Elements and Persistent Organic Pollutants in the Sediments of the Sava River

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Abstract Among various stressors, aquatic ecosystems are exposed also to different inorganic and organic pollutants. The pollution of the Sava River is related mainly to the release of industrial wastes, untreated effluents from municipalities, and contaminants arising from agricultural activities. To assess the geographical distribution of sediment pollution, sediments were analysed at selected sites along the Sava River. Total element concentrations were determined and mobile element fractions and anthropogenic inputs of elements assessed. Selected persistent organic pollutants: polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and chlorinated pesticides were also determined. In industrially exposed sites, Hg, Cr, and Ni were found in moderate concentrations (up to 0.6, 380 and 210 mg kg^{-1}, respectively). Since Cr and Ni exist in sparingly soluble forms, they do not represent an environmental burden. Elevated P concentrations up to 1,000 mg kg^{-1} were found at agricultural areas and big cities. Regarding elements, the environmental status of sediments of the Sava River is comparable to other moderately polluted rivers in Europe, if rivers impacted by mining are not considered. Among the organic pollutants PAH were present in moderate concentrations (sum of 16 PAH up to 2,000 ng g^{-1} with two exceptions with elevated PAH concentrations up to 4,000 ng g^{-1} located downstream the oil fields) and their concentrations increased downstream the river. Concentrations of PCB were low (the sum of 7 indicator PCB was below 4 ng g^{-1}). Among selected pesticides, p,p'-DDT were found in moderate concentrations in sediments at two sampling sites in Croatia (up to 3 ng g^{-1}) and HCB in high concentration in the city of Belgrade (91 ng g^{-1}), although the use of these persistent pesticides has been banned for many years. Considering the organic pollutants, Sava is a moderately polluted river. The results of this study contribute to knowledge on the extent of pollution of sediments of European rivers and are important for water management institutes

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and local authorities, which may use these data for sustainable use, management, and protection of the Sava River water resources.

Keywords Sava River • Sediments • Elements • Polyaromatic hydrocarbons • Polychlorinated biphenyls • Organochlorine pesticides

List of Abbreviations

Al	Aluminium
As	Arsenic
CCME	Canadian Environmental Quality Guidelines
Cd	Cadmium
Cr	Chromium
Cu	Copper
DDT	Dichlorodiphenyltrichloroethane
ECD	Electron capture detector
ERL	Effects range median
ERM	Effects range low
GC-MS	Gas chromatography–mass spectrometry
HCB	Hexachlorobenzene
Hg	Mercury
ICPDR	International Commission for the Protection of the Danube River
ICP–MS	Inductively coupled plasma mass spectrometry
ISQG	Interim Sediment Quality Guidelines
Ni	Nickel
OCP	Organochlorine pesticides
P	Phosphorous
PAH	Polycyclic aromatic hydrocarbons
Pb	Lead
PCB	Polychlorinated biphenyls
PEL	Probable effect levels
SARIB	Sava River Basin: Sustainable Use, Management and Protection of Resources
SQGs	Sediment quality guidelines
SRB	Sava River Basin
WFD	Water Framework Directive
Zn	Zinc

1   Introduction

The drinking water supply in the Sava basin relies mainly on the rich high-quality groundwater resources, which are directly influenced by the Sava River. Sediments are essential for the functioning of aquatic ecosystems. They serve as a source of nutrients for microorganisms and importantly contribute to the food web. On the other hand sediments represent also a sink for a variety of toxic inorganic and organic contaminants, nutrients, and pathogens. The accumulated contaminants may be remobilised to overlying waters and disrupt the ecosystem, acting as stressors, which can have harmful effects on freshwater habitat [1]. Therefore, sediment quality is of crucial importance to protect surface water quality and to maintain benthic ecosystem health. The quality of sediment is important also in preparing the management plans related to dredging activities for restoring water-ways or for the removal of sediments accumulated before dams of hydroelectric power plant accumulation basins.

Chemical analysis of sediments are commonly applied since they reflect spatial and temporal variation of contaminant concentrations of elements [2–6] and organic pollutants [7–9]. Among elements, Cd, Pb, Cu, Zn, Cr, Ni, Hg, and As are often accumulated in sediments as a consequence of industrial [10–12], municipal [3], and mining activities [13–15], while intensive rural land use and domestic sewage are a major source of P deposition in sediments [16, 17]. The most frequently investigated organic contaminants in sediments are polycyclic aromatic hydrocarbons (PAH) [7, 9, 18, 19], polychlorinated biphenyls (PCB) [8, 20], and pesticides [8, 9]. PAH, formed during the pyrolysis of virtually all organic matter, are ubiquitous organic contaminants in aquatic sediment. Their acute toxicity and sublethal effects on aquatic organisms, including the mutagenic and genotoxic potential of certain PAH once in the food chain, have generated interest in studying their composition and distribution in the environment and more specifically in river sediments [7, 9, 18, 19, 21–28]. PCB were once extensively used in industrial applications including transformers, electrical equipment, and ship painting. They have been banned in Europe for over three decades; however, being chemically stable, it is likely that their presence in sediments derives from their former use. Similarly, organochlorine pesticides are chlorinated hydrocarbons used extensively from the 1940s to the 1960s in agriculture and mosquito control. Representative compounds in this group include DDT, methoxychlor, dieldrin, chlordane, toxaphene, mirex, kepone, lindane, and benzene hexachloride. Organochlorine pesticides are now banned in the developed world, but due to their physicochemical properties and long range transport, they could be still entering our environment.

Once the concentration of the chemical contaminant reaches a point at which it causes adverse effects to the biota, the chemical contaminant is considered as a pollutant [29]. In past decades numerous sediment quality guidelines (SQGs) have been developed to estimate the environmental status of sediments and to determine management options for dredged material disposal [29–31]. Sediment quality was

assessed using chemical quality criteria [29], while biological effect-based assessment approaches have gained more interest. A group of Canadian researchers derived information on concentrations of selected chemicals that maintain healthy aquatic life associated with bed sediments, which is provided in the Canadian Environmental Quality Guidelines [32]. The Interim Sediment Quality Guidelines (ISQG) correspond to the threshold level effects below which adverse biological effects are not expected, while probable effect levels (PEL) characterise concentrations of pollutants that may affect the aquatic life [32]. For improving sediment quality assessment and sediment management alternatives, expert groups are still developing sediment quality criteria [1, 33, 34]. Recently, the European Commission (EC) has provided technical guidance for the derivation of SQGs as a part of common implementation strategy for the Water Framework Directive (WFD) [35].

In many cases the extent of pollution cannot be estimated solely on the basis of the determination of the total content of chemical substances in sediments because bioavailability and toxicity to organisms depend on their chemical forms. The use of fractionation procedures provide useful information on the partitioning of elements between easily and sparingly soluble fractions of sediments and enable assessment on the proportion of the potentially mobile and bioavailable element fractions.

Different fractionation procedures are applied in sediment and soil analysis, most frequently following Tessier's [36] or BCR [37] sequential extraction procedures [13, 38–40]. The leaching protocol of the first step of these sequential extraction procedures is also used to investigate the easily soluble elements fraction, applying aqueous solutions of ammonium chloride [36] or acetic acid [37] as extracting agents, respectively. Data on mobility and potential bioavailability of elements in sediments are useful for the estimation of the environmental burden [13, 38, 39] and represent a good basis for the management of dredged sediments [41] as well as remediation of polluted sediment sites. In order to estimate the natural and anthropogenic input of elements in sediments, normalisation approaches are commonly used based on correlations between the concentration of trace elements and the element that is naturally present in the environment investigated. For this purpose Al as a major constituent of aluminosilicates and Fe as a clay mineral indicator element have usually been applied [2, 42, 43]. However, these elements cannot be used in normalisation if they are present in sediments as a consequence of external contamination, e.g., mining or industrial activities [13].

In the present chapter ecological status of the Sava River sediments is assessed. Data on total element concentrations and highly mobile element fractions (extraction in 0.11 mol L^{-1} acetic acid) are given. Anthropogenic inputs of pollutants to sediments are identified by normalisation of total element concentrations to Al. In addition, information on occurrence of persistent organic pollutants, 16 PAH, 7 PCB, and selected chlorinated pesticides, in sediments is provided. The choice of pollutants investigated followed recommendations of the WFD [44], list of the priority substances and certain other pollutants from the WFD [45], as well as specific pollutants which have been recently listed in support to maintain physico-

chemical conditions in water that would prevent diverse biological effects on aquatic life [46]. Most data were obtained from results of the 6th FW EC project: Sava River Basin: Sustainable Use, Management and Protection of Resources (SARIB).

