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A complex investigation of the extent of pollution in sediments of the Sava River: part 2: persistent organic pollutants

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Abstract Sediment pollution of the biggest Danube tributary, the Sava River, was investigated within the sixth framework European Union project "Sava River Basin: Sustainable Use, Management and Protection of Resources" (SARIB). The extent of pollution was estimated by determining the amount of inorganic and persistent organic pollutants in sediment samples at 20 selected sampling sites along the Sava River. For the purpose of clarity, the findings are presented and published separately (part I: selected elements and part II: persistent organic pollutants). This study presents an investigation into the presence of organic pollutants in the Sava River sediment. According to the Water Framework Directive, the following persistent organic pollutants were investigated: polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), selected chlorinated pesticides and organotin compounds. The results reveal that PAHs were present in moderate concentrations (sum of 16 PAHs: up to 4,000 ng g^{-1}) and their concentrations increased downstream. Concentrations of PCB were low (sum of seven indicator PCBs: below 4 ng g^{-1}) and among the pesticides analyzed only *p,p*-dichlorodiphenyltrichloroethane was found in moderate concentrations at two sampling sites in Croatia (up to 3 ng g^{-1}) and hexachlorobenzene was found in a high concentration in the city of Belgrade (91 ng g^{-1}), although the use of these persistent pesticides has been banned for decades. Repeated sampling at the same location revealed point pollution near Belgrade. Among the organic pollutants surveyed, organotin compounds were not detected. Overall results reveal the presence of persistent organic pollutants in 20 of the Sava River sediments tested that is, in general, comparable or lower than the levels in the Danube River and other moderately polluted European rivers.

Keywords Sava River · Sediments · Persistent organic pollutants · Polyaromatic hydrocarbons · Polychlorinated biphenyls · Chlorinated pesticides · Organotin compounds

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Introduction

Persistent organic pollutants (POPs) are a group of organic chemicals that pose a threat to the environment despite no longer being in common use. Their properties that launched them on the market as miraculous are now the reason for their persistence in the environment despite a ban on production and application. Polyaromatic hydrocarbons (PAHs; Agarwal et al. 2007; Banjoo and Nelson 2005; Barth et al. 2007; Götz et al. 2007; Ho and Hui 2001; Ko et al. 2007; Lacorte et al. 2006; Liu et al. 2007; Oren et al. 2006; Škrbić et al. 2005; Ünlü and Alpar 2006; Xu et al. 2007), polychlorinated byphenilys (PCBs; El-Kady et al. 2007; Gómez-Gutiérrez et al. 2006; Götz et al. 2007; Ho and Hui 2001; Samara et al. 2006; Škrbić et al. 2007; Wang et al. 2007), chlorinated pesticides (Barth et al. 2007; Gómez-Gutiérrez et al. 2006; Götz et al. 2007; Lacorte et al. 2006; Škrbić et al. 2007), and organotin compounds (OTC; Hoch 2001) are examples of ubiquitous contaminants in several environmental compartments, particularly in aquatic ecosystems. Except OTC, they are frequently monitored in different river basins (Banjoo and Nelson 2005; El-Kady et al. 2007; Gómez-Gutiérrez et al. 2006; Götz et al. 2007; Ko et al. 2007; Liu et al. 2007; Oren et al. 2006; Samara et al. 2006; Ünlü and Alpar 2006; Xu et al. 2007). The occurrence of these contaminants is mostly related to the industrialization and urbanization (Baird 2003).

PAHs are a group of compounds that consist of two or more fused aromatic rings. Most of these are formed during incomplete combustion of organic material and the composition of PAH mixture varies with source(s) and selective weathering effects in the environment. PAHs also have a natural petrochemical origin and enter the environment from oil spills and during petroleum refinery operations. The persistence of the PAHs varies with their molecular weight. The low molecular weight PAHs are most easily degraded, and generally, as their complexity grows with number of rings, they become more persistent. This persistence has resulted in a widespread distribution in the environment—a fact that has aroused global concern. The acute toxicity of low PAHs is moderate, while International Agency for Research on Cancer has classified some higher molecular weight PAHs like for example benz[a]anthracene, benzo[a]pyrene, and dibenzo[a,h]anthracene as probable human carcinogens.

The Stockholm Convention is an international legally binding agreement on POPs (http://www.ciel.org/Chemicals/popsinternational.html). The agreement highlighted the so-called Dirty Dozen, a list of the potentially most hazardous POPs, and included PCB group, eight organochlorine pesticides: aldrin, chlordane, dichlorodiphenyltrichloroethane (DDT), dieldrin, endrin, heptachlor, mirex, and toxaphene; two industrial chemicals: hexachlorobenzene (HCB); and two groups of industrial by-products: dioxins and furans. PCBs are synthetic chemicals widely produced from the 1950s through to the 1980s and popular because of their outstanding physicochemical parameters and thermal properties. They were used in large amounts in numerous applications such as in the electrical industry in transformers and capacitors and elsewhere in lubricants, varnishes, dies, and glue production. In 1966, the Swedish scientist Sören Jensen discovered their presence in the environment while analyzing for dichlorodiphenyltrichloroethane (Jensen 1972). After a decade of use, the discovery of their harmful effects led to a ban on their production in North America in 1977 (Baird 2003). Chlorinated pesticides, some of them listed within the Stockholm convention, were used over decades to control pest insects worldwide. Despite being banned or restricted since the 1970s and 1980s in North America, Europe, and many other courtiers, highly toxic commercial mixtures are still produced and used in many developing countries. Organochlorine pesticides are a regular subject of research in different river basins around the world (Barth et al. 2007; Gómez-Gutiérrez et al. 2006; Ho and Hui 2001; ICPDR 2002; Škrbić et al. 2007; Wang et al. 2007).

