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Report on the contamination of the Sava River sediments with metals and organic pollutants

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Naročnik: SARIB - Sava River Basin: Sustainable Use, Management and Protection of Resources

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Introduction

The Sava River (945 km) is the biggest tributary to the Danube River. The 95551 km² large catchment is extended over Slovenia, Croatia, Bosnia and Herzegovina and Serbia and Montenegro. In the 6th FW EU project (INCO-CT-2004-509160): Sava River Basin: Sustainable Use, Management and Protection of Resources (SARIB) specific tools based on combination of chemical analysis and biological effect methods are developed and validated for the estimation of the pollution of sediments and impact on water biota. In order to assess the geographical distribution and historical trends in sediment contamination of the Sava River Basin, sediments were analysed in 20 selected sampling sites along the Sava River from its origin to its outfall into the Danube River. The extent of pollution was estimated by determination of the total element concentrations and by the identification of the most hazardous highly mobile element fractions and anthropogenic inputs of metals to sediments. In addition, selected persistent organic pollutants (e.g. polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated pesticides...) were also determined in sediments. The choice of pollutants followed the recommendations of the Water Framework Directive.

Experimental:

Sampling sites:

Sampling sites along the Sava River are presented in Fig.1 and corresponding GPS data in Table 1.



Fig. 1 Sediment sampling sites along the Sava River

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

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	–	Lukovec	(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°)

Collection of samples:

Sediments were taken using the piston corer which is released a set distance above the riverbed, penetrates the sediment by free fall, and sucks the sediment into the core barrel by an upward moving piston as the core is retrieved. Plastic core liners were placed inside the core barrels to contain the sediment core sample, and to avoid the problems of extrusion and contamination. After the corer was retrieved, the liner was removed from the barrel, the top was capped, and the core stored in a vertical position.

For sediment analysis corers were extruded in 1L polyethylene containers and transported to the laboratory.

Sample preparation:

For the determination of the total metal concentrations and organic pollutants sediment samples were homogenized in the laboratory, wet sieved through 63 μm sieve, dried at 40°C for three days (until constant weight) in dark, transferred into polypropylene containers and kept until the analysis at 4°C in dark.

Analytical procedures

Microwave assisted digestion of sediment samples for determination of total concentrations of As, Cd, Pb, Zn, Cu, Ni, Cr and P:

Before analysis sampling flasks were shaken virologously for one minute. Aprox. 0.25 g of sediment was weighted into Teflon vessel and 4 mL of conc. nitric acid s.p., 2 mL of hydrofluoric acid s.p. and 1 mL of hydrochloric acid s.p. were added, and samples gently mixed until all the sample has been wetted with acid. The Teflon vessels were then covered by vessel cups and submitted to colsed vessel microwave digestion on a CEM Corporation (Matthews, NC, USA) CEM MARS 5 Microwave Acceleration Reaction System using the following programme:

Ramp to temperature 30 min, T = 190 °C, hold 60 min (T = 190 °C), cool 30 min. After that the Teflon vessels were vented and vessel caps removed. 12.5 mL of boric acid s.p. (4% water solution) were added to each Teflon vessel in order to dissolve fluorides. Teflon vessels were covered by vessel cups and submitted to closed vessel microwave digestion again using the following programme: Ramp to temperature 15 min, T = 190 °C, hold 30 min (T = 190 °C), cool 30 min. After the digestion clear solution was obtained. The contents were quantitatively transferred to 30 mL graduated polypropylene tubes and filled to mark with water doubly distilled in quartz. The same procedure, with exception that no sample was added, was applied to determine blanks. Zn, Cu, Cd, Pb, Ni, Cr, As and P in digested sediment samples were determined under optimal measurent conditions by ICP-MS. All the analysis were made in duplicate.

The accuracy check was performed by the analysis of certified reference material CRM 320 (Trace elements in river sediment, BCR, Geel, Belgium). As it may be seen from Table 2 good agreement of results between determined and certified values were obtained, indicating that the analytical procedure applied was accurate and the results of sediment analysis reliable.

Table 2. Concentrations of elements in the sample of certified reference material CRM 320 (Trace elements in river sediment, BCR) determined by ICP-MS. Results represent average of two parallel samples and \pm standard deviation of measurements.

Element	Certified value (mg kg ⁻¹)	Determined value (mg kg ⁻¹)
Cu	44.1 \pm 1.0	44.9 \pm 0.9
Zn	142 \pm 3	140 \pm 2
Cd	0.533 \pm 0.026	0.546 \pm 0.022
Cr	138 \pm 7	139 \pm 6
Ni	75.2 \pm 1.4	74.3 \pm 0.9
Pb	42.3 \pm 1.6	41.2 \pm 1.0
As	76.7 \pm 3.4	74.3 \pm 3.0

Normalization to Al:

Normalization to Al was also performed to identify the anthropogenic inputs of elements. In the normalization procedure the total element concentrations were compared to the total concentration of Al.

