-56-7 Total PAHs (Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(g, h, i) perylene, Indeno(1,2,3-cd) pyrene)). Only the results of R for Anthracene are presented in Tables 9 and 10, for other PAHs a synthetic table was made, due to the big number of analyses showing values of R > 1.

There are thresholds for Anthracene specified in EQS dossiers and in the other standards for bottom sediments, except for the Rhine River basin. Regarding floodplain sediments, limit values are indicated only in the legislation of Bulgaria and Romania. Values of R > 1 are found in: Bosnia and Herzegovina, Bulgaria, Czech Republic, Republic of Moldavia, Romania and Slovakia.

In Bosnia and Herzegovina: at station 01 in all sediment types (suspended, bottom, floodplain (both TS and BS), in both laboratories). At station 02 only in bottom sediments and suspended sediments (Table 9).

In Czech Republic: at station 01 in bottom sediments and suspended sediments and at station 02 in bottom sediments BS and suspended sediments SS sampled with the barrel and the centrifuge.

In Bulgaria: at station 01 in bottom sediments.

In the Republic of Moldavia: one analysis at station 02 in bottom sediments (national laboratory).

In Romania: at station 01 in bottom sediments, in the centre of the transverse profile on the Danube, and in station 02 in bottom sediments in the left part of the profile.

In Slovakia: at station 01 in bottom and suspended sediments, and at station 02 only in bottom sediments.

It is worth noting the stricter Serbian target value for Anthracene in bottom sediments, compared with the rest of the standards for this type of sediments, a fact which produces R values of an order of magnitude higher for the Serbian standard. Regarding floodplain sediments, the thresholds in the Bulgarian legislation are much smaller than the Romanian value limits (Bulgarian normal value 0.005 mg/kg, intervention value 0.5 mg/kg. Romanian normal value 0.05 mg/kg, alert value 5 mg/kg, intervention value 10 mg/kg – sensible categories), which explains the high R values

Table 8. Risk ratio R for Pb in floodplain sediments FS

Sample Code	Lab. Type	FS-R. Serbia Max con.	FS-Bulgaria normal value	FS-Romania Alert values sensible categories	FS-Hungary Legislation	FS-Dutch Target value
AT02 FS BS	Nat.	2.33	7.61	3.95	1.98	2.33
AT02 FS BS	Ref.	2.33	7.62	3.96	1.98	2.33
AT02 FS TS	Ref.	1.95	6.38	3.32	1.66	1.95
AT02 FS TS	Nat.	2.06	6.74	3.51	1.75	2.06
SK02 FS BS	Nat.	1.47	4.81	2.50	1.25	1.47
SK02 FS TS	Ref.	1.31	4.27	2.22	1.11	1.31
SK02 FS TS	Nat.	1.61	5.26	2.73	1.37	1.61

Table 9. Risk ratio R for Anthracene in bottom sediments BS and suspended sediments SS

Sample Code	Lab. Type	BS-EQS benthic	BS-EQS sed.	BS-R. Serbia Target sed.	BS-US EPA lower limit	BS-Elbe Lower limit	BS-Rhine (poor)	SS-EQS
BG-01 BS	Ref.	1.04	< 1	25.00	< 1	< 1	n.d.	n.r.
CZ-01 BS	Ref.	4.04	< 1	97.00	< 1	3.23	n.d.	n.r.
CZ-01-SS	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	3.06
CZ-02 BS	Nat.	3.79	< 1	91.00	< 1	3.03	n.d.	n.r.
CZ-02 BS	Ref.	4.38	< 1	105	< 1	3.5	n.d.	n.r.
CZ-02-SS	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	1.87
CZ-02-SS centrif	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	1.50
MD-02 BS	Nat.	1.00	< 1	24.00	< 1	< 1	n.d.	n.r.
RO-01 BS-C	Ref.	1.08	< 1	26.00	< 1	< 1	n.d.	n.r.
RO-02 BS-L	Ref.	4.42	< 1	106.00	< 1	3.53	n.d.	n.r.
SBA01 SS/BR	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	28.80
SBA01/BS	Ref.	27.88	4.46	669.00	< 1	22.30	n.d.	n.r.
SBA01/BS	Nat.	29.04	4.65	697.00	< 1	23.23	n.d.	n.r.
SBA02 BS DR	Ref.	3.33	< 1	80.00	< 1	2.67	n.d.	n.r.
SBA02 BS DR	Nat.	3.88	< 1	93.00	< 1	3.10	n.d.	n.r.
SBA02 SS/BR	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	6.23
SK01 BS	Nat.	2.25	< 1	54.00	< 1	1.80	n.d.	n.r.
SK01 SS	Ref.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	3.17
SK02 BS	Nat.	2.67	< 1	64.00	< 1	2.13	n.d.	n.r.

