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Micro-pollutants in sediment samples in the middle Danube region, Serbia: occurrence and risk assessment

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Abstract This is the first comprehensive study on the occurrence of 940 semi-volatile organic compounds including sterols, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, plasticizers, and other emerging compounds in 10 river and canal sediments collected in northern Serbia. For quantification of investigated compounds GC-MS-MS (selected reaction monitoring) and GC-MS (using both selected ion monitoring and total ion monitoring) methods were used. The number of detected compounds was in the range of 85–117, while the sum of the concentrations varied from 959 μg/kg dry-wt to 84,445 μg/kg dry-wt. Sterols were quantified with high frequency in nearly 100% of investigated samples suggesting that the studied rivers and canals have been contaminated by sewage. Regarding persistent organic compounds, *p,p'*-DDE, *p,p'*-DDD, and *o,p'*-DDT were the dominant members of organochlorine pesticides (OCPs). The concentration range of 11 quantified pesticides of 452 analyzed was from 0.564 to 61.6 μg/kg dry-wt, while the concentration range of 47 quantified PCBs of 90 analyzed was from 0.928 to 32.1 μg/kg dry-wt. OCPs (DDE, DDD, and γ-HCH) and several PAHs (fluoranthene, pyrene, phenanthrene, chrysene, benzo(a)anthracene, benzo(a)pyrene) exceeded the maximum values of the sediment quality guidelines. Contents of domestic compounds comprise a large proportion of the total contaminant concentration. Overall, the study reveals that river sediments in Vojvodina Province were moderately polluted mainly by domestic wastewater. The toxic equivalent quantity (TEQ) relative to benzo(a)pyrene and 2,3,7,8-tetrachlorodibenzodioxin for seven carcinogenic PAHs and six quantified dioxin-like PCBs ranged from 3.59 to 103 μg TEQ/kg and from 0.001×10^{-3} to 2.10×10^{-3} μg TEQ/kg, respectively, and were in the range or lower than the literature published data.

Keywords Persistent compounds · Emerging compounds · Sterols · GC-MS · River sediment

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Introduction

Agricultural, industrial, and domestic activities use more than one third of the Earth's accessible renewable freshwater. Throughout these activities, water contamination certainly happens with numerous anthropogenic and natural occurring compounds (Schwarzenbach et al. 2009), which can be ascribed as micro-pollutants. Some of these micro-pollutants can be regarded as emerging pollutants (e.g., perfluorinated compounds, pharmaceuticals, personal care products); some of them are hydrophobic and degrade very slowly due to their persistent nature (e.g., organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs)), while some are polar and infiltrate into ground and drinking water (Loos et al. 2009; Pérez et al. 2014; Kong et al. 2016). The presence of

these compounds at low concentrations may raise considerable toxicological concern, adversely affecting surface, ground, and drinking water and sediment quality (Qi et al. 2011). River sediments provide foodstuff for living organisms and at the same time serve as medium for accumulation of a wide range of environmental contaminants especially hydrophobic organic substances such as persistent organic compounds (Antonijević et al. 2014; Kukučka et al. 2015). Many natural and anthropogenic processes such as high flow periods, floods, remediation of river bed, and urban redevelopment lead to secondary contamination of downstream (Salo et al. 2008; Qi et al. 2011; Kukučka et al. 2015).