Easily soluble element concentrations in 0.11 mol L⁻¹ acetic acid:

2 g of air dried sediment was shaken with 20 mL of 0.11 mol L⁻¹ acetic acid on a mechanical shaker (300 rpm) for 16 hours. Samples were then centrifuged (10000 rpm, 20 min) and filtered through 0.45 μ m membrane filter. Element concentrations were determined by ICP-MS under optimal measurement conditions.

Determination of total mercury in sediments by DMA-80 Direct Mercury Analyzer:

The DMA-80 Direct Mercury Analyzer performs thermal decomposition, catalytic reduction, amalgamation, desorption and atomic absorption spectroscopy to rapidly treat samples with no sample pretreatment.

About 50 mg of solid sediment sample was introduced into the DMA-80 Mercury Analyzer. Prior to combustion, the sample was initially dried in an oxygen stream passing through a quartz tube located inside a controlled heating coil. The combustion gases were further decomposed on a catalytic column at 750 °C. Mercury vapor was collected on a gold amalgamation trap and subsequently desorbed for quantitation. Mercury content was determined using atomic absorption spectrometry at 254 nm, and the results are displayed using a Pentium-based control terminal.

To control the accuracy of T-Hg determinations reference material (RM) IAEA 405, obtained from the International Atomic Energy Agency (IAEA) was used. All samples in a given batch, together with RMs were prepared in duplicate (or triplicate) and every measurement for each replicate was repeated 2-3 times. The determined value for Hg 794 \pm 21 ng g⁻¹ was in good agreement with the reference value 810 \pm 40 ng g⁻¹, indicating the accuracy of the analytical procedure applied.

Determination of organotin compounds (OTC):

For the analysis of OTC in sediments extraction with acetic acid was applied. Derivatization was performed with sodium tetraethylborate. Ethylated OTC species were extracted into

isooctane and their concentrations determined by gas chromatography – mass spectrometry (GC-MS). The accuracies of the analytical procedures were checked by the analysis of standard reference material PACS 2 (marine sediment). Results are presented in Table 3. Good agreement between certified and determined values was obtained for butyltin compounds.

Table 2: Concentrations of MBT, DBT and TBT ($\mu\text{g g}^{-1}$ Sn, dry mass basis) in certified reference materials PACS 2 (Marine Sediment) and CRM 477 (Mussel Tissue) determined by GC-MS. Results represent average of two parallel samples and \pm standard deviation of measurements.

Sample PACS 2	MBT ($\mu\text{g g}^{-1}$ Sn)	DBT ($\mu\text{g g}^{-1}$ Sn)	TBT ($\mu\text{g g}^{-1}$ Sn)
Determined	0.54 \pm 0.02	1.10 \pm 0.02	0.98 \pm 0.03
Certified	(0.6)*	1.047 \pm 0.064	0.890 \pm 0.105

* informative value only

Determination of Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB):

PAHs were determined by SFE with DCM. No cleaning procedure was applied before determination by GC-MSD (SIM mode).

PCBs and selected chlorinated pesticides were extracted by Soxhlet extraction and determined after cleaning and fractionation on Florisil column by GC-ECD.

Results

Analysis of total element concentrations in sediments along the Sava River

Analysis of total metal concentrations in the sediments along the Sava River are presented in Table 2, total mercury concentrations in Table 3 and total phosphorous concentrations in Table 4.