OTC represent a significant environmental burden, especially tributyltin (TBT) and triphenyltin (TPhT) that are used as biocides in antifouling paints and pesticides (Hoch 2001; Strand et al. 2003). Trisubstituted OTC, including TBT and TPhT, are among the most hazardous pollutants to enter aquatic ecosystems (Hoch 2001). The European Commission reacting to these new findings banned the use of TBT-containing antifouling paints (AFS Convention 2003; Commission Directive 2002/62/EC 2002) and added butyltin compounds to the list of priority pollutants under the European Union (EU) Water Framework Directive (Commission Directive 2000/60/EC 2000). Although OTC were intensively investigated in the marine environment (Coelho et al. 2002; Díez et al. 2005; Godoi et al. 2003; Gomez-Ariza et al. 2001; Harino et al. 1999; Milivojevič Nemanič et al. 2002, 2007; Ščančar et al. 2007), they are a rare subject of research in river sediments (Bancon-Montigny et al. 2004; ICPDR 2002; Lacorte et al. 2006; Scrimshaw et al. 2005).

In the case of all the aforementioned compounds, their high stability and medium-high hydrophobicity cause them to adsorb to organic particulate matter and accumulate in sediment compartments of rivers, lakes, coastal, and the estuarine environment. Despite their being banned, these compounds continue to persist in the environment and are transported over considerable distances from undeveloped areas where they are still in use. These compounds will be present in the environment for a long time.

One of the most complex investigations of river pollution is the Joint Danube Survey set up by International Commission for the Protection of the Danube River (ICPDR 2002). Investigation was performed in two campaigns (2002 and 2007) and included water, sediment, biology, suspended solids, mussels, and fish, each taken at three different sampling points at the station cross sections. After the first phase of sampling, the ICPDR (2002) issued a technical report showing point pollution with several inorganic and organic components, mostly a result of local industrialization (http://www.icpdr.org/jds/). These results indicate that each of the catchments has to be studied individually, taking into consideration local geography and historical sources of pollution. They also highlight the important contribution that tributaries make to the total pollution burden of the Danube River. The Sava River is the largest tributary of the Danube stretching for 945 km from the Slovene–Austrian border through Croatia, Bosnia, and ending in the Danube River in Belgrade, Serbia, covers over 95,551 km^2. Although the national environmental agencies monitor the quality of the Sava River on a regular basis, the sediment quality has not been assessed prior to our investigation supported by the EU FP6 Sava River Basin: Sustainable Use, Management and Protection of Resources (SARIB). The aim of our work was a comprehensive study to determine the extent of pollution according to Water Framework Directive recommendations (Commission Directive 2002/62/EC 2002; Commission Directive 2000/60/EC 2000) and includes selected elements (A complex investigation of the extent of pollution in sediments of the Sava River: part 1: selected elements; Milačič et al. 2009) and persistent organic pollutants (part 2, presented herein) in sediments along the Sava River.

Materials and methods

Instrumentation

The analysis of PAH in sediment extracts was performed using a gas chromatograph (GC) equipped with a split/splitless injector port and a mass selective detector (Hewlett-Packard model 6890 GC and 5972A mass spectrometry detector (MSD)) operating in the selected ion monitoring mode. The procedure is described in details elsewhere (Heath et al. 2006). In PAH analysis, an ISCO (Lincoln, NE, USA) supercritical fluid extractor (SFX2–10) was adopted (Notar and Leskovšek 2000). PCB and selected chlorinated pesticides were determined on a Hewlett-Packard 6890 GC-ECD (Polič et al. 2000). Soxhlet extraction was performed with Lab-line® multi-unit extraction heater (Barnstead/Lab-line, Dubuque, IA, USA) for PCB and pesticide analyses (EPA 3540C 1996; EPA 3620B 1996; EPA 8082A 1996; Polič et al. 2000). A WTW (Weilheim, Germany) 330 pH meter was employed to determine the pH.

The analyses of OTC were carried out on a Hewlett-Packard 6890 GC (Hewlett-Packard, Waldbronn, Germany) coupled to a Hewlett-Packard 5972A MSD. The GC was equipped with a 30 m × 25 mm HP-MS5 capillary column (film thickness 0.25 μm). The following temperature program was applied for the separation of OTC: The column temperature was held at 80°C for the first 4 min, raised to 280°C at the heating rate of 8°C min^{-1}, and held at 280°C for 4 min. The splitless injector port was kept at a temperature of 240°C and the transfer line at 280°C. Helium was used as a carrier gas (1 mL min^{-1}). The volume of injected sample was 1 μL. The MSD operated with the electron impact ion source at a temperature of 180°C. Single ion monitoring was conducted according to Morabito et al. (1995). A mechanical shaker Vibramax 40 (Tehtnica, Železniki, Slovenia) was used to agitate the sediment extracts while centrifugation of the sample extracts was performed on a Heraeus (Osterode, Germany) Model 17S Sepatech Biofuge centrifuge.