n.r. – not relevant; n.d. – not determined due to lack of limit value;

Table 10. Risk ratio R for Anthracene in floodplain sediments FS

Sample Code	Lab. Type	FS-R. Serbia Max con.	FS-Bulgaria normal value	FS-Romania Alert values sensible categories	FS-Hungary Legislation	FS-Dutch Target value
SBA01 FSSP/BS	Nat.	n.d.	187.60	< 1	n.d.	n.d.
SBA01 FSSP/BS	Ref.	n.d.	220.00	< 1	n.d.	n.d.
SBA01 FSSP/TS	Nat.	n.d.	222.80	< 1	n.d.	n.d.
SBA01 FSSP/TS	Ref.	n.d.	252.00	< 1	n.d.	n.d.

n.d. – not determined due to lack of limit value;

for floodplain sediments in Bosnia and Herzegovina at station 01 (Table 10).

The occurrence of R > 1 for all other measured PAHs, as well as total PAHs are presented in Table 11, which shows that these organic substances are accumulated in all types of sediments (bottom, suspended, floodplain), but not to the same extent. Limit values for listed PAHs in suspended sediments are specified in EQS dossiers, except for Indeno(1,2,3-cd) pyrene. It might seem that PAHs have a wider geographical distribution in bottom sediments, but two countries, Republic of Moldavia and Republic of Serbia sampled only bottom sediments, and so for them the concentrations of HSs in suspended and floodplain sediments could not be determined.

Metals, on the other hand, are captured in a great proportion in fine suspended sediments, but limit values of their concentration in suspended sediments exist only in EQS dossiers, for Pb and Ni. The risk ratios for the rest of the investigated metals could not be evaluated in suspended sediments, neither related to EQS dossiers, nor to the rest of the standards.

4.3. Pesticides

For the 6 pesticides listed in Table 3 either the measured concentration was below the detection limit in the laboratory, or there were no limit values in national standards in the European countries of the Danube River Basin, or, when there were, the computed risk ratio R values were < 1. This means that in the measured baseline stations we can assume there is no pollution due to agriculture at the sampling time.

5. CONCLUSIONS

The evaluation of results showed a good agreement

Table 11. Countries and frequency of analyses showing risk ratios R > 1 for metals and PAHs

Category	Substance	Total no. of analyses where R>1	No. of countries where R>1	Sediment Type			
				bottom sediments BS	suspended sediments SS	floodplain top layer FS TS	floodplain bottom layer FS BS
Metals	Arsenic	14	3	SK	n.d.	AT, HU, SK	AT, SK
	Cadmium	5	1	AT	n.d.	AT	AT
	Chromium	14	3	BH, RO	n.d.	BH, SK	BH
	Copper	7	2	SK	n.d.	SK	BG, SK
	Mercury	17	3	BH, SK	n.d.	BH, SK	AT, BH, SK
	Lead	35	9	AT, RO, SK, SR	AT, BG, BH, CZ, HR, HU, RO, SK	AT, SK	AT, SK
	Nickel	25	5	BH, RO, SR	BG, BH, CZ, RO	BG, BH, RO	BH, RO
	Zinc	17	3	AT	n.d.	AT, HR, SK	AT, SK
PAHs	Anthracene	23	6	BG, BH, CZ, MD, RO, SK	BH, CZ, SK	BH	BH
	Benzo(a)pyrene	65	10	AT, BG, BH, CZ, HR, MD, RO, SI, SK, SR	AT, BH, CZ, SK	BG, BH, CZ, SK	AT, BG, BH, CZ, RO, SK
	Benzo(b)fluoranthene	5	2	BG, RO	-	-	-
	Benzo(k)fluoranthene	3	2	BG, RO	-	-	-
	Benzo(g,h,i)perylene	38	6	BG, BH, CZ, MD, RO, SK	BH, CZ, SK	BG, BH, CZ, SK	BG, BH, CZ, SK
	Fluoranthene	88	11	AT, BG, BH, CZ, HR, MD, RO, SI, SK, SR	AT, BG, BH, CZ, HR, HU, SK	AT, BG, BH, CZ, RO, SK	AT, BG, BH, CZ, RO, SK
	Indeno(1,2,3-cd) pyrene	18	4	-	n.d.	BH, CZ, SK	BG, BH, CZ, SK
	Total PAHs	73	11	AT, BG, BH, CZ, HR, HU, MD, RO, SI, SK, SR	AT, BG, BH, CZ, HR, HU	BH, CZ	BG, BH, CZ,