Table 2: Determination of total element concentrations in sediments of the Sava River by ICP-MS. Results represent average of two parallel samples \pm 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)
1 –Mojstrana	11.5 \pm 0.1	55.4 \pm 0.7	14.4 \pm 0.4	12.6 \pm 3.9	23.1 \pm 1.3	0.28 \pm 0.01	6.9 \pm 0.6
2- HE Moste	40.9 \pm 0.6	118 \pm 1	33.1 \pm 0.4	70.1 \pm 1.1	184 \pm 4	0.58 \pm 0.02	14.7 \pm 0.1
3 – Jevnica	41.7 \pm 3.7	142 \pm 1	34.4 \pm 3.0	27.3 \pm 0.7	73 \pm 1	0.42 \pm 0.08	10.5 \pm 0.8
4 – Vrhovo	47.8 \pm 3.4	223 \pm 2	45.9 \pm 1.0	36.9 \pm 0.6	94 \pm 2	0.73 \pm 0.03	9.0 \pm 1.3
5- Brežice	27.3 \pm 2.7	113 \pm 1	18.6 \pm 3.0	17.6 \pm 1.9	48.2 \pm 0.6	0.24 \pm 0.01	9.6 \pm 2.1
6 - Jesenice na Dol.	29.2 \pm 6.6	106 \pm 13	13.6 \pm 1.9	12.3 \pm 0.1	50.3 \pm 0.8	0.22 \pm 0.01	8.4 \pm 0.8
7 – Oborovo	41.1 \pm 1.2	172 \pm 5	39.1 \pm 1.2	36.7 \pm 1.1	88 \pm 3	0.62 \pm 0.02	11.3 \pm 0.3
8 – Galdovo	13.8 \pm 0.4	77 \pm 2	10.9 \pm 0.3	16.3 \pm 0.5	43 \pm 1	0.40 \pm 0.01	2.9 \pm 0.1
9 – Črnac	32.5 \pm 1.0	155 \pm 5	27.1 \pm 0.8	30.8 \pm 0.9	85 \pm 3	0.55 \pm 0.02	7.7 \pm 0.2
10 – Lukovec	32.7 \pm 1.0	163 \pm 5	35.5 \pm 1.1	44.4 \pm 1.3	99 \pm 3	0.64 \pm 0.02	11.4 \pm 0.3
11 – Košutarica	41.5 \pm 1.2	224 \pm 7	30.3 \pm 0.9	39.5 \pm 1.2	127 \pm 4	0.83 \pm 0.02	20.1 \pm 0.6
12 – Gradiška	36.0 \pm 1.1	220 \pm 7	29.8 \pm 0.9	41.9 \pm 1.3	167 \pm 5	1.02 \pm 0.03	12.1 \pm 0.4
13 – Srbac	25.5 \pm 0.5	84 \pm 2	27.1 \pm 0.5	79 \pm 2	236 \pm 5	0.43 \pm 0.01	11.2 \pm 0.2
14 - Slavonski brod	25.5 \pm 0.8	118 \pm 4	31.9 \pm 1.0	102 \pm 3	186 \pm 6	0.58 \pm 0.02	16.5 \pm 0.5
15 – Županja	33.9 \pm 1.0	134 \pm 4	31.1 \pm 0.9	212 \pm 7	381 \pm 11	0.47 \pm 0.01	19.8 \pm 0.6
16 – Brčko	52 \pm 1	165 \pm 3	43.4 \pm 0.8	185 \pm 4	312 \pm 6	0.62 \pm 0.01	16.7 \pm 0.3
17 - Bosanska Rača	122 \pm 1	184 \pm 4	47.1 \pm 0.9	186 \pm 4	273 \pm 6	0.66 \pm 0.01	17.9 \pm 0.4
18 – Sremska Mitr.	79 \pm 1	275 \pm 6	44.9 \pm 0.9	177 \pm 4	276 \pm 6	0.84 \pm 0.02	23.6 \pm 0.5
19 – Šabac	117 \pm 1	361 \pm 7	49.6 \pm 1.0	163 \pm 3	232 \pm 5	1.40 \pm 0.03	25.1 \pm 0.6
20 – Beograd	97 \pm 1	173 \pm 4	46.2 \pm 0.9	82 \pm 2	151 \pm 3	0.84 \pm 0.02	15.7 \pm 0.3
ISQG	30.2	124	18.7	/	52.3	0.7	7.24
PEL	112	271	108	/	160	4.2	41.6

Canadian Sediment Quality Guidelines for the Protection of Aquatic Life, 1999:

Interim Sediment Quality Guidelines (ISQG) correspond to the threshold level effects below which adverse biological effects are not expected.

Probable effects levels (PEL) characterize concentrations of pollutants that may affect the aquatic life.

Table 3: Determination of total Hg concentrations in sediments of the Sava River by CV AAS. Results represent average of two parallel samples \pm standard deviation.

Sampling site	Hg (mg kg ⁻¹)
1- Mojstrana	0.035 \pm 0.001
2 – Moste	0.134 \pm 0.004
3 – Jevnica	0.388 \pm 0.043
4 – Vrhovo	0.397 \pm 0.011
5 – Brežice	0.247 \pm 0.006
6 - Jesenice na Dol.	0.235 \pm 0.042
7- Oborovo	0.390 \pm 0.007
8 – Galdovo	0.091 \pm 0.005
9 – Črnac	0.366 \pm 0.004
10 – Lukovec	0.282 \pm 0.010
11 – Košutarica	0.585 \pm 0.015
12 – Gradiška	0.629 \pm 0.025
13 – Srbac	0.376 \pm 0.009
14 - Slavonski brod	0.347 \pm 0.012
15 – Županja	0.269 \pm 0.010
16 – Brčko	0.297 \pm 0.031
17 - Bosanska Rača	0.374 \pm 0.004
18 - Sremska Mitr.	0.444 \pm 0.091
19 – Šabac	0.624 \pm 0.012
20 – Beograd	0.275 \pm 0.030
ISQG	0.17
PEL	0.486

Canadian Sediment Quality Guidelines for the Protection of Aquatic Life, 1999:

Interim Sediment Quality Guidelines (ISQG) correspond to the threshold level effects below which adverse biological effects are not expected.

Probable effects levels (PEL) characterize concentrations of pollutants that may affect the aquatic life.

Table 4: Determination of total P concentrations in sediments of the Sava River by ICP-MS. Results represent average of two parallel samples \pm standard deviation.