2 Sampling of Sediments: The Sava River Profile and Grain-Size Distribution

Sampling was performed in April 2005, October 2005, and May 2006. Twenty sampling locations (Fig. 1, Table 1) were selected along the Sava River considering the sample accessibility and representativeness in terms of different anthropogenic sources of pollution like the industry, agriculture, urban activities, and traffic.

In the Slovenian part of the basin, the riverbed is relatively steep and formed from solid rock. So, samples were taken from the reaches where sediment deposition occurs, a few meters from the riverbank. At the locations of hydroelectric power plants Moste and Vrhovo, sediments were sampled just before the hydroelectric dams. Downstream from the Slovenian–Croatian border, the Sava River turns into a flatland river with fine-grained sediments covering the riverbed. From each location, about 3 kg of the top 15 cm sediment layer was collected using the piston corer with plastic core liners (Fig. 2).
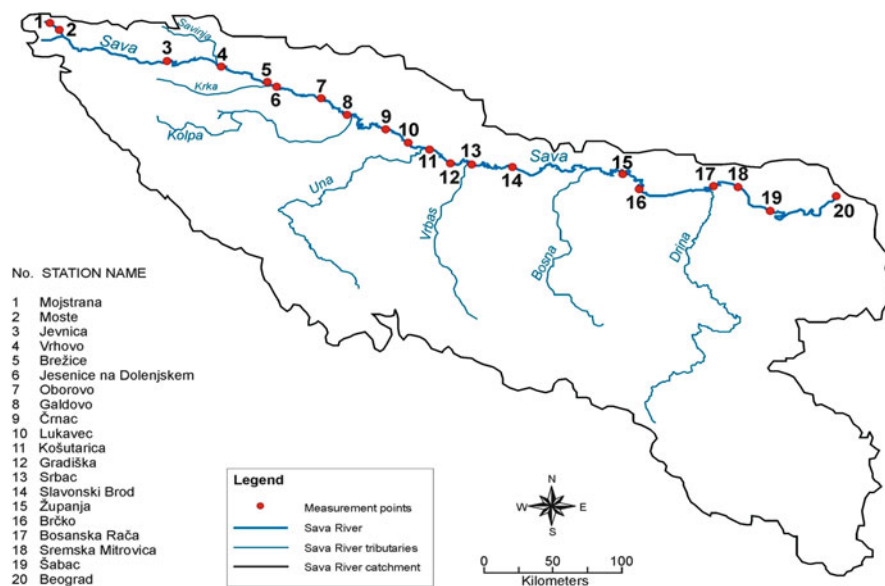

No.	STATION NAME
1	Mojstrana
2	Moste
3	Jevnica
4	Vrhovo
5	Brežice
6	Jesenice na Dolenjskem
7	Oborovo
8	Galdovo
9	Črnac
10	Lukavec
11	Košutarica
12	Gradiška
13	Srbac
14	Slavonski Brod
15	Županja
16	Brčko
17	Bosanska Rača
18	Sremska Mitrovica
19	Šabac
20	Beograd

Legend

• Measurement points
— Sava River
— Sava River tributaries
— Sava River catchment

Fig. 1 Sava River basin: sediment sampling sites along the Sava River

Table 1 GPS data for sediment sampling sites along the Sava River

Sample no.	Sampling site	GPS
1	Mojstrana	N46.0644°; E13.959822°
2	Moste	N46.415057°; E14.105334°
3	Jevnica	N46.105710°; E14.787503°
4	Vrhovo	N46.045294°; E15.215272°
5	Brežice	N45.897421°; E15.591798°
6	Jesenice na Dolenjskem	N45.861740°; E15.683890°
7	Oborovo	N45.41217°; E16.14.810°
8	Galdovo	N45.28922°; E16.23155°
9	Črnac	N45.26304°; E16.25520°
10	Lukavec	N45.24087°; E16.32339°
11	Košutarica	N45.15062°; E16.57157°
12	Gradiška	N45.09°; E17.15°
13	Srbac	N45.10876°; E17.51570°
14	Slavonski Brod	N45.08380°; E18.04441°
15	Županja	N45.02389°; E18.41924°
16	Brčko	N44.88220°; E18.80366°
17	Bosanska Rača	N44.90960°; E19.29548°
18	Sremska Mitrovica	N44.97481°; E19.59324°
19	Šabac	N44.76057°; E19.70745°
20	Beograd	N44.81456°; E20.44646°

Sampling and sample preservation followed the recommendations of the Guidance Document No. 25 on chemical monitoring of sediment and biota under the WFD [46]. For comparability of analytical data to other river basins, wet sieving through 63 μm sieve was applied [46–48].

From the Sava River profile and grain-size distribution of sediments (Fig. 3), it can be seen that in Slovenia the Sava River is a mountain river containing between 40 and 60 % of fine particles in the sediment (<63 μm). At the Slovenian–Croatian border, the Sava River turns into a flatland river and the percentage of the fine particles in sediments (<63 μm) is gradually increased, reaching up to 90 % of the total sediment content.

3   Elements in the Sediments of the Sava River

3.1   Total Element Concentration of Sediments in the Sava River and Normalisation to Aluminium

Total element concentrations were determined after microwave-assisted digestion of sediments by ICP–MS and total Hg by oxidative combustion using DMA-80

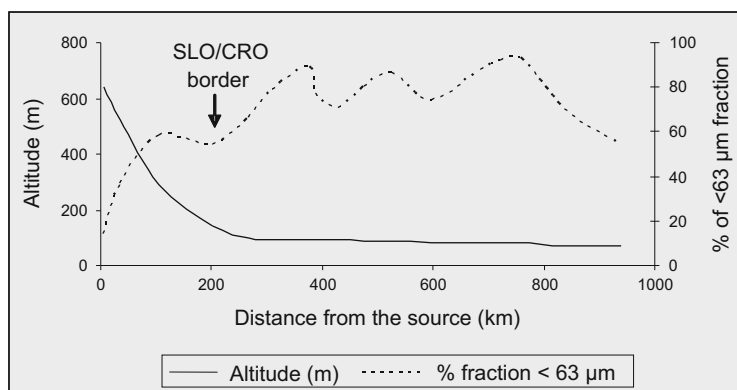**Fig. 2** Sediment sampling and piston corer used for sampling of sediments

Fig. 3 The Sava River profile and grain-size distribution of sediments

Direct Mercury Analyzer. The sampling protocol, sample preparation, and analytical procedures are described in detail in the study of Milačič et al. [49]. In the sediment of the Vrhovo impoundment, Hg speciation was also performed. Total Hg (THg) in solid part was determined by acid digestion, oxidation, reduction, gold amalgamation, and cold vapour atomic absorption spectrometry (CV AFS). MeHg was determined by CH_2Cl_2 extraction, ethylation, and detection by cold vapour atomic fluorescence spectrometry (CV AFS) [50, 51]. Methylation and reduction

potential of inorganic Hg were determined using spikes of inorganic radioactive isotope [197]Hg. After incubation MeHg was extracted. Radioactive decay of the isotope [197]Hg was measured [52]. The data on total element concentrations in the sediments of the Sava River are presented in Table 2. To evaluate the quality of the Sava River sediments, ISQG and PEL values are also given, considering the Canadian Quality Guidelines [32].

In order to account for geochemical variations along the Sava River, the normalisation by a conservative element Al, as a major constituent of aluminosilicates, was applied (Fig. 4). Significant deviations from the linear relationship may be used to differentiate between natural against anthropogenic inputs [42, 43, 49].

From the data of Table 2, it can be seen that the lowest concentrations of elements, which represent a natural background, were observed at the mountain village Mojstrana, an unpolluted site close to the Sava Dolinka River spring. Ščančar et al. [53] reported similar low concentrations of elements along the Sava Dolinka River from Mojstrana up to Jesenice, an industrial city with well-developed steelmaking industry. As a consequence of dredging of sediments, low element concentrations were found also at Galdovo. So this sampling site may not represent the actual ecological status of sediments. In general, the concentrations of elements in sediments of the Sava River gradually increase from the Sava River spring to its outflow to the Danube River.