Reagents

A PAH standard mixture (PAHs Mix 4-8905) was purchased from Supelco (Bellefonte, PA, USA). Deuterated PAHs were obtained from Ultra Scientific Inc. (North Kingston, RI, USA). All solvents (SupraSolv grade), except solvents for organic residue analysis (Baker ultra resi-analyzed) which were purchased from J.T. Baker (Deventer, Holland), and reagents (activated copper powder, anhydrous sodium sulfate) were supplied by Merck (Darmstadt, Germany). The wet support was obtained from ISCO (Lincoln, NE, USA). Carbon dioxide (99.9995% purity) was delivered by Messer Griesheim (Gumpoldskirschen, Austria). Individual PCB congeners and pesticides were supplied by Dr. Ehrenstorfer GmbH (Ausburg, Germany) and Florisil by Supelco (PR 60/100 mesh, Bellefonte, PA, USA).

Suprapure acids (Merck, Darmstadt, Germany) and Milli-Q water (Direct-Q 5 Ultrapure water system, 18 MΩ, Millipore Watertown, MA, USA) were used for the preparation of samples and standard solutions. All other chemicals were of analytical-reagent grade or higher purity.

Monobutyltin trichloride chloride (MBT; 95%), monophenyltin trichloride (MPhT; 98%), and diphenyltin dichloride (DPhT; 96%) were purchased from Aldrich (Milwaukee, WI, USA). Dibutyltin dichloride (DBT; 97%), tributyltin chloride (96%), triphenyltin chloride (95%), and tripropyltin chloride (98%) were obtained from Merck. Monooctyltin trichloride (MOcTCl_3, 98%) and dioctyltin dichloride (DOcTCl_2, 98%) were purchased from LGC Promochem (Wesel, Germany) and trioctyltin chloride (TOcTCl, 95%) from Fluka (Buchs, Switzerland). Organotin standard stock solutions (1,000 mg L^{-1} as Sn) were prepared in methanol. Anhydrous sodium acetate was purchased from Kemika (Zagreb, Croatia). Acetic acid, methanol, and isooctane were supplied by Merck. Sodium tetraethylborate (NaBEt_4) was purchased from Strem Chemicals (Newburyport, MA, USA).

Quality control

To verify the quality of our data, we analyzed a reference material IAEA-408: organochlorine compounds, petroleum hydrocarbons, and sterols in a sediment sample from mudflats of the Tagus Estuary (IAEA, Analytical Quality Control Services, and Vienna, Austria). To check the quality of data in OTC determinations, a reference material PACS 2 (Marine Sediment Reference Material for Metals and Other Constituents, National Research Council, Ottawa, Canada) was analyzed.

Sampling procedure, sampling location, and sample preparation

River sediment samples were collected during three sampling campaigns (April 2005, October 2005, and May 2006) from 20 different sampling locations along the Sava River. The sampling procedure, sampling locations, and sample preparation are described in detail in part I of this investigation (Milačič et al. 2009).

Determination of PAH

PAH were determined by accelerated solvent extraction–supercritical fluid extraction (ASE–SFE) with methylene chloride and carbon dioxide. Disposable 10-mL high temperature crystalline polymer extraction cartridges (ISCO, Lincoln, NE, USA) packed with 5 g of sediment sample and 2 g (or the mass needed to fill up the cartridge volume) of sodium sulfate or wetsupport™ (ISCO, Lincoln, NE, USA). The ASE–SFE extraction procedure with a total extraction time of 30 min is presented in detail elsewhere (Heath et al. 2006). The method validation is also described in full elsewhere (Notar and Leskovšek 2000).

Determination of PCB and chlorinated pesticides

PCB and selected chlorinated pesticides were extracted by Soxhlet extraction (ca. 10 g of dried sediment) with hexane and analyzed after cleaning and fractionation on a Florisil column by GC-ECD (EPA 3540C 1996; EPA 3620B 1996; EPA 8082A 1996; Polič et al. 2000).

Determination of OTC

For the analysis of OTC, approximately 0.5 g of sediment sample was extracted in 20 mL acetic acid. Derivatization was performed with sodium tetraethylborate. Ethylated OTC species were extracted into isooctane and their concentrations determined by GC–MS (Ščančar et al. 2007).

Results and discussion

The accuracy check

The accuracies of the analytical procedures applied were checked by analyzing certified reference materials and reference materials. The average values obtained are summarized in Tables 1, 2, 3, and 4. In general, good agreements with the certified, reference, and/or information values were obtained, giving confidence in the accuracy of the results reported in this study.

The Sava River sedimental grain size distribution

The grain size distribution in the sediments is described in detail in part I of this study (Milačič et al. 2009).

Analysis of PAH

Sediment samples collected downstream from the Sava River were analyzed and the content of 16 PAHs: naphthalene, anthracene, phenanthrene, fluoranthene, benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(g,h,i)perylene, benzo(k) fluoranthene, indeno(1,2,3)pyrene, acenaphtylene, benzo(b)fluoranthene, acenaphthene, fluorene, dibenzo(a,b)anthracene, and phenanthrene (Table 5) and their methylated analogs were determined. For this method, the limit of detection for a single PAH was determined to be between 0.002 and 0.01 ng g^{-1}.