Sampling site	P (mg kg ⁻¹)
1- Mojstrana	170 \pm 5
2 – Moste	275 \pm 10
3 – Jevnica	625 \pm 20
4 – Vrhovo	1190 \pm 30
5 – Brežice	360 \pm 10
6 - Jesenice na Dol.	315 \pm 10
7- Oborovo	950 \pm 30
8 – Galdovo	380 \pm 10
9 – Črnac	750 \pm 20
10 – Lukovec	930 \pm 30
11 – Košutarica	670 \pm 20
12 – Gradiška	910 \pm 30
13 – Srbac	400 \pm 10
14 - Slavonski brod	860 \pm 25
15 – Županja	690 \pm 20
16 – Brčko	730 \pm 20
17 - Bosanska Rača	760 \pm 20
18 - Sremska Mitr.	800 \pm 25
19 – Šabac	930 \pm 30
20 – Beograd	1060 \pm 30
ISQG	/
PEL	/

Canadian Sediment Quality Guidelines for the Protection of Aquatic Life, 1999: **Interim Sediment Quality Guidelines** (ISQG) correspond to the threshold level effects below which adverse biological effects are not expected. **Probable effects levels** (PEL) characterize concentrations of pollutants that may affect the aquatic life.

Normalization to Al

Normalization data for total metal concentrations to Al in sediments of the Sava River are presented in Fig. 2.

Analysis of the easily soluble element fractions of sediment of the Sava River

Data of the analysis of the percentage of the easily soluble element fraction (extraction in 0.11 mol L⁻¹ acetic acid) of the total element content in sediments of the Sava River are presented in Fig. 3.

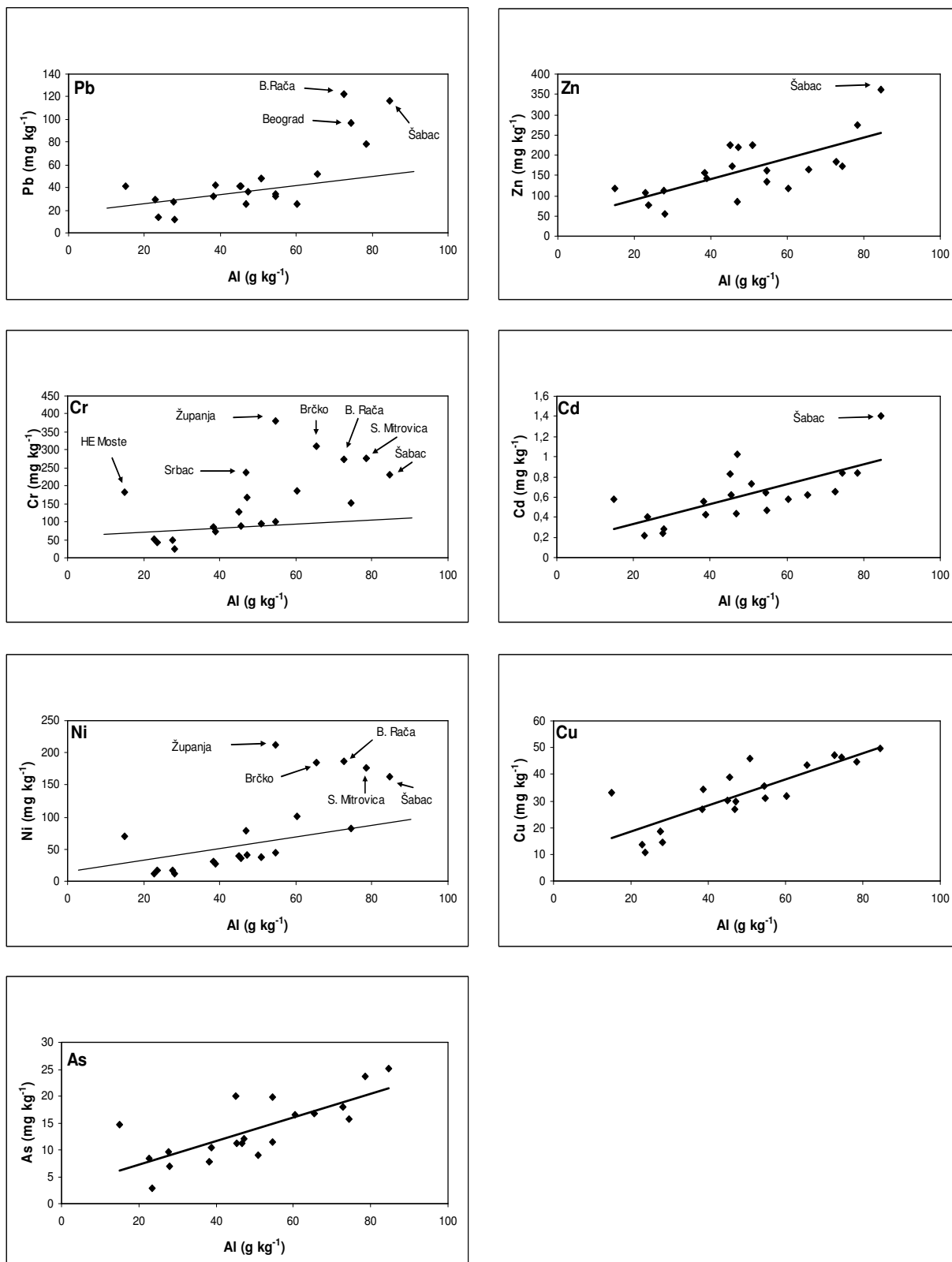


Fig. 2 Relationship of Pb, Zn, Cu, Ni, Cr, As and Cd with Al in sediments from the Sava River.