Among metals, Hg concentrations in sediments in general ranged from 0.2 to 0.6 mg kg^{-1} and in most sampling sites exceeded the ISQG value (0.17 mg kg^{-1} Hg). In Košutarica, Gradiška, and Šabac, Hg concentrations were around 0.6 mg kg^{-1} and exceeded also the PEL value (0.486 mg kg^{-1} Hg). Normalisation to Al (Fig. 4) also indicated that higher Hg concentrations in Košutarica and Gradiška are most probably related to the oil refinery activities, while in Šabac the Hg input is most likely associated to pollution from the chemical industry. Slightly elevated Hg levels in Vrhovo (the Slovenian part of the river) were associated to former industrial pollution from a chemical plant in Hrastnik (the use of Hg cells in chlor-alkali production until 1997), while in Jevnica the impact of Ljubljana city is evident. In our previous work [42], comparable Hg concentrations at the same sampling sites in Slovenia were also determined. A similar concentration of Hg as in Jevnica was determined in Oborovo (Croatia), a sampling site, which reflects the pollution of the Zagreb city. In general lower concentrations than in the Sava River (between 0.1 and 0.3 mg kg^{-1} Hg) were reported by Sakan et al. [12, 54] for the canal sediments from the Danube alluvial formation and the Tisa River in Serbia. The extent of pollution of Hg in sediments from the Sava River is comparable to the majority of sampling sites in the Danube River (around 0.4 mg kg^{-1} Hg) [48, 55, 56] and is similar to the concentrations reported in Odiel River in Spain (from 0.1 to 0.7 mg kg^{-1} Hg) [57]. Hg concentrations from the Sava sediments are lower than reported by Meybeck et al. [5] for the Seine River, France (around 1 mg kg^{-1} Hg), and for the polluted Bílina River, Czech Republic (1–3 mg kg^{-1} Hg) [58], and are much lower than those determined in contaminated sediments of the Soča River (10–20 mg kg^{-1} Hg) due to former mercury mining activities in Idrija, Slovenia [14, 59].

Table 2 Determination of total element concentrations in sediments of the Sava River by ICP-MS and Hg by DMA-80 Direct Mercury Analyzer. Concentrations are expressed on a dry mass basis. Results represent average of two parallel samples ± standard deviation

Sampling site	Pb (mg kg^{-1})	Zn (mg kg^{-1})	Cu (mg kg^{-1})	Ni (mg kg^{-1})	Cr (mg kg^{-1})	Cd (mg kg^{-1})	As (mg kg^{-1})	Hg (mg kg^{-1})	P (mg kg^{-1})
1. Mojstrana	11.5 ± 0.1	55.4 ± 0.7	14.4 ± 0.4	12.6 ± 3.9	23.1 ± 1.3	0.28 ± 0.01	6.9 ± 0.6	0.035 ± 0.001	170 ± 5
2. Moste	40.9 ± 0.6	118 ± 1	33.1 ± 0.4	70.1 ± 1.1	184 ± 4	0.58 ± 0.02	14.7 ± 0.1	0.134 ± 0.004	275 ± 10
3. Jevnica	41.7 ± 3.7	142 ± 1	34.4 ± 3.0	27.3 ± 0.7	73 ± 1	0.42 ± 0.08	10.5 ± 0.8	0.388 ± 0.043	625 ± 20
4. Vrhovo	47.8 ± 3.4	223 ± 2	45.9 ± 1.0	36.9 ± 0.6	94 ± 2	0.73 ± 0.03	9.0 ± 1.3	0.397 ± 0.011	1,190 ± 30
5. Brežice	27.3 ± 2.7	113 ± 1	18.6 ± 3.0	17.6 ± 1.9	48.2 ± 0.6	0.24 ± 0.01	9.6 ± 2.1	0.247 ± 0.006	360 ± 10
6. Jesenice na Dol.	29.2 ± 6.6	106 ± 13	13.6 ± 1.9	12.3 ± 0.1	50.3 ± 0.8	0.22 ± 0.01	8.4 ± 0.8	0.235 ± 0.042	315 ± 10
7. Oborovo	41.1 ± 1.2	172 ± 5	39.1 ± 1.2	36.7 ± 1.1	88 ± 3	0.62 ± 0.02	11.3 ± 0.3	0.390 ± 0.007	950 ± 30
8. Galdovo	13.8 ± 0.4	77 ± 2	10.9 ± 0.3	16.3 ± 0.5	43 ± 1	0.40 ± 0.01	2.9 ± 0.1	0.091 ± 0.005	380 ± 10
9. Črnac	32.5 ± 1.0	155 ± 5	27.1 ± 0.8	30.8 ± 0.9	85 ± 3	0.55 ± 0.02	7.7 ± 0.2	0.366 ± 0.004	750 ± 20
10. Lukavec	32.7 ± 1.0	163 ± 5	35.5 ± 1.1	44.4 ± 1.3	99 ± 3	0.64 ± 0.02	11.4 ± 0.3	0.282 ± 0.010	930 ± 30
11. Košutarica	41.5 ± 1.2	224 ± 7	30.3 ± 0.9	39.5 ± 1.2	127 ± 4	0.83 ± 0.02	20.1 ± 0.6	0.585 ± 0.015	670 ± 20
12. Gradiška	36.0 ± 1.1	220 ± 7	29.8 ± 0.9	41.9 ± 1.3	167 ± 5	1.02 ± 0.03	12.1 ± 0.4	0.629 ± 0.025	910 ± 30
13. Srbac	25.5 ± 0.5	84 ± 2	27.1 ± 0.5	79 ± 2	236 ± 5	0.43 ± 0.01	11.2 ± 0.2	0.376 ± 0.009	400 ± 10
14. Slavonski Brod	25.5 ± 0.8	118 ± 4	31.9 ± 1.0	102 ± 3	186 ± 6	0.58 ± 0.02	16.5 ± 0.5	0.347 ± 0.012	860 ± 25
15. Županja	33.9 ± 1.0	134 ± 4	31.1 ± 0.9	212 ± 7	381 ± 11	0.47 ± 0.01	19.8 ± 0.6	0.269 ± 0.010	690 ± 20
16. Brčko	52 ± 1	165 ± 3	43.4 ± 0.8	185 ± 4	312 ± 6	0.62 ± 0.01	16.7 ± 0.3	0.297 ± 0.031	730 ± 20
17. Bosanska Rača	122 ± 1	184 ± 4	47.1 ± 0.9	186 ± 4	273 ± 6	0.66 ± 0.01	17.9 ± 0.4	0.374 ± 0.004	760 ± 20
18. Sremska Mitrovica	79 ± 1	275 ± 6	44.9 ± 0.9	177 ± 4	276 ± 6	0.84 ± 0.02	23.6 ± 0.5	0.444 ± 0.091	800 ± 25
19. Šabac	117 ± 1	361 ± 7	49.6 ± 1.0	163 ± 3	232 ± 5	1.40 ± 0.03	25.1 ± 0.6	0.624 ± 0.012	930 ± 30
20. Beograd	97 ± 1	173 ± 4	46.2 ± 0.9	82 ± 2	151 ± 3	0.84 ± 0.02	15.7 ± 0.3	0.275 ± 0.030	1,060 ± 30
ISQG	30.2	124	18.7	/	52.3	0.7	7.24	0.17	/
PEL	112	271	108	/	160	4.2	41.6	0.486	/