The Danube River is the second-largest river in Europe (2857 km long) that flows through 10 countries and receives a vast volume of untreated wastewater from domestic sources, industrial activities, and agricultural activities. Together with its tributaries, the Danube River provides a necessary resource for water supply, sustaining biodiversity, agriculture, industry, fishing, recreation, tourism, power generation, and navigation (Natchkov and Case Study IX, 1997). In the scientific literature, there is little information available on the occurrence of semi-volatile organic contaminants in sediment of the Danube River and its tributaries. JDS1, Summary of the Final Report Joint Danube Survey (2002), Micić and Hofmann (2009), JDS2, Joint Danube Survey 2 (2008), JDS3, Joint Danube Survey 3, (2015), Matić-Bujagić et al. (2016), and Kukučka et al. (2015). Matić-Bujagić et al. (2016) investigated source pollution of the sediments of the Danube River and its tributaries using sterol ratios. Kukučka et al. (2015) analyzed chlorinated and brominated persistent organic pollutants in sediment samples collected on a monthly basis during a period of 1 year in the upper catchment of the Danube River. The Joint Danube Survey 2 (JDS2) study conducted in autumn 2007 investigated more than 280 individual parameters in water, sediment, and mussel samples collected from 124 sites covering the total length of the Danube River and important tributaries from Germany until the Black Sea (JDS2, Joint Danube Survey 2, 2008). The Joint Danube Survey 3 (JDS3) study was the world's biggest river research expedition of its kind in 2013, which investigated 800 individual parameters in the Danube River basin (most of them not covered in the ongoing monitoring practice) (JDS3, Joint Danube Survey 3, 2015).

Besides these findings, monitoring data on river sediment status in Serbia are still scare and limited in the terms of sampling sites and number of compounds. Additionally, most of those studies have focused on a small number of targeted substances or a group of substances (such as OCPs). It is therefore difficult to obtain a complete picture of chemical pollution of the Danube River and its tributaries. Widespread screening of hundreds of organic micro-pollutants in environmental matrices is technically and financially challenging. For example, during the JDS3 study, 36 cooperating laboratories from the European Union participated in the survey during which 800 individual parameters were measured and 100 semi-volatile organic compounds (SVOCs) were targeted.

In order to overcome this gap, an automated screening gas chromatographic–mass spectrometric (GC-MS) method was developed by Kadokami et al. (2005) capable to operate in both selected ion monitoring (SIM) and total ion monitoring (TIM) mode and, in conjunction with a mass spectral database, is able to identify and quantify nearly 1000 SVOCs. Thus, GC-MS together with gas chromatography–triple quadrupole mass spectrometry (GC-MS-MS) (selected reaction monitoring, SRM) was employed in this study, enabling for the first time the screening of 940 SVOCs in sediment samples of the middle Danube region covering the Serbian part of the Danube River.

Therefore, the aims of this study were (1) to obtain concentrations of a wide variety of substances using the GC-MS database method and GC-MS-MS, (2) to recognize the contribution ratios made by human activities, and (3) to identify characteristic substances and their sources (domestic, business, industrial, and agricultural activities). Additionally, the risk assessment of persistent organic compounds was evaluated through a comparison with sediment quality guidelines for assessing adverse biological effects associated with exposure to contaminated sediments.

Materials and methods

Reagents and materials

All solvents, n-hexane, acetone, and dichloromethane, were of pesticide residue analysis grade supplied by J.T. Baker (Deventer, the Netherlands). Sodium chloride and sodium sulfate were of pesticide residue analysis grade supplied by Fluka (St. Louis, USA). Before the analysis, anhydrous sodium sulfate and sodium chloride were heated at 700 °C for 6 h and stored in a desiccator prior to use. Copper granular (reduced copper, granular, super grade) was obtained from Acros Organics (Geel, Belgium). Internal standards (IS) and surrogate standards (SS) were purchased from Kanto Chemical Co., Wako Pure Chemical Industries (Osaka, Japan), Wellington Laboratories (Ontario, Canada), Sigma-Aldrich Japan K.K. (Tokyo, Japan), and Hayashi Pure Chemical Ind. (Osaka, Japan). IS and SS working solutions were prepared in a concentration of 10 μg/mL using acetone or hexane. Before using, water was purified with a Millipore Milli-Q Advantage (Millipore, Molsheim, France). Silica–gel cartridges were purchased from Waters Corporation (Sep-Pak VAC 2 g/12 mL; Waters Associates, Milford, MA, USA). Activated carbon columns were obtained from SUPELCO (ENVI-Carb; SUPELCO, Bellefonte, PA, USA). Diatomaceous earth and

cellulose filters were purchased from Thermo Fisher Scientific (Sunnyvale, California, USA).