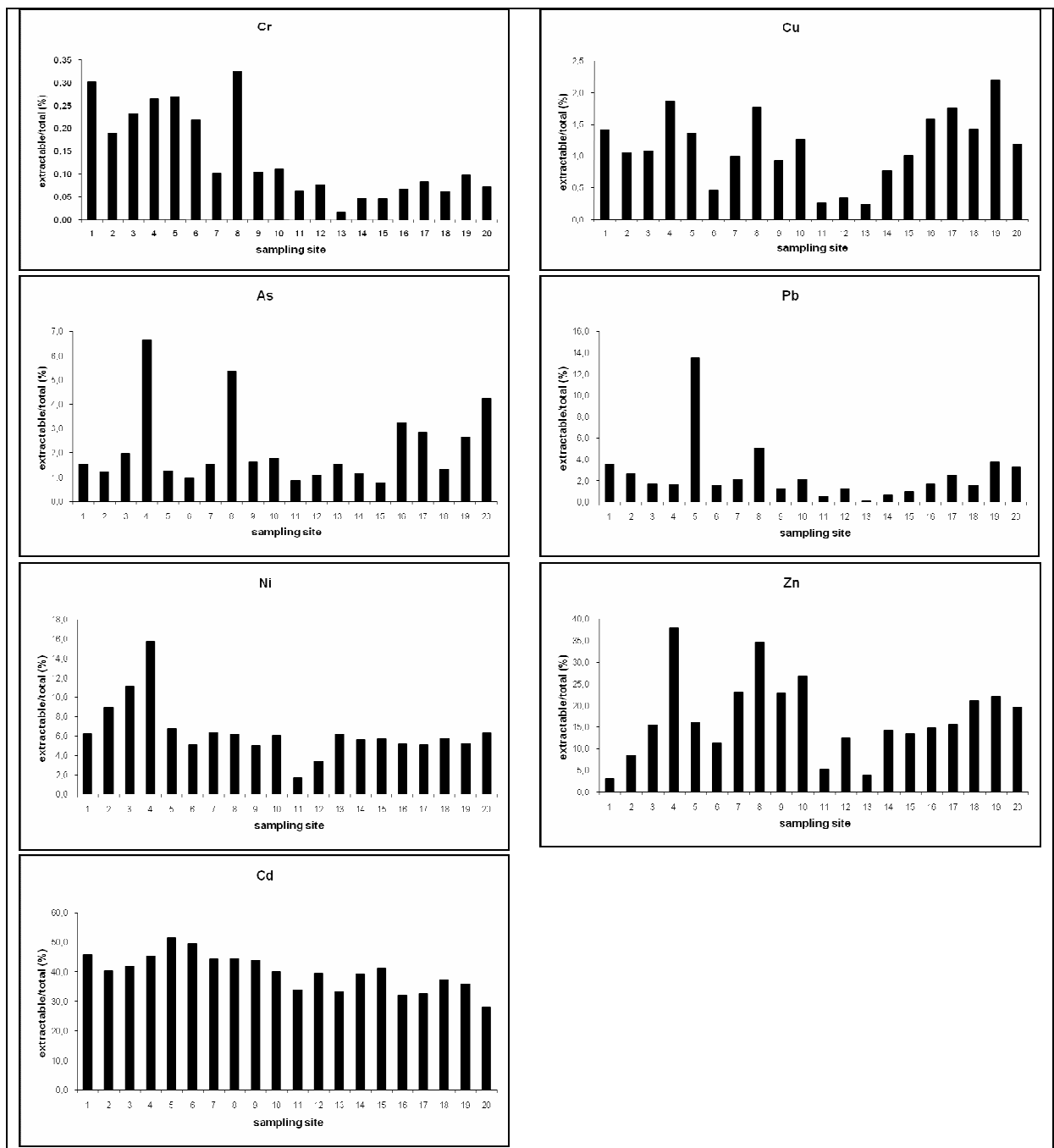


Fig. 3: Percentage of element extracted from sediments of the Sava River with 0.11 mol L⁻¹ acetic acid.

Analysis of OGRANOTIN COMPOUNDS in sediments of the Sava River

Analysis of sediments from 20 locations in the Sava River by GC-MS indicated that concentrations of butyltins, octyltins and phenyltins were below limits of detection:

Butyltins < 2 ng Sn g⁻¹

Octyltins < 3 ng Sn g⁻¹

Phenyltins < 10 ng Sn g⁻¹

Analysis of organic pollutants in sediments of the Sava River

Concentrations of organic pollutants of the Sava River are presented in Tables 5-7. (Table 5 selected chlorinated pesticides, Table 6 selected PCB congeners and sum of 7 most toxic congeners and Table 7 concentrations of selected PAHs and sum of 16 PAHs).