Canadian Sediment Quality Guidelines for the Protection of Aquatic Life [32]
Interim Sediment Quality Guidelines (ISQG) corresponds to the threshold level effects below which diverse biological effects are not expected
Probable effect levels (PEL) characterize concentrations of pollutants that may affect the aquatic life
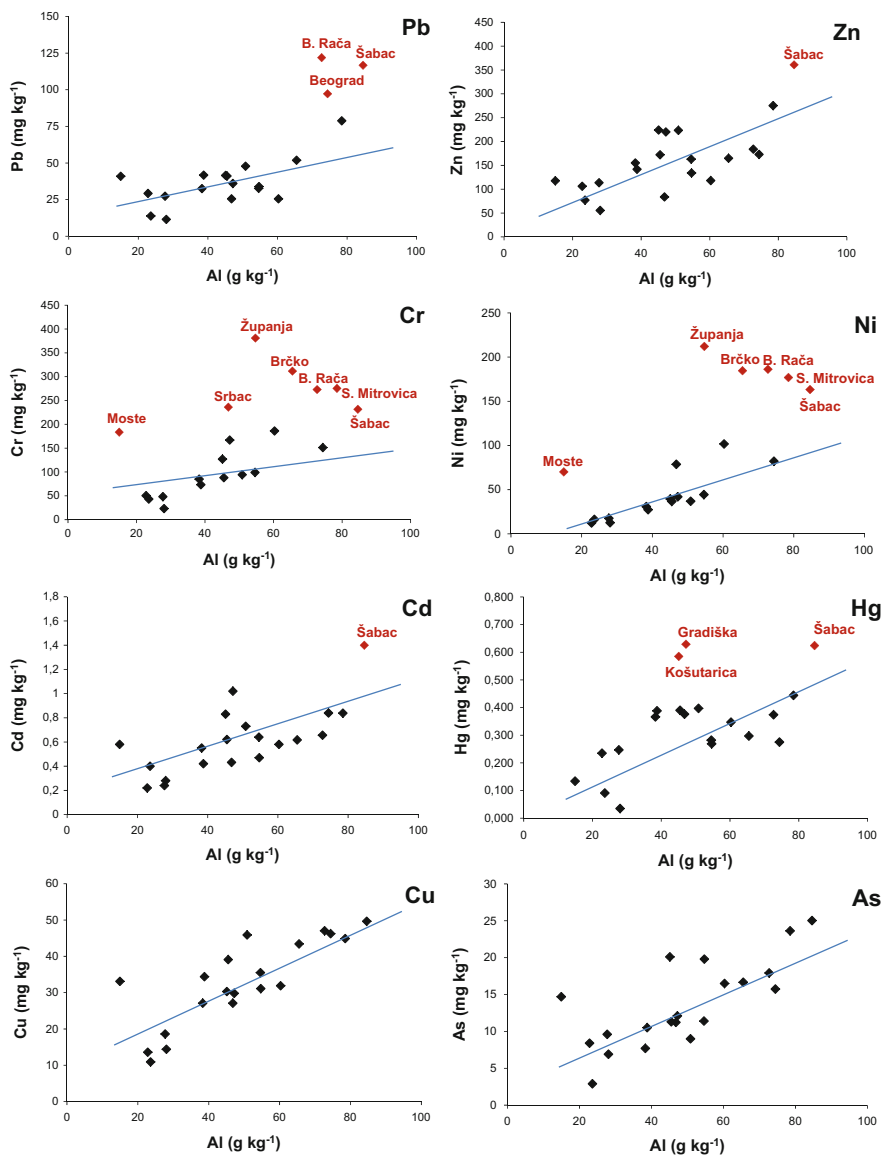/ data not provided

Fig. 4 Relationship of Pb, Zn, Cr, Cd, Ni, Cu, Hg, and As with Al in the sediments from the Sava River

It is well known that Hg can be transformed from inorganic to more toxic organic form—monomethylmercury (MeHg), which is bioaccumulative form of Hg. Moreover, mobility of mercury can also be enhanced due to oxidation/reduction processes in the aquatic environment [60], particularly in impoundments. In order to assess the potential for these transformations speciation of mercury was

Table 3 Some parameters measured in sediment core sample from accumulation basin of HP Vrhovo

Parameter	Value
Redox potential (mV)	−170
THg (ng g^{-1}), dry weight	283 ± 14
MeHg (ng g^{-1}), dry weight	7.5 ± 0.6
Methylation Hg (ng g^{-1} day^{-1})	6.78
Reduction Hg (ng g^{-1} day^{-1})	0.021

done. In addition, experiments using radioactive tracer ^{197}Hg were performed to estimate reduction and methylation potential of the impoundment sediment.

THg in the impoundment sediment core from hydropower plant (HP) Vrhovo (Table 3) was slightly higher in comparison to the Slovenian background [61, 62]. The percentage of Hg present as MeHg exceeded 2.5 % of THg. That proportion is relatively high compared to the literature data where less than 1 % of Hg as MeHg is normally reported [63, 64].

Tracer experiments also confirmed very high ability for methylation of Hg in sediment of the HP Vrhovo. For instance, in one day per gram of sediment 6.8 ng of MeHg can be formed, which is 200 higher, than in 1 L of river water from same sampling location [65]. This indicates extreme sensitivity of the impoundment sediment of the system for free Hg(II) loads.

For comparison, the sediment of the Idrijca River, which is heavily impacted by the past mercury mining, has shown much lower methylation capacity (about 10 times lower) [52, 66]. Consequently, MeHg in water and fish of the HP Vrhovo were also elevated [65]. These results indicate that for the river systems, total mercury is not a good indicator, but the speciation is of paramount importance to understand the potential risk of Hg.

Data from Table 2 also demonstrate that the Sava River is moderately polluted with Cr and Ni at sampling site Moste in Slovenia (steelworks Acroni) and at sampling sites in Croatia, Bosnia and Herzegovina, and Serbia, from Gradiška up till Šabac. At these sampling locations the concentrations of Cr are higher than those of PEL values (160 mg kg^{-1} Cr) and, at most sampling sites investigated, higher also from ISQG values (52.3 mg kg^{-1} Cr). For Ni there are no data on Canadian sediment quality standards. Normalisation to Al exhibited the same pattern of Cr and Ni inputs to sediments. At the sampling site in Moste, the Cr and Ni contamination arises from steelworks Acroni, while sampling sites from Gradiška up till Šabac indicate the influence of the heavy metal and chemical industry activities along the Sava River in this region. Cr concentrations in industrial-impacted sites range from 180 up to 380 mg kg^{-1} Cr and of Ni from 70 up to 200 mg kg^{-1} Ni. Similar concentrations were found in the sediments of the Po River, Italy (from 120 to 230 mg kg^{-1} of Cr and from 100 to 240 mg kg^{-1} of Ni) [67]. However, the concentrations of Cr and Ni in the Sava River sediments influenced by the industrial activities are higher than most of Cr and Ni values reported for the Danube River [48, 55, 56, 68] and Tisa River [69] sediments, in

which concentrations of Ni in general did not exceed 100 mg kg^{-1} and Cr 150 mg kg^{-1}. Concentration levels of Cr and Ni in the Sava sediments are also higher from those determined in sediments of the Odiel River, Spain (30–150 mg kg^{-1} Cr and 15–40 mg kg^{-1} Ni) [57].

From the data on Table 2, it can be further seen that most of Pb concentrations in the Sava sediments exceeded ISQG value (30.2 mg kg^{-1}) and at Bosanska Rača and Šabac sampling sites, the sediments exceeded also PEL value (112 mg kg^{-1} Pb). From data on normalisation to Al (Fig. 4), the anthropogenic input of Pb in Belgrade arises presumably due to heavy city traffic, while in Bosanska Rača high Pb concentrations in sediments are related to heavy traffic on the border between Bosnia and Herzegovina and Serbia. In Šabac anthropogenic input of Pb in sediments is most probably related to the activities of the chemical industry. By comparing the amount of Pb in the sediment from the Sava River at Šabac (sampling on May 2006, 117 mg kg^{-1}) with that reported by Vuković et al. [70] for the same location (around 30 mg kg^{-1}), a significant decrease in Pb concentration is evident most likely due to reduced emissions from the chemical plants. Pb concentrations in the Sava River are in general comparable to concentrations of Pb (40–70 mg kg^{-1}) in River Po, Italy [67], and Tisa River, Serbia [69], and are similar to Pb concentrations reported for the Danube River (30–100 mg kg^{-1} Pb) [48, 54–56, 68] as well as for the Bílina River, Czech Republic [58], but are much lower than those reported for the mining area (100–9,000 mg kg^{-1} Pb [13] and 500–5,000 mg kg^{-1} Pb [57]).

Cd concentrations in sediments of the Sava River (Table 2) in general did not exceed ISQG value (0.7 mg kg^{-1}). Anthropogenic input (data on normalisation to Al, Fig. 4) in Šabac is most probably related to the emissions from the chemical industry. Cd concentrations in the sediments of the Sava River are comparable to River Po, Italy (0.4–1.4 mg kg^{-1}) [67], and are lower than those reported for the Tisa River, Serbia (around 3 mg kg^{-1}) [69]. Slightly higher Cd concentrations than in the Sava River sediments were found in the Seine River, France (1–2 mg kg^{-1}) [5], and Bílina River, Czech Republic (around 3 mg kg^{-1}) [58], but appreciably higher Cd concentrations were determined in the sediments of the Danube River (around 2–3 mg kg^{-1} Cd) [48, 56]. However, recent reports on Cd concentrations in the Danube River indicate on the reduced pollution with Cd (concentrations between 1 and 10 mg kg^{-1}) [54, 55, 68]. In comparison to mining area sites (2–130 mg kg^{-1} Cd [13] and 2–9 mg kg^{-1} Cd [57]), the concentrations of Cd in the Sava River sediments are significantly lower.