Sample collection

The Serbian part of the Danube is 588 km long, and the second largest one (20.6% of total length). It begins at the border with Hungary (km 1433 of the Danube flow) and ends at the mouth of the Timok River, at the border with Bulgaria (km 845 of the Danube flow). It defines Serbia's border with Croatia over a length of 138 km and Serbia's border with Romania over a length of 230 km (Babić-Mladenović et al. 2013). This study is focused on the 200-km-long middle Danube segment, i.e., of the Pannonian Danube, within the Vojvodina Province, the northern Serbian Province. The Tisza River is the largest one in the Danube River basin (157,200 km^2), and it is the longest tributary (966 km) of the Danube River. The Begej River rises in the Carpathian region in Romania and flows through Banat as the left tributary of the River Tisza. The river is 254 km long, 76 km of which is in Serbia. The Great Bačka Canal is a part of the Danube–Tisza–Danube (DTD) canal system for irrigation in Vojvodina Province. It runs from Bezdan (on the Danube River) to Bečej (on the Tisza River). The canal is 118 km long. The Krivaja River (109 km) is a river in northern Serbia which flows fully within the borders of the Serbian province of Vojvodina.

In this study, 10 sampling sites were chosen, including points at the Danube, Tisza, Begej, and Krivaja rivers, and the Danube–Tisza–Danube canal (Fig. 1). These locations were selected to represent the different water systems in Vojvodina Province. Descriptions of the locations and water system types are given in Table 1. Sediment samples (coded from S1 to S10, Table 1, Fig. 1) were taken to the depth of 10 cm at the shallow water from the surface layer of sediment in September 2014. Three grab samples were collected from each sampling site in order to obtain composite samples. Sampling was provided by the Vode Vojvodine d.o.o. responsible for the water system in the Vojvodina Province, the northern part of Serbia. The samples were transferred into stainless steel bottles previously washed successively with detergent, purified water, acetone, and hexane in a laboratory. The bottles containing sediment samples were kept in an ice box and were transported to the lab. Sediment samples were stored in the dark at a temperature of 4 °C and extracted within 2 weeks after sampling. Determination of moisture contents was carried out by measuring the weight loss in 10 g sub-sediment samples after oven-drying at 105 °C for 2 h (Pan et al. 2014).

Sample preparation and chemical analysis

The analytical processes for determination of the 940 SVOCs (Table S1) in sediment samples were performed according to Kadokami et al. (2012). A detailed description of sample preparation, quality control, and analysis is provided in Sections S1–S3 of the Supplementary Material; only a brief summary is provided here. All samples were extracted in stainless-steel extraction cells (33 mL) using an accelerated solvent extractor (ASE 350, Dionex 350, Thermo Fisher Scientific, USA). After extraction, the extracts were loaded to silica–gel cartridges and separated into three fractions. The first fraction was eluted with 15 mL of hexane, the second with 15 mL of 5% acetone–hexane solution, while the third fraction was eluted with 15 mL of 30% acetone–hexane solution. In order to remove sulfur and colored substances, fraction 1 was treated with copper powder while fraction 3 was loaded on activated carbon columns.

The targeted 940 analytes were measured using GC–MS–SIM/TIM (QP2010 Plus, Shimadzu, Kyoto, Japan). SIM was applied to PCBs, OCPs, polycyclic aromatic hydrocarbons (PAH), and sterols. Additionally, 81 compounds including OCPs and PCBs were measured using GC–MS–MS–SRM (TSQ Quantum XLS, Thermo Fisher Scientific, Yokohama, Japan). Before the analysis, internal standards (Table S1) were added in each analyzed sample (at each fraction). GM–MS–SIM/TIM and GC–MS–MS–SRM settings are presented in Tables S2 and S3. The GC–MS identification/quantification system (Kadokami et al. 2005) was used for identification and quantification of the 940 SVOCs throughout the analysis of total ion current chromatograms obtained by a GC–MS–TIM (Table S1). Micro-pollutants analyzed in SIM and SRM mode are presented in Tables S4 and S5, respectively. For substances which were quantified by multiple methods (GC–MS (TIM/SIM) and/or GC–MS–MS (SRM)), results obtained by GC–MS–MS (SRM) were preferentially used followed by the results of GC–MS (SIM) and GC–MS (TIM).