Our results reveal increasing PAH values downstream from Črnac with four sites having significantly elevated PAH (the sum of 16 PAHs) levels, e.g., Županja, Brčko (up to 4,000 ng g^{-1}), and Bosanska Rača, Gradiška (approximately 2,000 ng g^{-1}; Table 5). All four locations with elevated concentrations are situated downstream of the oil fields of Črnac and Lukavec. The Canadian Environmental Quality Guidelines (1999) for separate PAHs in sediments quotes Interim Freshwater Sediment Quality Guidelines (ISQG; dry weight) 6–111 ng g^{-1} and probable effect level (PEL; dry weight) 88–2355 ng g^{-1}. Therefore, except for the aforementioned locations, pollution with PAHs in sediments can be considered moderate along the Sava River.

PAHs are the frequent subject of research in river sediments (Agarwal et al. 2007; Banjoo and Nelson 2005; Barth et al. 2007; Götz et al. 2007; Ho and Hui 2001; Ko et al. 2007; Lacorte et al. 2006; Liu et al. 2007; Oren et al. 2006; Škrbić et al. 2005; Ünlü and Alpar 2006; Xu et al. 2007). Vertical profiles of river sediments (Götz et al. 2007) shows that the highest content of 16 EPA PAHs occurs in the 1960s reaching 43,580 ng g^{-1} in 1964. Liu et al. (2007) studied the distribution and sources in surface sediments of the rivers in Shanghai, China and found total PAH concentrations between 107 and 1,707 ng g^{-1}. Surface sediments from the Yellow River, China (Xu et al. 2007) revealed slightly higher total PAH concentrations (up to 2,621 ng g^{-1}), while Taiwanese research found up to 9.8 μg g^{-1} of total PAH concentrations in the surface sediments of the Susquehanna River (Ko et al. 2007). Total PAH contents in downstream, the sediment of the Kishon River in Israel (Oren et al. 2006), were up to 299 ng g^{-1}, which is comparable to Ebro River PAH sediment levels (1.07–224 ng g^{-1}; Lacorte et al. 2006). Our results for the Sava River sediment lie within the above reported values.

Based on the sediment quality guideline of effects (Ko et al. 2007), the contents of total PAHs

Table 1 Concentrations of selected PAHs (ng g^{-1}) in reference material IAEA-408 (organochlorine compounds, petroleum hydrocarbons, and sterols in a sediment sample)

PAHs (ng g^{-1})	Naphthalene	Acenaphtylene	Acenaphtene	Fluorene
Determined value (ng g^{-1})	29.78 ± 3.33	4.03 ± 0.12	3.95 ± 0.18	5.41 ± 0.34
Recommended value (ng g^{-1})	27			
Information value (ng g^{-1})		3.6	3.3	6.7
95% confidence interval (ng g^{-1})	16–47	2.1–4.7	2.0–17	4.6–24
	Phenanthrene	Anthracene	Fluoranthene	Pyrene
Determined value (ng g^{-1})	36.93 ± 1.77	8.86 ± 0.16	85.01 ± 3.48	73.90 ± 2.73
Recommended value (ng g^{-1})	35	9.8	84	77
Information value (ng g^{-1})				
95% confidence interval (ng g^{-1})	21–43	8.0–13	53–110	57–93
	Benzo(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene
Determined value (ng g^{-1})	36.83 ± 1.81	30.75 ± 1.29	35.78 ± 5.79	28.20 ± 6.08
Recommended value (ng g^{-1})	53	35	46	46
Information value (ng g^{-1})				
95% confidence interval (ng g^{-1})	35–60	25–56	32–69	26–61
	Benzo(a)pyrene	Indeno(1,2,3 cd)pyrene	Dibenzo(a,h)anthracene	Benzo(g,h,i)perylene
Determined value (ng g^{-1})	49.48 ± 2.27	39.81 ± 2.23	12.68 ± 0.79	30.24 ± 1.42
Recommended value (ng g^{-1})	48			38
Information value (ng g^{-1})		51	11	
95% confidence interval (ng g^{-1})	30–63	45–53	7.8–14	20–52

Results represent a mean of three parallel sample determinations

Table 2 Concentrations of selected PCBs (ng g^{-1}) in reference material IAEA-408 (organochlorine compounds, petroleum hydrocarbons, and sterols in a sediment sample)

Congeners (ng g^{-1})	PCB 18	PCB 28	PCB 31	PCB 52	PCB 44	PCB 101	PCB 149
Determined value (ng g^{-1})	0.411 ± 0.051	0.447 ± 0.056	0.451 ± 0.058	0.715 ± 0.044	0.464 ± 0.036	1.208 ± 0.113	1.244 ± 0.056
Recommended value (ng g^{-1})		0.79		0.6		1.2	1.4
Information value (ng g^{-1})	0.74		0.43		0.47		
95% confidence interval (ng g^{-1})	0.13–1.9	0.35–0.98	0.09–1.5	0.38–0.93	0.23–3.0	0.81–1.7	1.3–1.6