Zn concentrations in sediments of the Sava River (Table 2) in general exceeded ISQG value (124 mg kg^{-1} Zn) and at two sampling sites also PEL value (271 mg kg^{-1} Zn). Anthropogenic input of Zn in Šabac (normalisation data on Al concentration, Fig. 4) most probably arise from activities of the chemical industry. Zn concentrations in the sediments of the Sava River are comparable to most data reported for the Danube River (200–500 mg kg^{-1} Zn) [47, 54–56, 68]; Tisa River, Serbia [69]; and River Po, Italy [57] and are slightly lower than Zn concentrations in the sediments of the Seine River in France [5] and Bílina River, Czech Republic [58] (600–800 mg kg^{-1} Zn). These concentrations are much lower than those

determined in the sediments at the mining areas of the Mežica valley, Slovenia (400–16,000 mg kg^{-1} Zn) [13], and Odiel River, Spain (1,000–8,000 mg kg^{-1} Zn) [57].

Concentrations of Cu in the Sava River sediments in general ranged from 30 to 50 mg kg^{-1} and exceeded ISQG value (18.7 mg kg^{-1} Cu) but were lower than the PEL value (108 mg kg^{-1} Cu). Concentrations of Cu in sediments of the Sava River do not represent anthropogenic inputs (see normalisation to Al, Fig. 4) and are lower than reported for sediments of the Danube River [47, 55, 56, 68]; River Po, Italy [67], Seine River, France [5]; and Tisa River, Serbia [69] (50–200 mg kg^{-1} Cu). Cu concentration levels in the Sava River sediments are much lower than at contaminated sites (Cu exploiting) in the Odiel River, Spain (200–2,800 mg kg^{-1} Cu) [57].

Concentrations of As in the sediments of the Sava River range from 7 to 25 mg kg^{-1} As (Table 2) and in general exceeded the ISQG value (7.24 mg kg^{-1} As). However, these As concentrations do not reflect anthropogenic inputs (see normalisation data in Fig. 4) but are characterised by its natural background. As concentrations in the sediments of the Sava River are lower than most of those reported for the Danube River [47, 55, 56] and Bílina River, Czech Republic [58] (40–80 mg kg^{-1} As).

Finally, data from Table 2 indicate that concentrations of total P in the sediments along the Sava River tend to increase from spring toward the inflow into the Danube River. The highest concentrations (around 1,000 mg kg^{-1} of total P) were found mainly due to the use of P-containing fertilisers in rural areas and also due to the influence of the municipal sewage outflow (use of P-containing detergents in household) in big cities, e.g., sampling site in Oborovo (outflow of the municipal sewage system in Zagreb, Croatia) and sampling site in the city of Belgrade before the Sava River merges with the Danube River. The influence of municipal sewage system on the quality of river sediments was observed also by House and Denison [16], who reported that sewage outflows at the Blackwater River in United Kingdom importantly contributed to P input to the river sediments. Concentrations of P downstream the sewage outflows reached concentrations up to 4,000 mg kg^{-1} of the total P. Similar P concentrations to those in the Sava River sediments (around 1,000 mg kg^{-1} of total P) were found in the sediments of the Danube River [47].

3.2 Partitioning of Elements in Sediments from the Sava Dolinka River

In sequential extraction procedures various extractants are applied successively to the sediment or soil for selective leaching of the particular chemical forms of elements from samples analysed. Due to its simplicity, short time of analysis, and the amount of information obtained, the BCR sequential extraction scheme [37] is most commonly applied. In step I (extraction in 0.11 mol L^{-1} acetic acid, pH 2.8) of the BCR scheme, metals present in ionic form bound to carbonates and the exchangeable fraction is released. In step II (extraction in 0.1 mol L^{-1} hydroxylamine

hydrochloride, pH 2), metals bound to amorphous Fe and Mn oxides and hydroxides are leached. In step III (oxidation in acid-stabilised 30 % hydrogen peroxide and extraction in 1 mol L^{-1} ammonium acetate, pH 2, adjusted with nitric acid) metals bound to organic matter and sulphides are separated. For the determination of the metal fraction associated with aluminosilicates to the original BCR scheme, step IV is added in which the residue is digested with nitric, perchloric, and hydrofluoric acids.

To estimate the applicability of the BCR extraction procedure to the sediments of the Sava River, two representative sediments from the Sava Dolinka River— contaminated sediment from the basin of the hydroelectric power plant Moste (impacted also by the steelmaking industry) and non-contaminated sediment from Mojstrana site (close to Sava Dolinka spring)—were analysed. The results of the partitioning of elements by applying the modified BCR extraction scheme are presented in Fig. 5.
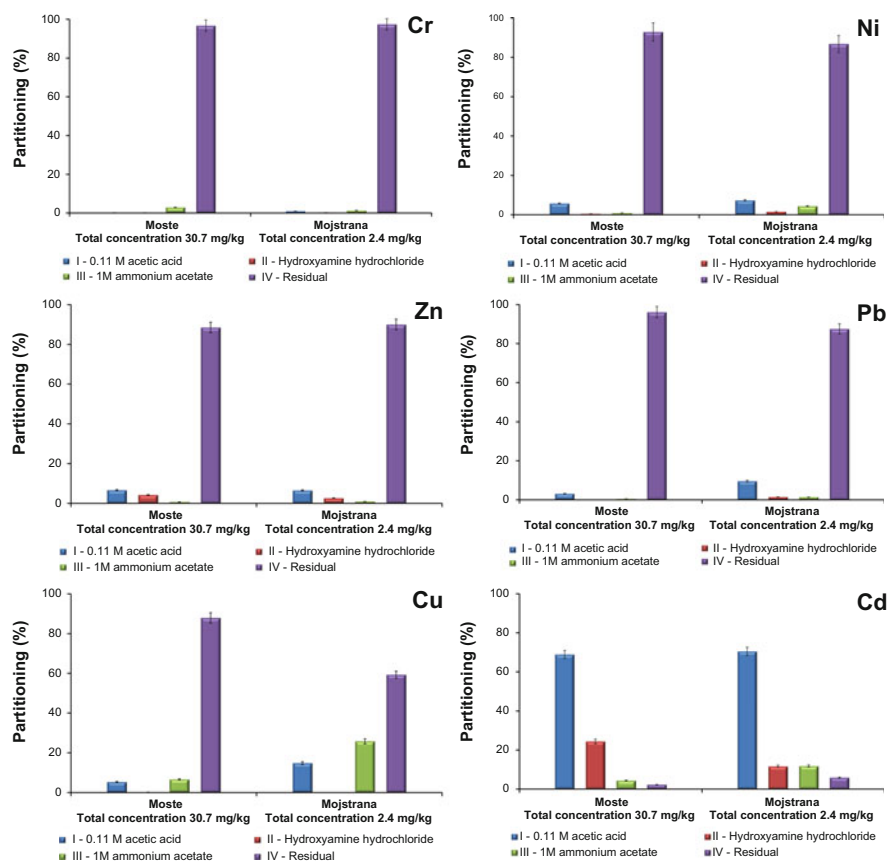

Fig. 5 Partitioning of Cr, Ni, Zn, Pb, Cu, and Cd in sediments from Moste and Mojstrana sampling sites of the Sava River by applying the modified BCR extraction scheme

The data from Fig. 5 indicate that Cr, Ni, Zn, Pb, and Cu from contaminated site are incorporated mainly into the silicate lattice, while the easily soluble fraction of the elements is negligible, meaning low hazard of these elements for the biota and environment. Cu from non-contaminated site is distributed between easily soluble fraction (about 15 %), bound to amorphous Fe and Mn oxides and hydroxides (about 25 %), and incorporated into the silicate lattice (about 60 %). Different distribution of Cu between sediment compartments in comparison to contaminated site represents its different association with sediment minerals and larger extent of Cu mobility in non-contaminated sediment. A completely different distribution pattern is evident for Cd, which is in contaminated and non-contaminated sediments present in about 70 % in the form of carbonates. This fraction is easily soluble and highly mobile in the environment and represents also the potential environmental burden, if the total Cd concentration is high.

Therefore, for the estimation of the environmental burden, the most important is the highly mobile and bioavailable metal fraction, which was further examined in sediments along the Sava River.