Table 5: Concentrations of selected chlorinated pesticides determined in the sediments of the Sava River

Pesticide (ng/g)*	HCB	Heptachlor	Aldrine	p,p DDE	Lindane	p,p DDD	p,p DDT	Dieldrine	Endrine
Mojstrana	0.007	0.014	0.005	0.004	0.021	0.001	0.002	0.004	0.092
Moste	0.076	0.089	0.107	0.095	0.017	0.004	0.171	0.081	0.558
Jevnica	0.195	0.028	0.057	0.095	0.002	0.028	0.005	0.099	0.003
Vrhovo	0.035	0.044	0.058	0.055	0.066	0.021	0.116	0.011	0.256
Brežice	0.096	0.056	0.059	0.062	0.012	0.015	0.281	0.001	0.291
Jesenice	0.051	0.072	0.050	0.042	0.070	0.003	0.036	0.001	0.059
Oborovo	0.011	0.408	0.042	0.282	0.057	0.156	0.173	0.111	0.206
Galdovo	0.002	0.145	0.012	0.082	0.016	0.201	2.562	0.027	0.196
Crnac	0.008	0.161	0.023	0.131	0.039	0.016	0.163	0.064	0.176
Lukavec	0.130	0.303	0.039	0.350	0.068	0.206	0.145	0.170	0.294
Košutarica	0.859	0.101	0.115	0.277	0.032	0.256	1.288	0.060	0.252
Gradiška	0.476	0.064	0.020	0.092	0.020	0.084	0.248	0.058	0.071
Srbac	0.161	0.021	0.005	0.023	0.009	0.018	0.033	0.041	0.021
Slavonski Brod	0.341	0.059	0.016	0.187	0.077	0.091	0.063	0.049	0.467
Županja	0.096	0.164	0.011	0.283	0.058	0.130	0.203	0.087	0.977
Brčko	0.162	0.001	0.007	0.099	0.034	0.186	0.220	0.120	0.093
Rača	0.109	0.001	0.014	0.559	0.030	0.136	0.182	0.103	0.089
Sremska Mitrovica	0.612	0.001	0.007	0.090	0.096	0.151	0.259	0.068	0.044
Šabac	1.101	0.005	0.006	0.287	0.069	0.230	0.486	0.074	0.049
Beograd	90.823	0.041	0.014	0.582	0.094	0.233	0.649	0.316	0.029
ISQGs	/	/	/	1.42	0.94	3.54	1.19	2.85	2.67
PEL	/	/	/	6.75	1.38	8.51	4.77	6.67	62.4

*MDL for single chlorinated pesticide: 0.01-0.006 ng/g (GC-ECD) , rel.std.dev up to 8%

Table 6: Concentrations of selected PCB congeners and sum of 7 most toxic congeners (28, 52, 101, 118, 138, 153 and 180) determined in the sediments of the Sava River

Congeners (ng/g)*	PCB 18	PCB 28	PCB 31	PCB 52	PCB 44	PCB 101	PCB 149	PCB 118	PCB 153	PCB 138	PCB 180	PCB 170	PCB 194	Sum 7 PCBs**	Aroclor 1254	Total PCBs
Mojstrana	0.071	0.079	0.065	0.050	0.036	0.027	0.031	0.032	0.038	0.041	0.041	0.011	0.003	0.308		
Moste	0.140	0.094	0.077	0.249	0.107	0.449	0.304	0.355	0.328	0.412	0.027	0.067	0.022	1.912		
Jevnica	0.832	0.430	0.406	0.227	0.054	0.018	0.162	0.131	0.165	0.206	0.044	0.080	0.025	1.221		
Vrhovo	0.024	0.033	0.068	0.069	0.065	0.021	0.182	0.253	0.237	0.081	0.074	0.105	0.042	0.768		
Brežice	0.106	0.031	0.019	0.074	0.057	0.029	0.073	0.091	0.098	0.125	0.097	0.034	0.011	0.545		
Jesenice	0.377	0.149	0.069	0.211	0.058	0.033	0.064	0.033	0.066	0.065	0.074	0.123	0.043	0.631		
Oborovo	0.251	0.166	0.162	0.470	0.175	0.281	0.171	0.247	0.751	0.852	1.078	0.643	0.252	3.844		
Galdovo	0.097	0.069	0.057	0.337	0.092	0.052	0.103	0.039	0.095	1.348	0.118	0.069	0.051	2.057		
Crnac	0.147	0.119	0.094	0.490	0.157	0.173	0.398	0.221	0.368	0.464	0.406	0.259	0.076	2.242		
Lukavec	0.023	0.026	0.031	0.044	0.017	0.032	0.036	0.026	0.042	0.049	0.037	0.021	0.009	0.255		
Košutarica	0.107	0.074	0.036	0.369	0.101	0.301	1.240	0.393	1.078	1.967	1.299	0.818	0.173	5.482		
Gradiška	0.068	0.027	0.038	0.145	0.036	0.072	0.585	0.321	0.418	0.609	0.718	0.414	0.136	2.310		
Srbac	0.058	0.058	0.035	0.050	0.051	0.059	0.158	0.094	0.184	0.235	0.164	0.112	0.023	0.843		
Slavonski Brod	0.102	0.043	0.084	0.213	0.151	0.254	0.350	0.185	0.456	0.494	0.356	0.206	0.058	2.001		
Županja	0.035	0.053	0.107	0.062	0.020	0.193	0.322	0.199	0.360	0.422	0.336	0.208	0.060	1.624		
Brčko	0.141	0.124	0.154	0.152	0.126	0.409	0.321	0.242	0.348	0.450	0.397	0.237	0.054	2.123		
Rača	0.306	0.328	0.271	0.422	0.296	0.689	0.591	0.667	0.442	0.447	0.361	0.235	0.063	3.357		
Sremska Mitrovica	0.309	0.330	0.337	0.448	0.323	0.596	0.449	0.375	0.404	0.563	0.558	0.403	0.149	3.273		
Šabac	0.324	0.235	0.219	0.271	0.123	0.300	0.393	0.362	0.452	0.606	0.574	0.453	0.155	2.800		
Beograd	0.246	0.215	0.189	0.322	0.129	0.274	0.548	0.318	0.619	1.054	0.607	0.378	0.153	3.410		
ISQGs	/	/	/	/	/	/	/	/	/	/	/	/	/	/	60	34
PEL	/	/	/	/	/	/	/	/	/	/	/	/	/	/	340	277