	PCB 118	PCB 153	PCB 138	PCB 180	PCB 170	PCB 194	
Determined value (ng g^{-1})	1.086 ± 0.012	1.089 ± 0.002	1.264 ± 0.005	0.843 ± 0.012	0.356 ± 0.005	0.133 ± 0.001	
Recommended value (ng g^{-1})	1.2	1.9	1.6	1.1	0.47	0.2	
Information value (ng g^{-1})							
95% confidence interval (ng g^{-1})	0.9–1.6	0.98–2.1	1.1–2.1	0.85–1.2	0.34–0.59	0.2–0.23	

Results represent a mean of three parallel sample determinations

Table 3 Concentrations of selected pesticides (ng g^{-1}) in reference material IAEA-408 (organochlorine compounds, petroleum hydrocarbons, and sterols in a sediment sample)

Pesticide (ng g^{-1})	HCB	Heptachlor	Aldrine	*p*,*p*-DDE	Lindane	*p*,*p*-DDD	*p*,*p*-DDT	Dieldrine	Endrine
Determined value (ng g^{-1})	0.481 ± 0.015	0.354 ± 0.003	0.253 ± 0.037	0.883 ± 0.019	0.154 ± 0.001	0.505 ± 0.080	0.320 ± 0.034	0.359 ± 0.022	0.169 ± 0.018
Recommended value (ng g^{-1})	0.41			1.4	0.19		0.67	0.3	
Information value (ng g^{-1})		0.42	0.41			0.87			0.57
95% confidence interval (ng g^{-1})	0.3–0.57	0.23–0.7	0.2–2.3	0.88–2.0	0.11–0.2	0.56–1.7	0.48–0.98	0.3–0.48	0.14–1.2

Results represent a mean of three parallel sample determinations

Table 4 Concentrations of MBT, DBT, and TBT (ng g^{-1} Sn) in certified reference material PACS 2 (marine sediment) determined by GC–MS

Sample	MBT (ng g^{-1} Sn)	DBT (ng g^{-1} Sn)	TBT (ng g^{-1} Sn)
PACS 2			
Determined	540 ± 20	1,100 ± 20	980 ± 30
Certified	600[a]	1,047 ± 64	890 ± 105

Results represent a mean of two parallel sample determinations

[a] Informative value only

are bellow the effects range median of 44.8 μg g^{-1}, while some exceed the effects level low (ERL) of 4.02 μg g^{-1} (Ko et al. 2007). According to the literature (Götz et al. 2007; Ko et al. 2007; Lacorte et al. 2006; Liu et al. 2007; Oren et al. 2006; Xu et al. 2007), we believe that except at certain locations, where levels exceed the ERL (Ko et al. 2007), PAHs should not cause adverse ecological effects; this is also the case for those Sava River sediments tested.

When comparing PAH pollution in the Danube River sediments (ICPDR 2002) with the Sava River sediments, the Sava River sediment samples have a lower PAH content. For instance, in the Danube sediment, the PAH contamination profile (ICPDR 2002) is dominated by phenanthrene and anthracene (up to 8 mg kg^{-1}); however, the sum of the 16 PAHs rarely reaches 2 mg kg^{-1}. The Sava sediments (Table 5) were more evenly polluted with regards to individual PAHs, and concentrations of individual PAHs were in all cases below 1 mg kg^{-1}. In agreement with the above observations, the four most polluted sites have the highest contents of phenantherene, fluoranthene, pyrene, benzo(a)anthracene, and chrysene (Table 5).

A common method for estimating the source of PAH pollution is by calculating the specific ratios of the alkylated PAH and the parent PAH (methylphenanthrene/phenanthrene and methylpyrene/pyrene; Notar et al. 2001; Ünlü and Alpar 2006). If the ratio between methylphenanthrene/phenanthrene (MePh/Ph) is between 0.5 and 1 and the ratio between methylpyrene and pyrene (MePy/Py) is smaller than 1, it can be assumed that the main sources of pollution are from combustion processes. If the MePh/Ph ratio is between 2 and 6 and the ratio of MePy/Py is greater than 2, there is a strong indication of fossil fuel pollution. The presence of retene tends to indicate forest fires as a source of PAH. Calculations of the MePh/Ph ratios (Table 6) show values between 0.5 and 1 at the following locations: Moste, Vrhovo, Brežice, and Jesenice, which is consistent with MePy/Py values below 1 (Table 6).

These data 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 (MePh/Ph 2–6 and MePy/Py >2) which is surprising since heavy petrochemical industry is located around Sisak (Croatia). The elevated retene concentrations indicate six potential spots (Table 6) polluted with PAHs as a result of forest fires (Moste, Vrhovo, Brežice, Jesenice, Brèko, and Raèa); however, there is as yet insufficient data available to confirm these results.

Analysis of PCB

As an indicator for PCB pollution, seven indicator PCBs were determined (seven congeners: 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, 180: 2,2′,3,4,4′,5,5′-heptachlorobiphenyl). The limit of detection for selected PCBs was between 0.0005 and 0.001 ng g^{-1}.

Our results show no elevated concentrations in the sediments at the sampling sites downstream of the Sava River (up to 6 ng g^{-1}). Even though Canadian Environmental Quality Guidelines (1999) quotes for total PCBs ISQG to be 34.1 ng g^{-1} and PEL as 277 ng g^{-1}, we can say that the PCB pollution is not present downstream of the Sava River in significant levels (Table 7). However, slightly elevated values were found in sediments taken at the Košutarica sampling site, which might be the influence of industrial activities.