3.3 Assessment of Element Mobility in Sediments from the Sava River

For the investigation of the potential bioavailability of elements in sediments of the Sava River, the leaching protocol of the first step of the BCR sequential extraction procedure was used. By applying 0.11 mol L^{-1} acetic acid as an extracting agent, it is possible to estimate the easily soluble elements fraction, which has the highest impact on the environment. The portions of elements in sediments extractable in acetic acid, together with the total element concentrations, are presented in Fig. 6.

The data from Fig. 6 demonstrate extremely low mobility of Cr and low mobility of Ni. The proportions of the easily soluble metal fractions were below 0.3 % for Cr and 16 % for Ni. Since these two elements exist primarily in the sparingly soluble forms, it can be assumed that total Cr and Ni concentrations in sediments at industrially exposed sites (Moste in Slovenia and sites along the Sava River from Košutarica to Šabac) do not represent an environmental burden.

The mobile fractions of Cu in the sediments of the Sava River represent less than 2 % of its total contents, of As less than 6 %, and of Pb (with exception of Brežice site) less than 4 %, indicating their low mobility into the aquatic environment and low environmental burden.

On the contrary, high proportions of the mobile fractions in sediments were found for Cd (30–50 %) and in about half of the sampling sites also for Zn (20–40 %). However, despite the high proportion of the easily soluble Cd content, these concentrations do not represent an environmental hazard, since total Cd concentrations were low. The extractable, easily soluble Zn fraction in the sampling sites
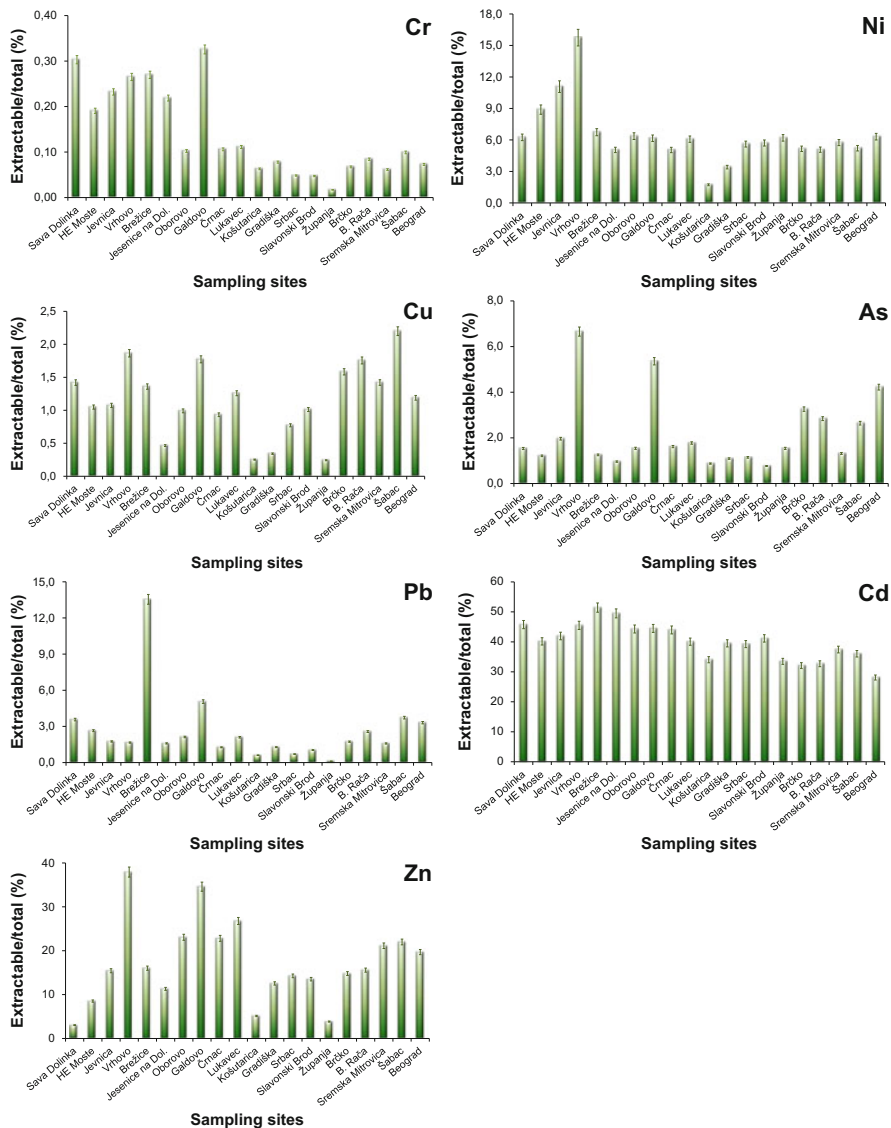
Fig. 6 Percentages of Cr, Cu, As, Pb, Ni, Zn, and Cd from sediments of the Sava River extracted with 0.11 mol L^{-1} acetic acid

investigated represented less than 90 mg kg^{-1} of Zn. This concentration is below ISQG level (124 mg kg^{-1} Zn). Therefore, regarding mobile concentrations of Zn, the potential environmental hazard and threat for the aquatic life is estimated to be low.

4 Organic Pollutants in the Sediments of Sava River

Between organic pollutants, the presence of PAH, PCB, and OCP was determined in surface Sava River sediments (Table 4).

4.1 PAH in Sava River Sediment

In this study 16 EPA priority list PAH were determined in the Sava River sediment samples. They included naphthalene, acenaphthene, acenaphthylene, anthracene, phenanthrene, fluorene, fluoranthene, benzo(*a*)anthracene, chrysene, pyrene, benzo (*a*)pyrene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, dibenzo(*a,h*)anthracene benzo(*g,h,i*)perylene, and indeno(1,2,3 *cd*)pyrene. Selected PAH were determined by GC-MSD (Hewlett-Packard model 6890 GC and 5972A MSD) after extraction by an ISCO supercritical fluid extractor (SFX2-10, Lincoln, NE, USA). The sample preparation and analytical procedures including quality control are described in detail in the study by Heath et al. [71, 72].

Sava River sediments contained total PAH concentrations of between 51 and 1,963 ng g^{-1}. The two exceptions were Županja and Brčko ($\leq$3,965 ng g^{-1}) (Table 4, Fig. 7). Table 4 also reveals increasing PAH values downstream from Črnac with four sites having significantly higher PAH (the sum of 16 PAH) levels, e.g., Županja, Brčko ($\leq$4,000 ng g^{-1}), and Bosanska Rača, Gradiška (approx. 2,000 ng g^{-1}). All four are situated downstream of the Črnac and Lukavec oil fields.

Liu et al. [25] studied the distribution and sources in surface sediments of the rivers in Shanghai, China, and found the total PAH concentration to be between 107 and 1,707 ng g^{-1}. Surface sediments from the Yellow River, China [28], revealed slightly higher total PAH concentrations ($\leq$2,621 ng g^{-1}), while Taiwanese research found 9.8 μg g^{-1} of total PAH concentrations in the surface sediments of the Susquehanna River [19]. Total PAH content in the sediments downstream of the Kishon River in Israel [26] were $\leq$299 ng g^{-1}, which is comparable to Ebro River PAH sediment levels (1.07–224 ng g^{-1} [24]). In the Danube samples the total amount of PAH was 130–1,850 ng g^{-1} with the highest amount of total PAH in the bottom sediment layers in the Morava tributary (5,150 ng g^{-1} [48]).

A comparison of Sava River sediment's PAH content with reported values [19, 24–26, 28, 48] shows that the PAH pollution levels of sediment top layers are comparable (Table 4). By vertical profiling of river sediments Götz et al. [22] found that the highest concentration of the 16 EPA PAH occurred in the 1960s (43,580 ng g^{-1} in 1964) which confirms better sediment quality status in recent years.

The Canadian Environmental Quality Guidelines [32] for separate PAH in sediments quotes ISQG (Interim Freshwater Sediment Quality, dry weight) 6.71–111 ng g^{-1} and PEL (probable effect level, dry weight) 88.9–2,355 ng g^{-1}. With the exception of Županja and Brčko, pollution with PAH in sediments can be considered moderate along the Sava River.