The data on the analytical quality control could be found in Pan et al. (2014). The method detection limits (MDLs) (Table S1) were ≤ 2 μg/kg dry-wt for 84% of the chemicals in the database, while the MDLs of the substances measured by SIM or SRM were ≤ 0.2 and ≤ 0.02 μg/kg dry-wt, respectively.

Quality controls were performed by blank analysis, as well as reproducibility and repeatability tests. Despite precautions to avoid contamination, 17 chemicals were still detected at concentrations higher than instrumental quantification limits in field blank samples during the analysis (Table S6). The concentration detected in the samples within two times of the value observed in the field blank was reported to be not detected; otherwise, a blank value was subtracted from the detected concentration. The surrogate standards with the similar physico-chemical properties as investigated compounds

Fig. 1 Locations of sediment sampling (description in Table 1)

(Table S7) were spiked to all samples (sediment and blank samples) before extraction, and the average recoveries were

used to check the applicability of the applied method. Obtained recovery values for surrogate standards were in the

Table 1 Description of the sampling locations and samples collected throughout the Vojvodina Province

Sample code Latitude/ longitude	Sampling locations	Description of samples
S1[a]	Great Bačka Canal[b] before Vrbas town	Near sewage effluent of the Kula town into the Great Bačka Canal
S2	Small canal (belonging to the DTD canal system) close to inlet in the Great Bačka Canal, Vrbas town	Near meat industry and confectionery plants
S3	Inlet of the Krivaja River[c] into the Great Bačka Canal, between Srbobran town and Bačko Gradište.	Near operating oil wells, wastewater from municipal solid waste landfill, slaughterhouse, and farm meat industry
S4	Great Bačka Canal after inlet of the Krivaja River, between Srbobran town and Bačko Gradište.	Near operating oil wells
S5	Tisza River[d], between Novi Bečej town and Titel town	Downstream wastewater cardboard industry and slaughterhouse
S6	Danube river, Bačka Palanka town (at 1299 km of the Danube flow)	Public beach
S7	Danube river, Čelarevo village (at 1287 km of the Danube flow)	Downstream from industrial plants in Bačka Palanka town
S8	Danube river, Futog village (at 1269 km of the Danube flow)	Place at river bank as a station of transfer boat (srb. "skela")
S9	Danube river, Novi Sad town (at 1255 km of the Danube flow)	Downstream the oil refinery
S10	Begej River[e], Titel town	Downstream from edible oil production plant, slaughterhouse, detergent industry in Zrenjanin town

[a] S1 (45° 35′ 55″ N; 19° 36′ 13″ E); S2 (45° 35′ 7″ N; 19° 38′ 25″ E); S3 (45° 32′ 47″ N; 19° 50′ 57″ E); S4 (45° 32′ 42″ N; 19° 25′ 28″ E); S5 (45° 23′ 42″ N; 20° 12′ 38″ E); S6 (45° 14′ 8″ N; 19° 25′ 28″ E); S7 (45° 15′ 21″ N; 19° 31′ 56″ E); S8 (45° 14′ 3″ N; 19° 43′ 5″ E); S9 (45° 15′ 48″ N, 19° 53′ 1″ E); S10 (45° 12′ 39″ N, 20° 20′ 50″ E)

[b] Great Bačka Canal—a part of the Danube–Tisza–Danube (DTD) Canal system for irrigation in Vojvodina Province. It runs from Bezdan (on the Danube) to Bečej (on the Tisza). The canal is 118 km long

[c] The Krivaja is a river in northern Serbia. With the length of 109 km, it is the longest river that flows completely within the borders of the Serbian province of Vojvodina. It empties into the Great Bačka Canal. It is not navigable

[d] Tisza is one of the main rivers of Central Europe (966 km long). It starts in Ukraine and flows through Romania, Hungary, and Serbia, where it empties into the Danube River

[e] Begej (or Bega) river is a 254-km-long river that starts in Romania (178 km) and flows to Serbia (76 km) before it empties into the Tisza River

range from 60 to 120% for 22 of 38 surrogate standards analyzed. Presented results were not corrected for recovery values.