The sum of PCBs in river sediment showed that Danube and the Sava sediments have a lower content than in the sediment of the rivers Rhine (200 ng g^{-1}), Volga (up to 40 ng g^{-1}; Winkels

Table 5 Concentrations of selected PAHs (ng g^{-1}), sum of 16 PAHs determined in the sediments of the Sava River and ISQG and PEL values (Canadian Environmental Quality Guidelines 1999)

PAHs (ng g^{-1})	Naphthalene	Acenaphtylene	Acenaphtene	Fluorene	Phenanthrene	Anthracene
Mojstrana	6.94	0.89	1.31	1.59	9.93	0.48
Moste	12.34	8.19	2.19	14.69	67.93	13.75
Jevnica	5.50	1.53	1.17	2.34	11.76	1.53
Vrhovo	12.95	3.36	6.11	10.74	30.16	3.99
Brežice	1.65	0.46	0.65	1.24	3.55	0.41
Jesenice na Dolenjskem	2.60	0.74	1.28	0.86	4.05	0.43
Oborovo	20.48	10.52	3.52	9.86	61.80	7.91
Sremska Mitrovica	2.30	5.17	7.59	4.47	153.71	12.32
Črnac	14.31	11.76	3.52	8.63	266.26	36.26
Lukavec	24.48	14.54	5.73	19.44	154.07	25.20
Košutarica	92.70	181.74	61.25	12.74	118.68	46.29
Gradiška	23.68	42.04	4.45	10.83	97.56	29.69
Srbac	46.90	16.08	7.76	2.41	4.90	10.63
Slavonski brod	10.04	8.15	4.56	8.51	114.32	19.38
Županja	57.47	41.10	16.73	45.03	280.60	116.53
Brčko	76.08	39.71	24.68	44.46	299.88	81.33
Bosanska Rača	51.61	27.30	12.62	25.29	141.04	38.13
Sremska Mitrovica	39.68	10.80	9.05	22.25	133.62	16.00
Šabac	47.38	15.71	7.69	16.71	112.06	11.18
Beograd	22.93	5.64	5.45	11.67	82.89	2.07
ISQGs	34.6	5.87	6.71	21.2	41.9	46.9
PEL	391	128	88.9	144	515	245

PAHs (ng g^{-1})	Fluoranthene	Pyrene	Benzo(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene
Mojstrana	4.83	3.88	3.32	6.04	5.94	2.47
Moste	59.61	65.35	36.29	45.16	33.47	22.50
Jevnica	21.33	15.90	12.15	22.03	24.86	14.29
Vrhovo	39.67	33.01	19.62	30.25	25.81	16.14
Brežice	7.45	5.66	4.00	5.91	7.15	3.45
Jesenice na Dolenjskem	8.49	6.10	3.87	6.10	7.69	4.70
Oborovo	59.04	31.08	49.79	46.26	41.92	31.93
Sremska Mitrovica	5.60	22.40	14.50	10.88	8.75	6.00
Črnac	47.42	64.76	91.99	328.68	34.53	67.32
Lukavec	92.55	104.02	137.67	209.82	85.29	47.18

Table 5 (continued)

PAHs (ng g^{-1})	Fluoranthene	Pyrene	Benzo(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene
Košutarica	66.14	69.06	119.11	220.00	68.79	60.69
Gradiška	263.24	203.49	188.08	326.95	224.00	137.30
Srbac	142.56	102.53	74.10	74.63	144.59	33.71
Slavonski brod	71.22	83.23	64.23	152.20	40.82	53.70
Županja	518.93	435.36	454.96	437.16	276.12	369.95
Brčko	601.79	461.71	379.46	287.61	433.50	111.58
Bosanska Rača	318.66	239.97	211.78	170.90	250.21	85.49
Sremska Mitrovica	158.62	148.14	69.11	67.96	106.97	30.07
Šabac	141.36	101.95	81.89	69.99	161.77	32.09
Beograd	48.38	30.72	17.01	26.81	43.65	11.07
ISQGs	111	53.0	31.70	57.1	/	/
PEL	2,355	875	385	862	/	/

PAHs (ng g^{-1})	Benzo(a)pyrene	Indeno(1,2,3 cd)pyrene	Dibenzo(a,h)anthracene	Benzo(g,h,i)perylene	Sum 16 PAH
Mojstrana	1.95	1.95	0.65	3.31	55.46
Moste	31.72	23.47	6.92	23.45	467.01
Jevnica	11.09	15.88	2.54	14.46	178.35
Sremska Mitrovica	16.17	20.97	3.81	18.69	291.47
Brežice	2.34	2.92	0.74	3.73	51.30
Jesenice na Dolenjskem	2.90	3.65	0.42	3.41	57.28
Oborovo	26.44	19.52	6.34	22.09	448.48
Galdovo	5.28	2.71	0.87	2.15	264.69
Črnac	63.06	32.88	35.53	78.99	1,185.90
Lukavec	52.43	17.97	16.08	37.79	1,044.25
Košutarica	53.88	32.75	17.26	33.52	1,254.62
Gradiška	133.93	95.08	36.44	83.60	1,900.37
Srbac	63.30	0.00	0.00	0.00	724.11
Slavonski brod	41.99	26.69	15.79	36.45	751.30
Županja	417.18	238.37	62.16	197.55	3,965.22
Brčko	237.90	250.97	55.91	163.80	3,550.37
Bosanska Rača	146.15	132.16	20.81	90.56	1,962.68
Sremska Mitrovica	49.31	57.97	8.28	38.95	966.77
Šabac	66.00	76.92	10.63	51.46	1,004.80
Beograd	15.16	4.64	4.02	2.30	334.43
ISQGs	31.9	/	6.22	/	/
PEL	782	/	135	/	/