n.d. – not determined due to lack of limit value

between analyses performed in the national laboratories and those done in the reference laboratory. Metals in measured sediment samples are likely to be related to past and present mining activities in Austria, Slovakia, Bosnia and Herzegovina and Republic of Serbia (higher concentration in As, Cd, Cu, Hg, Pb, Zn). Transboundary impact of environmental pollution from mining was mentioned also by Nagy (2012). Higher concentration in Cr and Ni are believed to be due to the geological background of ultrabasic and metamorphic rocks in Bosnia and Herzegovina, Republic of Serbia and Romania. From metals, Pb is the most widely spread and it can come also from PAHs processing.

Anthracene comes from fuel burning and it shows pollution from industry or navigation on Danube (Czech Republic, Slovakia, Bosnia and Herzegovina, Bulgaria and Romania,). Other revealed high concentration of PAHs, as well as total measured PAHs indicate industrial activities and wastewater discharges into the Danube River Basin. From PAHs, Fluoranthene has the widest spread (bottom, suspended and floodplain sediments), followed by Total PAHs.

In all 12 countries, pesticides from agriculture were below the detection limit or below the thresholds, suggesting that at least in the measured baseline stations, there are no pressures on the environment due to agriculture at the sampling time. The following concluding remarks are listed at country level, from Austria downstream, ending to Romania.

5.1. Austria

In Austria, no environmental quality standards have been set for sediments. As concerns the calculated risk ratios R, these are far higher in suspended sediments than in bottom sediments. The risk ratios for Pb in bottom and suspended sediment samples are the result of past mining activities (Pirkl et al., 2015). For example, the sampling station 02 (Lavamünd) is located downstream of an ancient iron and copper mine, 2 km ENE from Ettendorf. Pb, Zn, As, Hg and Cd risk ratios R exceed the value of 1 in top layer and bottom layer of floodplain sediments at both sampling stations, when applying Romanian, Bulgarian, Serbian or Hungarian QS values. The high risk ratios of individual and total PAHs may originate from industrial activities.

5.2. Czech Republic

The high level of PAHs in bottom and suspended sediments is connected with various causes, namely: burning materials for heating and other industrial purposes; airborne transboundary transmission of PAHs; surface runoff of PAHs; traffic.

5.3. Slovakia

In Slovakia the calculated risk ratios for floodplain sediments are often overpassing the national Environmental Quality (EQ) limits for soils (no national legislation for floodplains). The main sources of pollution by metals and PAHs in bottom and suspended sediments are the long lasting mining activities (Horná Nitra region, a source of metals like arsenic, cadmium, zinc etc.) and fossil fuel and coal combustion in a neighbouring power plant and in ore processing. The collapsing of a coal ashes retaining dam, a few decades ago, still nowadays acts as a long term source of PAHs and heavy metals.

Pesticides used in agriculture (long term agricultural activity in whole region of Nitra River) and also municipal waste incoming along the rivers are other sources of pollution with PAHs.

5.4. Slovenia

Ni concentrations are higher in bottom sediments compared to some QS, but stay below the intervention values. The higher concentration in Ni is partly related to the regional geology (Carboniferous-Permian shales and sandstones). The bottom sediments are evaluated as riskier than floodplain sediments for total PAHs, Benzo(a)pyrene and Fluoranthene All of these have a natural or anthropogenic origin (both locations are located close to Ljubljana, in the area of agricultural land). The high concentration of PAHs, as well as total measured PAHs indicate industrial activities and wastewater discharges.

5.5. Croatia

The sources of metal contamination are most likely the effluent water discharged into the rivers. Elevated concentrations of Pb and its compounds were determined in suspended sediment, on the expense of weathering of rocks and mineralization upstream of Drava River. Industrial and mining activities were also present in the upper part of the river. The top layer at Sutla River was contaminated with elevated concentrations of Zinc and its compounds (201.36 mg/kg), specifically caused by rail traffic over the bridge near the sampling site.

5.6. Hungary

In the bottom, suspended and overbank sediments in Hungary, there is no hazard for the benthic or water related ecosystems as concerns metals. All the PAHs concentrations measured in the river bottom sediment are below all the considered quality standards, so that the benthic and water related ecosystem are not at risk. The elevated PAHs concentrations in suspended sediments at both stations can be explained by sampling after a winter period (heating by burning wood, pallet or gas) and by remobilized PAHs from bottom sediment to suspended sediment. No burning factory such as waste incinerator, power plant or cement factory are known in these areas.