*MDL for single PCBs: 0.09-0.009 ng/g (GC-ECD) , rel.std.dev. up to 9%

**congeners 28, 52, 101, 118, 138, 153, 180

Table 7: Concentrations of selected PAHs and sum of 16 PAHs determined in the sediments of the Sava River

PAHs (ng/g)	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzofluoranthene	Chrysene	Benzofluoranthene	Benzofluoranthene	Benzofluoranthene	Indeno(1,2,3-cd)pyrene	Dibenzo(a,h)anthracene	Benzofluoranthene	Sum 16 PAH
Mojstrana	6.94	0.89	1.31	1.59	9.93	0.48	4.83	3.88	3.32	6.04	5.94	2.47	1.95	1.95	0.65	3.31	55.46
Moste	12.34	8.19	2.19	14.69	67.93	13.75	59.61	65.35	36.29	45.16	33.47	22.50	31.72	23.47	6.92	23.45	467.01
Jevnica	5.50	1.53	1.17	2.34	11.76	1.53	21.33	15.90	12.15	22.03	24.86	14.29	11.09	15.88	2.54	14.46	178.35
Vrhovo	12.95	3.36	6.11	10.74	30.16	3.99	39.67	33.01	19.62	30.25	25.81	16.14	16.17	20.97	3.81	18.69	291.47
Brežice	1.65	0.46	0.65	1.24	3.55	0.41	7.45	5.66	4.00	5.91	7.15	3.45	2.34	2.92	0.74	3.73	51.30
Jesenice na Dolenjskem	2.60	0.74	1.28	0.86	4.05	0.43	8.49	6.10	3.87	6.10	7.69	4.70	2.90	3.65	0.42	3.41	57.28
Oborovo	20.48	10.52	3.52	9.86	61.80	7.91	59.04	31.08	49.79	46.26	41.92	31.93	26.44	19.52	6.34	22.09	448.48
Galdovo	2.30	5.17	7.59	4.47	153.71	12.32	5.60	22.40	14.50	10.88	8.75	6.00	5.28	2.71	0.87	2.15	264.69
Crnac	14.31	11.76	3.52	8.63	266.26	36.26	47.42	64.76	91.99	328.68	34.53	67.32	63.06	32.88	35.53	78.99	1185.90
Lukavec	24.48	14.54	5.73	19.44	154.07	25.20	92.55	104.02	137.67	209.82	85.29	47.18	52.43	17.97	16.08	37.79	1044.25
Košutarica	92.70	181.74	61.25	12.74	118.68	46.29	66.14	69.06	119.11	220.00	68.79	60.69	53.88	32.75	17.26	33.52	1254.62
Gradiška	23.68	42.04	4.45	10.83	97.56	29.69	263.24	203.49	188.08	326.95	224.00	137.30	133.93	95.08	36.44	83.60	1900.37
Srbac	46.90	16.08	7.76	2.41	4.90	10.63	142.56	102.53	74.10	74.63	144.59	33.71	63.30	0.00	0.00	0.00	724.11
Slavonski brod	10.04	8.15	4.56	8.51	114.32	19.38	71.22	83.23	64.23	152.20	40.82	53.70	41.99	26.69	15.79	36.45	751.30
Županja	57.47	41.10	16.73	45.03	280.60	116.53	518.93	435.36	454.96	437.16	276.12	369.95	417.18	238.37	62.16	197.55	3965.22
Brčko	76.08	39.71	24.68	44.46	299.88	81.33	601.79	461.71	379.46	287.61	433.50	111.58	237.90	250.97	55.91	163.80	3550.37
Bosanska Rača	51.61	27.30	12.62	25.29	141.04	38.13	318.66	239.97	211.78	170.90	250.21	85.49	146.15	132.16	20.81	90.56	1962.68
Sremska mitrovica	39.68	10.80	9.05	22.25	133.62	16.00	158.62	148.14	69.11	67.96	106.97	30.07	49.31	57.97	8.28	38.95	966.77
Šabac	47.38	15.71	7.69	16.71	112.06	11.18	141.36	101.95	81.89	69.99	161.77	32.09	66.00	76.92	10.63	51.46	1004.80
Beograd	22.93	5.64	5.45	11.67	82.89	2.07	48.38	30.72	17.01	26.81	43.65	11.07	15.16	4.64	4.02	2.30	334.43
ISQGs	34.6	5.87	6.71	21.2	41.9	46.9	111	53.0	31.70	57.1	/	/	31.9	/	6.22	/	/
PEL	391	128	88.9	144	515	245	2355	875	385	862	/	/	782	/	135	/	/