Table 6 PAH origin downstream Sava River

Sediment	MePh/Ph	MePy/Py	Ph/An	Retene (ng g^{-1})
Sava Moste	0.53	0.07	4.94	41.24
Sava Mojstrana	0.22	0.28	20.80	3.17
Sevnica	0.28	0.18	7.69	6.60
Vrhovo	0.89	0.34	7.56	56.73
Brežice	0.67	0.21	8.59	32.28
Jesenice	0.69	0.15	9.44	23.82
Oborovo	0.01	0.04	5.90	under detection limit
Galdovo	0.00	0.00	12.48	under detection limit
Črnac	0.00	0.00	7.34	under detection limit
Lukavac	0.02	0.03	6.11	under detection limit
Košutarica	0.01	0.06	2.56	under detection limit
Gradiška	0.02	0.02	3.29	under detection limit
Slavonski brod	0.01	0.04	5.90	under detection limit
Županja	0.01	0.01	2.41	under detection limit
Srbac	6.93	0.09	0.46	9.32
Brčko	0.24	0.07	3.69	37.91
Rača	0.31	0.09	3.70	24.32
Sremska Mitrovica	0.25	0.06	8.35	9.83
Šabac	0.27	0.09	10.02	8.89
Beograd	0.35	0.09	39.98	2.68

Me methyl, *Ph* phenanthrene, *Py* pyrene, *An* anthracene

et al. 1998), and Niagara (up to 124 ng g^{-1}; Samara et al. 2006). In depth sediment analysis found the highest PCB concentrations to correlate to the year 1980 (sum PCBs 322 ng g^{-1}) and in the period 1964–1970 (sum PCBs 224 ng g^{-1}) at two different locations on the Elbe River in Germany (Götz et al. 2007); detailed research in the Danube (ICPDR 2002) revealed that the sum of the indicator PCBs does not exceed 0.005 mg kg^{-1}. In the Sava River, this number was exceeded only at Košutarica sampling site. At all other locations, the values were significantly below 5 mg kg^{-1}. Therefore, the pollution of both river basins is at comparable levels and insignificant compared to values reported in the literature (Götz et al. 2007; Samara et al. 2006; Škrbić et al. 2007; Winkels et al. 1998).

Analysis of selected chlorinated pesticides

The presence of selected halogenated pesticides (hexachlorobenzene, heptachlor, aldrine, *p*,*p*-DDE, lindane, *p*,*p*-DDD, *p*,*p*-DDT, dieldrine, and endrine) was also evaluated in the Sava River sediments. The limit of detection for selected chlorinated pesticides was between 0.0005 and 0.001 ng g^{-1}. According to our results (Table 8), with the exception of the sample taken near Belgrade where HCB was determined to be 90.8 ng g^{-1}, there are no elevated concentrations of the other selected pesticides.

HCB was widely used as a pesticide and also as a component for ammunition production. Even though no evidence exists, the high HCB content in the sediment from Belgrade could be a result of recent military conflict. Repeated sampling in June 2007 at the same location showed low HCB values (0.39 ng g^{-1}). To exclude any possible analytical error, sediment collected during previous fieldwork was reanalyzed. The high HCB content was confirmed (98.98 ng g^{-1}). These results (Table 8) indicate a point source of pollution near Belgrade. Among the other chlorinated pesticides studied, most of the values were below 1 ng g^{-1}, except *p*,*p*-DDT at Galdovo (2.56 ng g^{-1}) and Košutarica (1.29 ng g^{-1}) and Endrine at Županja (0.98 ng g^{-1}) which may be a side effect of intense agricultural activities in these areas of the Sava River basin. The Canadian Environmental Quality Guidelines (1999) for separate pesticides are reported to be 1–4 (ISQG) and 4–65 ng g^{-1} (PEL) which confirms that there is no significant organochlorine compound pollution in the Sava River basin.

Comparison with the literature data revealed that the levels of identified organochlorine

Table 7 Concentrations of selected PCB congeners (ng g^{-1}), sum of seven most toxic congeners (28, 52, 101, 118, 138, 153, and 180) determined in the sediments of the Sava River, and ISQG and PEL values (Canadian Environmental Quality Guidelines 1999)

Congeners (ng g^{-1})	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[a]	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		
Črnac	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	34.1
PEL	/	/	/	/	/	/	/	/	/	/	/	/	/	/	340	277

[a] Sum of seven indicator PCB congeners: 28, 52, 101, 118, 138, 153, 180

Table 8 Concentrations of selected chlorinated pesticides (ng g^{-1}) determined in the sediments of the Sava River and ISQG and PEL values (Canadian Environmental Quality Guidelines 1999)

Pesticide (ng g^{-1})	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
Črnac	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

pesticides in Sava and Danube are in the same order as the lower values found in the Buffalo River, South Africa (Fatoki and Awofolu 2003), the River Queme (UNEP 2003), Elbe, Spain (Barth et al. 2007; Lacorte et al. 2006), and the Daliaohe River, China (Wang et al. 2007). The depth concentration profiles of chlorinated pesticides (Götz et al. 2007) give the maximum contaminant concentrations correlating to the year 1964, the year that organochlorine pesticides reached peak production in Germany.