Table 4 Concentrations of PAH (sum of 16 EPA PAH), PCB (7 indicator congeners), DDTs (the sum of *p-p* DDT, *p-p* DDE, and *p-p* DDD), and selected organochlorine pesticides (HCB, heptachlor, aldrin, lindane, dieldrin, and endrin) in Sava River sediments. All concentrations are expressed as ng g^{-1} on a dry mass basis

| Sampling site	Sum 16 PAH	Sum 7 PCB	Sum DDT	HCB	Heptachlor	Aldrin	Lindane	Dieldrin	Endrin
1. Mojstrana	56	0.31	0.007	0.007	0.014	0.0050	0.021	0.0040	0.092
2. Moste	470	1.9	0.27	0.076	0.089	0.11	0.017	0.081	0.60
3. Jevnica	180	1.2	0.13	0.20	0.028	0.057	0.0020	0.099	0.0030
4. Vrhovo	290	0.77	0.19	0.035	0.044	0.058	0.066	0.011	0.26
5. Brežice	51	0.55	0.36	0.096	0.056	0.059	0.012	0.0010	0.29
6. Jesenice na Dol.	58	0.63	0.081	0.051	0.072	0.050	0.070	0.0010	0.059
7. Oborovo	450	3.9	0.61	0.011	0.41	0.042	0.057	0.11	0.21
8. Galdovo	260	2.1	2.8	0.0020	0.15	0.012	0.016	0.027	0.20
9. Črnac	1,200	2.2	0.31	0.008	0.16	0.023	0.039	0.064	0.18
10. Lukavec	1,000	0.26	0.70	0.13	0.30	0.039	0.068	0.17	0.29
11. Košutarica	1,300	5.5	1.8	0.86	0.10	0.12	0.032	0.060	0.25
12. Gradiška	1,900	2.3	0.42	0.50	0.064	0.020	0.020	0.058	0.071
13. Srbac	720	0.84	0.074	0.16	0.021	0.0050	0.0090	0.041	0.021
14. Slavonski Brod	750	2.0	0.34	0.34	0.059	0.016	0.077	0.049	0.47
15. Županja	4,000	1.6	0.62	0.10	0.16	0.011	0.058	0.087	0.98
16. Brčko	3,600	2.1	0.51	0.16	0.0010	0.0070	0.034	0.12	0.093
17. Bosanska Rača	2,000	3.4	0.88	0.11	0.0010	0.014	0.030	0.10	0.089
18. Sremska Mitrovica	1,000	3.3	0.50	0.61	0.0010	0.070	0.096	0.068	0.044
19. Šabac	1,000	2.8	1.0	1.1	0.0050	0.0060	0.069	0.074	0.049
20. Beograd	330	3.4	1.5	91	0.041	0.014	0.094	0.32	0.029
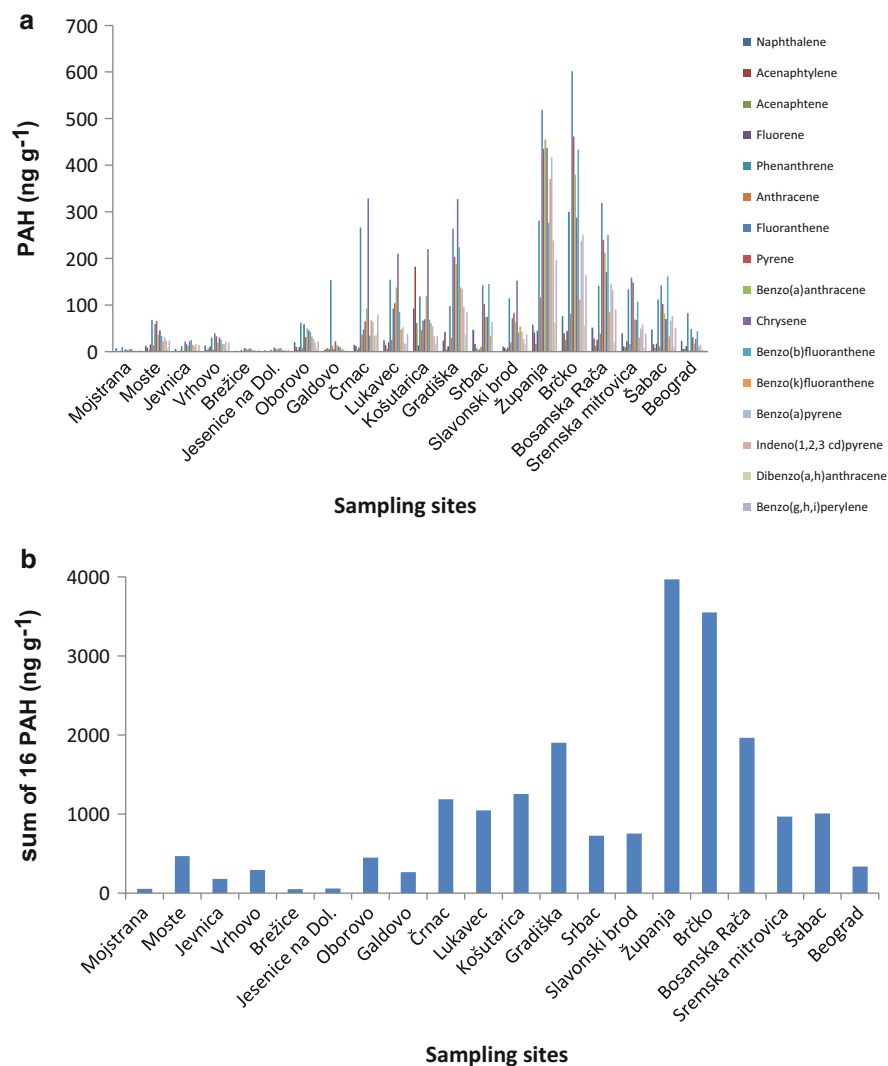
Fig. 7 The concentration of single PAH (**a**) and their sum (**b**) in sediment samples from the Sava River

Based on the sediment quality guideline of effects [19], the contents of total PAH are below the effect range median (ERM) of 44.8 μg g^{-1}, while some exceed the effect range low (ERL) of 4.02 μg g^{-1} [19]. According to the literature [19, 22, 24–26, 28], we believe that except at those locations, where levels exceed the ERL [19], PAH should not cause adverse ecological effects.

An attempt was also made to estimate the source of PAH pollution by calculating the ratio of alkylated PAH to its parent PAH (methylphenanthrene/phenanthrene

and methylpyrene/pyrene, [72]). Results suggest that the main pollution in the northern part of the Sava River (Slovenia) is the direct result of combustion processes from local coal and wood heating. There was no data to show that fossil fuels were the source of PAH, which is surprising since a heavy petrochemical industry is located around Sisak (Croatia). The presence of retene is indicative of forest fires, and its elevated concentrations indicate sites possibly polluted by PAH resulting from forest fires [72].

4.2   PCB in Sava River Sediments

Polychlorinated biphenyls exist in 209 congeners sharing the same chemical skeleton but varying in the number and position of the chlorine atoms. Environmental monitoring usually concentrates on a set of seven marker or indicator PCB. These congeners were selected because they are ubiquitous in all environmental compartments [73] and cover the range of toxicological properties of the group [74]. The seven indicator PCB are 28: 2,4,4′-trichlorobiphenyl, 52: 2,2′5,5-′-tetrachlorobiphelyl, 101: 2,2′,4,5,5′-pentachlorobiphenyl, 118: 2,3′,4,4′5-pentachlorobiphenyl, 138: 2,2,3,4,4′,5′-hexachlorobiphenyl, 153: 2,2′,4,4′,5,5-′-hexachlorobiphenyl, and 180: 2,2′,3,4,4′,5,5′-heptachlorobiphenyl. Selected PCB were determined in Sava River sediments by GC-ECD (Hewlett-Packard 6890) after Soxhlet extraction with Lab-line® multi-unit extraction heater (Barnstead/Lab-line, Dubuque, IA, USA). The sample preparation and analytical procedures including quality control are described in detail in the study of Heath et al. [72].

The presence of each of the seven indicator PCB determined along the Sava River catchment is presented in Fig. 8a, while their sum is shown in Fig. 8b and Table 4. Results show no elevated concentrations in the sediments at the sampling sites downstream of the Sava River (≤ 6 ng g^{-1}). Among the samples, elevated values occur at Moste (≤ 2 ng g^{-1})—a likely result of historical steel industry pollution from Jesenice and at Košutarica (≤ 6 ng g^{-1}), resulting from local industrial activities.