*MDL for single PAHs: 0.1 – 0.02 ng/g (GC-MSD). rel.std.dev. up to 9%

Discussion

Among metals, Hg was found to be present in elevated concentrations in the sediments of the Sava River (concentrations in general ranged from 0.2 to 0.6 mg kg⁻¹). Results also indicated that the Sava River is moderately polluted with Cr and Ni in sampling site HE Moste in Slovenia (basin of the hydroelectric power plant) and in sampling sites in Croatia, BIH and Serbia from Gradiška up till Šabac. (Concentrations of Cr higher than those of probable effect levels (PEL)).

Normalization data indicated the anthropogenic inputs of Cr and Ni in sediments. The origin of pollution with metals is most probably related to industrial activities.

However, the data of the extraction in 0.11 mol L⁻¹ acetic acid showed that the percentage of the easily soluble metal fraction of Cr and Ni were low (below 0.3% of total Cr and below 16% of total Ni, respectively). Analysis of the easily soluble concentrations of other elements were in general below 10%. Exceptions were Cd (30 – 50%) and Zn (5 – 40%). Despite high percentage of the easily soluble Cd content, these concentrations do not represent environmental hazard, since the total Cd concentrations were low.

Organotin analysis showed that the Sava River sediments are not polluted with butyltins, phenyltins or octyltins.

Phosphorous concentrations in the sediments along the Sava River tend to increase from origin toward the inflow to the Danube River. The highest concentrations was observed in the accumulation basin of the Hydropower plant Vrhovo (Slovenia) and in agricultural areas of Croatia, Bosnia and Herzegovina and Serbia, most probably due to the use of P-containing manures in agriculture. High P concentrations were found also found in sampling sites Oborovo (influence of the municipal sewage system of the Zagreb city) and at sampling point in the center of Belgrade before Sava merge with Danube River.

Data of the analysis of OTC indicated that sediments of the Sava River are not polluted with butyltin, phenyltin or octyltin compounds.

Regarding the PAH content of the Sava River sediments it may be seen that the amount of PAHs increases downstream the Sava River and reach the highest concentration around Brčko. For PCB concentrations in sediments no augmented values were found. In case of studied pesticides two locations with exceeded p,p-DDT values (Galdovo: 2,562 ng g⁻¹ and Košutarica (1,288 ng g⁻¹) were noticed even though this persistent pesticide should not have been in use for many years. However, these values are not unusual since p,p-DDT chemical is very persistent and transboundary pollutant. Besides this chlorinated pesticide, also HCB was determined in augmented values in two locations: Šabac (1,101 ng g⁻¹) and Beograd (90,823 ng g⁻¹) where the later one was present in extremely high concentration. HCB is a chemical that does not dissolve in water very well so most of it remains in particles at the bottom sediment.

Conclusion

Data of the analysis of the sediments sampled at 20 locations along the Sava River from its origin to its inflow to the Danube River indicate moderate pollution of sediments with Hg and on industrially exposed sites of Cr and Ni. However, the latter two elements exist primarily in sparingly soluble forms and therefore do not represent critical environmental burden. Phosphorous concentrations in elevated concentrations were found in agricultural areas and in big cities (Zagreb, Belgrade). Analysis of OTC indicated that Sava River is not polluted with butyltin, phenyltin or octyltin compounds.

Among organic pollutants PAH's were present in sediments of the Sava River. Their concentrations increased downstream the Sava River. Concentrations of PCB in sediments of the Sava River were low. Among selected pesticides p,p-DDT were found in sediments of Galdovo and Košutarica although the use of this persistent pesticide is banned for many years. HCB pesticide was also determined in high concentration at Šabac and in particularly high concentration in Belgrade sampling sites. The origin at these two locations is not explored yet.