When comparing chlorinated pesticides values in sediments of the Danube (ICPDR 2002) and Sava River basins, it may be seen that HCB, which was elevated near Belgrade (90.8 ng g^{-1}) Sava River sampling site, was also present at elevated values near Budapest (23 ng g^{-1}) on the Danube River. This exceeds the Canadian "lowest effect level" for HCB (ICPDR 2002) in sediments. However, repeated sampling showed significantly lower HCB values, again indicating a point source of pollution of the Sava sediments. Among the remaining chlorinated pesticides analyzed in the Sava and Danube sediments, the Sava sediments contained lower levels of chlorinated pesticides.

OTC in sediments of the Sava River

The major pathway of entry of OTC into the terrestrial environment and surface waters is the use of agricultural pesticides or wood preservatives (TBT and TPhT) and from manufacturing of plastic, glass, paper, and leather (Bancon-Montigny et al. 2004). The most important nonpesticidal route is the leaching of organotin-stabilized polyvinylchloride (PVC) by water (DBT and octyltins) and accumulation of OTC in the waste water treatment plants. In order to estimate the extent of pollution with OTC, sediments from 20 locations in the Sava River were analyzed by GC–MS. The results indicate that the concentrations of butyltins, octyltins, and phenyltins are below the limits of detection (<2 ng Sn g^{-1} for butyltins, <3 ng Sn g^{-1} for octyltins, and <10 ng Sn g^{-1} for phenyltins, respectively). Therefore, we consider the Sava River sediments not to be polluted with OTC. Similar observations for the Danube River sediments (ICPDR 2002) also found mainly undetectable levels of TBT. Concentrations of TBT above 10 ng Sn g^{-1} were found in only two sediment samples of the Danube. There are river sediments contaminated with OTC in Europe and these include the rivers from the Adour–Garonne basin (Bancon-Montigny et al. 2004) where the concentrations of butyltin in river sediments are from 1 to 125 ng Sn g^{-1} for MBT, 1 to 87 ng Sn g^{-1} for DBT, and 1 to 125 ng Sn g^{-1} for TBT. Phenyltin concentrations are lower, between 0.5 and 49 ng Sn g^{-1} for MPhT, 0.2 and 8 ng Sn g^{-1} for DPhT, and 0.1 and 0.5 ng Sn g^{-1} for TPhT, while octyltins concentrations were lower than 0.5 ng Sn g^{-1}. Scrimshaw et al. (2005) investigated the historical deposition of butyltins in bed sediments from the harbor in the River Thames (UK). Results from sediment cores demonstrated that in most samples, TBT concentrations of 20–60 ng Sn g^{-1} accounted for less than 10% of the total butyltin species present. This indicates the degradation of TBT compounds in the sediments. Pilot survey of the OTC concentrations in sediments from the Ebro river basin (NE Spain; Lacorte et al. 2006) indicated that in contaminated sites, the TBT concentrations ranged from 25 to 38 ng Sn g^{-1} for TBT, 40 to 512 ng Sn g^{-1} for DBT, and 18–156 ng Sn g^{-1} for MBT. MBT and DBT as predominant species occurred not only as degradation product of TBT but also from leaching and weathering of PVC materials containing these OTC. Our study demonstrates that OTC are not present in measurable concentrations in the sediments of the Sava River. This indicates that in the area investigated, there was not widespread use of these toxic compounds, neither for agriculture nor in the manufacturing of products containing OTC.

Conclusions

Sava River sediments were investigated for the presence of inorganic pollutants (Milačič et al. 2009) and organic pollutants presented herein at 20 downstream locations from the Sava River spring to its inflow into the Danube River. Among other persistent organic pollutants, PAH were present in the sediment samples and their concentrations increased downstream. Concentrations of PCB in the sediments were low and among the selected pesticides *p*,*p*-DDT was found in the river sediments collected at Galdovo and Košutarica, although its use has been banned for many years. We also found the HCB pesticide in a higher concentration at Šabac and in a particularly high concentration at the Belgrade. However, from repeated sampling, it was confirmed that near Belgrade, the HCB derives from a point source of pollution. Analysis of organic pollutants indicated that the Sava River is not polluted with butyltin, phenyltin, or octyltin compounds.

The environmental status of sediments of the Sava River is in general comparable to other moderately polluted rivers in Europe. According to targeted organic analyses (PAHs, PCBs, selected chlorinated pesticides, and organotin compounds) performed within the SARIB project, we make a general conclusion that, with the exception of certain sampling sites (Županja, Brèko, Bosanska Raèa, Gradiška, and Belgrade), the pollution of the Sava River sediments is low and generally lower than the pollution in the Danube River sediments (ICPDR 2002).

The findings of our investigation contribute to the sum of knowledge of the extent of pollution in the sediments of European rivers. The results are also significant for the International Sava River Basin Commission, stakeholders, water management bodies, and local authorities of the riparian countries, which may use our data as a basis for sustainability purposes, management, and protection of the Sava River water resources.

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