Multivariate statistical analysis

For statistical analysis, commercially available software products Microsoft Excel 2007 (Microsoft Office) and DEL 13.2 Statistica (Tulsa, Oklahoma, USA) were used. In the environmental analysis of a wide number of micro-pollutants, multivariate statistical techniques such as cluster analysis (CA) and principal component analysis (PCA) are often used. These techniques are able to simplify and interpret the data in a more clear way. PCA was used to clarify the main emission sources of targeted substances, which had been previously divided into 12 groups based on their chemical similarities (e.g., polycyclic aromatic hydrocarbons (PAHs)) or according to their similarities in usage (such as pesticides, intermediate). Half of the detection limit value was substituted for the sample individual component concentration that was below the method detection limit (Škrbić et al. 2005a; Škrbić and Đurišić-Mladenović 2007). On the same data used for PCA, CA was applied (Ward's agglomerative clustering with Euclidean squared distances) in order to classify sampling locations according to their similarities in contamination. Log transformation was performed to all data as presence of outliers and data distribution have a severe effect on those statistical methods and in order to correct the skewness of data typical for environmental contaminants (Cachada et al. 2012; Škrbić et al. 2017).

Risk assessment

In order to evaluate the level of ecological toxicity on aquatic biota relating the investigated compounds (PAHs, PCBs, OCPs), the obtained results were compared with sediment quality guidelines (SQGs) proposed by the Florida Department of Environmental Protection and some non-regulatory published sediment quality guidelines (Smith et al. 1996; Long and Morgan 1991) summarized in MacDonald et al. (2003). The most used targeted values for the effect characterization are (i) the effects range approach (ERA) including the effects range low (ERL) and the effects range medium (ERM) (Long and Morgan 1991) and (ii) the effects level approach (ELA) including the threshold effect level (TEL) and the probable effect level (PEL) (Smith et al. 1996).

Additionally, toxicity assessment was evaluated for persistent organic compounds (PAHs and PCBs) by calculating the total toxic equivalent quantity ($\sum TEQ_{PAH}$, $\sum TEQ_{PCB}$) for seven carcinogenic PAHs (benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (InP),

dibenzo(a,h)anthracene (DahA)) and 12 dioxin-like PCBs (PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189) (as they have the same structure as those of dioxins and furans and pose similar risk for human and animal health) (Škrbić et al. 2005b; Oliva et al. 2015; Montuori et al. 2016a; Montuori et al. 2016b). Additionally, the TEQ was also estimated for 16 US EPA PAHs as priority environmental pollutants. The calculation was done using

$$\sum TEQ_{PAH/PCB} = \sum C_i \times TEF_i$$

where C_i is concentration of individual PAH or dioxin-like PCB ($\mu g/kg$ dry-wt), and TEF_i is the toxic equivalency factor of PAHs and PCBs relative to benzo(a)pyrene (BaP) and 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD), respectively. The TEF_i used for TEQ calculation is given in Section S4 of the Supplementary material.

Results and discussion

Micro-pollutants in sediment samples

None of the sediment samples tested was free of organic micro-pollutants. Rather, a similar number of compounds were quantified in the sediment samples collected at 10 locations (Fig. S1) ranging from 85 (S9) to 117 (S10) compounds detected, in average 104, representing about 15% targeted compounds (940). The number of chemicals detected only once was 11.