When the content of PCB in Sava sediments is compared to sediments from the Danube (average concentration 4.3 ng g^{-1}, maximal concentration 46 ng g^{-1} [48]), Rhine (≤ 200 ng g^{-1} [75]), Volga (≤ 40 ng g^{-1} [75]), and Niagara (≤ 124 ng g^{-1} [76]), the Sava river is clearly less polluted. Only at Košutarica does the amount exceed 5 ng g^{-1}. With closer look at Danube river basin as a whole, of which the Sava River Basin is part of, we find that the Danube river basin is less polluted compared to values reported in the literature [8, 22, 75–77].

Vertical profiling of river sediments by Götz et al. [22] found that the highest PCB concentration correlates to the year 1980 (sum PCB: 322 ng g^{-1}) and in the period 1964–1970 (sum PCB: 224 ng g^{-1}) at two different locations on the Elbe River in Germany [22] confirms the intensive use of these compounds before 1980.
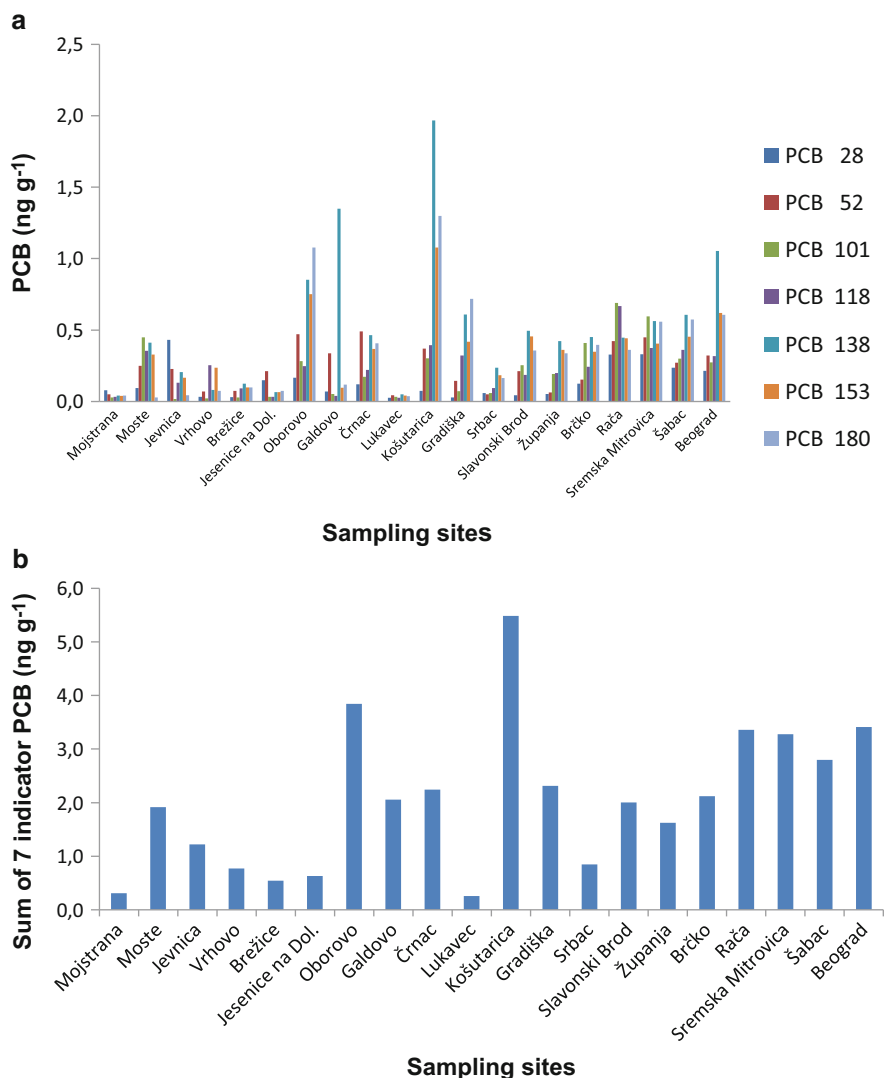
a

b

Fig. 8 The concentration of seven indicator PCB (**a**) and their sum (**b**)

According to the Canadian Environmental Quality Guidelines [32], the total PCB Interim Freshwater Sediment Quality (ISQG, dry weight) is 34.1 ng g^{-1}, while probable effect level (PEL, dry weight) is 277 ng g^{-1} [32]. According to the Sava River PCB contents determined within this study (Table 4), we can conclude that PCB pollution is not significant downstream the Sava River.

4.3   OCP in Sava River Sediments

The presence of a representative group of halogenated pesticides (hexachloro-benzene, heptachlor, aldrin, p,p' DDE, lindane, p,p'-DDD, p,p'-DDT, dieldrin, and endrin) was evaluated in Sava River sediments (Table 4, Fig. 9). Selected organochlorine pesticides (OCP) were determined by GC-ECD (Hewlett-Packard 6890) after Soxhlet extraction with Lab-line® multi-unit extraction heater (Barnstead/Lab-line, Dubuque, IA, USA). The sample preparation and analytical procedures including quality control are described in detail in the study by Heath et al. [72].

The concentrations of OCP have different spatial distribution, resulting from different inputs, rates of degradation, and sediment texture [77]. Residues of hexachlorobenzene (HCB) occur in the environment as a result of past manufacture and as a by-product during the production of certain chlorinated compounds and is used as a pesticide and in ammunition [72, 77]. Our results are presented in Table 4. Other than in the one sample from near Belgrade, where HCB was 90.8 ng g^{-1}, we found no elevated concentrations of individual pesticides. The high HCB content in the sediment from Belgrade could be a result of the recent military conflict [72]. For most of the OCP, their levels are below 1 ng g^{-1}. Exceptions include DDT at Galdovo (2.845 ng g^{-1}) and Košutarica (1.82 ng g^{-1}) and endrin at Županja (0.98 ng g^{-1}), which is a likely consequence of intensive farming activities.
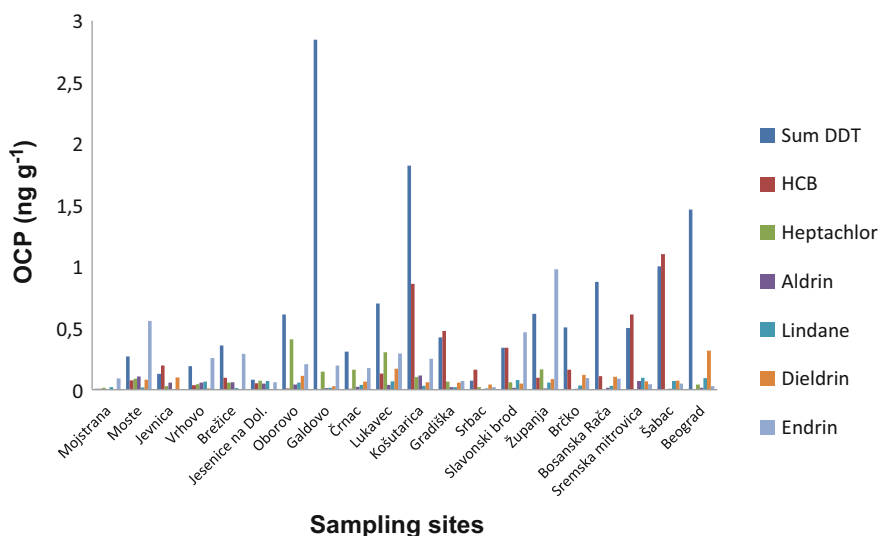

Fig. 9 The presence of selected organochlorine pesticides in the Sava River sediments. The highest OCP concentration (HCB; 90.823 ng g^{-1}) determined in a sediment sample from Belgrade is not shown on this figure

When looking at OCP levels in the Danube catchment as a whole [47], elevated levels of HCB occur near Belgrade (90.8 ng g^{-1}) on the Sava and near Budapest (23 ng g^{-1}) on the Danube with both values exceeding the Canadian "Lowest effect Level" for HCB [47] for sediments. Repeat sampling of the Sava sediments found significantly lower HCB levels and that the original high value was due to a point source of pollution [72]. When compared with other reported values, the levels of identified OCP in the Sava and Danube [48] are in the same order as the lower values found in the Buffalo River in South Africa [78], the Elbe in Spain [9, 24], and the Daliaohe River in China [20]. Overall, the levels of OCP determined in the Sava and Danube sediments shows they are not significant pollutants for the Danube catchment as whole [48].

The Canadian Environmental Quality Guidelines [32] for separate OCP are reported to be 0.6–3.54 ng g^{-1} (ISQG) and 2.74–62.4 ng g^{-1} (PEL). This confirms that there is no significant pollution by OCP in the Sava River Basin.

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