5.7. Montenegro

From all the countries which took part in this study, only Montenegro has no concentrations for all HSs above the limit values of EQS dossiers. Regarding other standards, all samples are below the intervention value or even the normal value.

5.8. Bosnia and Herzegovina

In Bosnia, for the station 01 Karanovac, the Ni, Cr and Hg high levels are explained by the extended ultrabasic rocks in the Spreča River basin, upstream of the sampling site. The increased concentration of Hg in the sediments is due to the anthropogenic factor (industrial plants upstream).

The increased contents of PAHs can certainly be attributed to the anthropogenic factor, i.e. industrial wastewater.

At sampling station 02 Rudanka, downstream from Karanovak site, the same ultrabasic rock source explains the high content in Ni and Cr. Here the increased content of Pb and Hg are caused by the discharge of industrial wastewater. At Rudanka, in the Bosna River, the contents of PAHs are up to several times lower than in the sediments of the river Spreča at Karanovac. So that the vast majority of PAHs are brought to the Bosna River by the Spreča River.

5.9. Republic of Serbia

In Republic of Serbia the quality of sediments may be considered to be within the national standards and is not to be considered to be a source of risk. Some exceptions were signaled. Ni and its compounds are higher than the threshold values set in national legislation, requiring revision of the national standards. Pb and its compounds at station 02 (Ram) is classified at risk, requiring also additional analysis and evaluation to establish the cause of the violation.

Total PAHs are above threshold values and represent a risk. The source of contamination is from air pollution and erosion and the main sources are probably from the coal fired in power stations and from steel mills in the vicinity of the sampling stations.

5.10. Bulgaria

There is no hazard for any damages for the benthic or water related ecosystems from Hg, As, Cd, Pb, Cu, Ni, Zn and Cr. Only at station 01 (Silistra) R =1.71 for Pb in suspended sediments and it is interpreted as being due to navigation. Ogosta and Iskar River (station 02) obviously settle their hazardous metals before, or close to the junction with the Danube River. Burning wood, pallet or gas of households is partly responsible for the observed elevated PAHs concentrations. Other possible sources might be related to industrial wastewater discharge and naval traffic. Waste waters from industrial plants of Veliko Tarnovo and Gabrovo may come into consideration as possible sources of contamination.

5.11. Republic of Moldavia

Regarding metals, there are no risk values > 1 in the investigated bottom sediment samples. Higher values were found only for anthracene, fluoranthene and total PAHs, being due to anthropogenic factors.

5.12. Romania

The risk ratios for Pb and its compounds in bottom and suspended sediment samples are a result of mining activities in the catchment area and may also be due to naval traffic. The higher content of Ni and Cr in bottom sediments at station 01 Bazias probably reflects the geological background.

At station 02 Sulina, the list of HSs in bottom sediments with values of R > 1 compared to EQS dossiers is shorter than at station 01 Bazias. An explanation could be the fact that the Danube at Bazias has the regime of a lake, where finer sediments were deposited in time, trapping many HSs. At Sulina, the waterbody has the regime of a river polluted by human activities. As concerns the bottom sediments, the PAHs concentration can be explained by pollution from the heavy naval traffic along the Danube River. These pollutants result by incomplete combustion of organic materials as fuel in ship engines or plants, and are released in air as gas-phase or aerosols and then in soil, water and biota.

5.13. Final remarks

Due to the very heterogeneous character of threshold values for metals, PAHs and pesticides in different countries along the Danube River, it appears necessary to revise the Quality Standards (QS) of sediments, including in the national legislations previsions for suspended and floodplain sediments, so that QS should not differ across countries. Quality Standards for metals, PAH and pesticides (i.e. limits above which a concentration can cause harm to humans, animals, plants) should not differ across countries.

In relation to the thresholds established by QS, the geochemical anomalies for Ni, Cr, etc. caused by the local geological background, should be considered in setting the levels of intervention, as was suggested also by Albanese et al., (2007).

Acknowledgements

This study was funded by the Project DTP2-093-2.1. **SIMONA** (Sediment-quality Information, Monitoring and Assessment System to Support Transnational Cooperation for Joint Danube Basin Water Management) financed by the European Union through the Danube Transnational Programme.

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Received at: 25. 07. 2022
Revised at: 18. 08. 2022
Accepted for publication at: 30. 08. 2022
Published online at: 31. 08. 2022