The total contents of all detected micro-pollutants in each of the sediment samples are presented in Fig. 2. Total concentration was calculated without summing the impact of n-alkanes as the main source of n-alkanes was terrestrial plants. The sum of the concentrations varied from 959 $\mu g/kg$ dry-wt (S9) to 84,445 $\mu g/kg$ dry-wt (S2). The highest total content of 84,445 $\mu g/kg$ dry-wt was found at sampling location S2 (small canal belonging to the DTD canal system, Vrbas town), followed by sampling location S3 (inlet of the Krivaja River into Great Bačka Canal) 19,854 $\mu g/kg$ dry-wt and sampling location S4 (Great Bačka Canal after inlet of the Krivaja River) 12,086 $\mu g/kg$ dry-wt. In all other sediment samples, total contents of micro-pollutants ranged from 959 $\mu g/kg$ dry-wt (S9) to 4019 $\mu g/kg$ dry-wt (S10). The total micro-pollutant content at each site decreased towards the inflow of the DDT canal into the Tisza River, from Vrbas town (S2) to the Great Bačka Canal after the inlet of the Krivaja River (S4). An exception was sediment sample S1 taken at the Great Bačka Canal before Vrbas town. Regarding the sediment samples taken from the Danube River, the total contents of micro-pollutants in four sediment samples decreased along the downstream flow, from sample S6 (at 1299 km of the Danube flow), followed by sample S7 (at 1287 km of the Danube flow), sample S8 (at 1269 km

Fig. 2 The total content of the detected micro-pollutants in sediment samples (logarithmic scale)
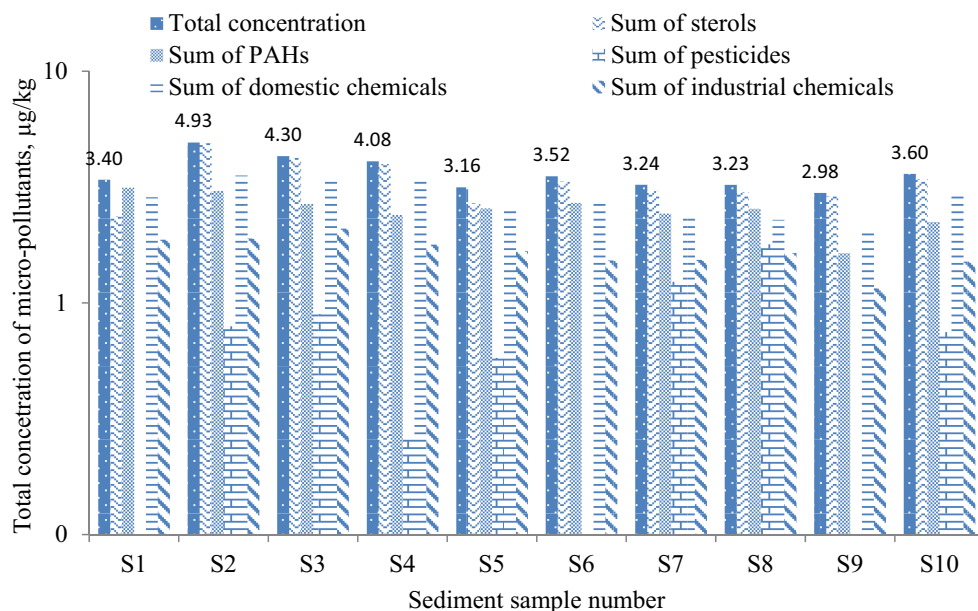
of the Danube flow), and sample S9 (at 1255 km of the Danube flow) (Figs. 1 and 2).

A total of 143 compounds were detected in all the samples, including n-alkanes, PAHs, industrial and domestic chemicals, persistent organic compounds, and sterols. The distribution of four classes of chemicals (PAHs, pesticides, domestic chemicals, and industry chemicals) within the total contents determined in each of the sediment sample is given in Fig. 3. Three groups of samples with similar distribution might be observed: the group with the dominant domestic chemicals (sediment samples S2–4 and S9–10), the group with unique distribution of domestic chemicals and PAHs (sediment samples S5–7), and the group of the samples with the dominant PAHs chemicals (S1 and S8).
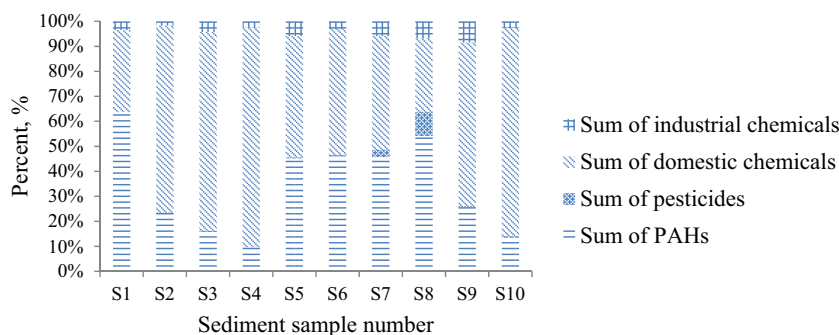
n-Alkane

The total concentrations of the n-alkanes $\sum(nC_9$ to $nC_{33})$ ranged from 3858 μg/kg dry-wt (S4) to 23,882 μg/kg dry-wt (S2) in the sediments with the mean value of 10,160 μg/kg dry-wt (Table S8). Among the n-alkanes examined, C_{27}, C_{29}, and C_{31} were prevalent. Obtained concentrations for the sum

of n-alkanes were lower than those announced for comparable samples from rivers in Vietnam and Dokai Bay, Japan (1056–61,839 μg/kg dry-wt, average 17,033 and 1208–37,671 μg/kg dry-wt, average 17,798 μg/kg dry-wt, respectively) (Kadokami et al. 2013; Duong et al. 2014), and higher than in sediment samples from Tokyo Bay, Japan (1513–9257 μg/kg dry-wt, average 4980 μg/kg dry-wt) (Pan et al. 2014).

The data used for distinguishing the sources of n-alkanes (biogenic or petrogenic source) are summarized in Table S9. The ratio of the sum of <C21 and the sum of >C21 much lower than 1 indicates n-alkanes produced by higher plants, marine animals, or sedimentary bacteria. The ratio close to 1 indicates algae, plankton, or crude oil origin. Additionally, biogenic samples show a large value (i.e., 50) for the ratio of the sum of all identified n-alkane concentrations and C16, while oily samples show a small value (i.e., 15). The concentration ratio of odd n-alkanes (the sum of C27 and C29 n-alkanes multiplied by 2; (C27 + C29))×2) and even n-alkanes (the sum of C26, C28 multiplied by 2 and C30; C26 + 2 × C28 + C30) between 3 and 6 indicates vascular plants origin of n-alkanes. If the calculated ratio of odd and even n-alkanes is around 1, it indicates petrogenic

Fig. 3 Distribution of four classes of micro-pollutants in sediment samples

hydrocarbon origin. As the dominant n-alkanes were C27, C29, and C31, the ratio of the sum of <C21 concentration and the sum of >C21 concentration was much lower than 1, while the ratio of the sum of all identified n-alkanes and C16 concentration showed large values, and the ratio of the sum of odd and the sum of even alkane concentration was between 1.4 and 11; it could be concluded that the main source of n-alkanes is terrestrial plants (Table S9).

Sterols

Ten separate sterols were identified during this study; the sum of sterol concentrations ranged from 231 μg/kg dry-wt (S1) to 79,608 μg/kg dry-wt (S2) (average 11,431 μg/kg dry-wt). Among the chemical groups evaluated in the presented study, sterols showed the highest concentration levels (Table S8). Coprostanol, cholesterol, corpostanone, campesterol, stigmasterol, beta-sitosterol, and stigmastanol were detected in every sediment sample in a wide range of concentrations: the relative standard deviations (RSDs) were higher than 100%, even when the outlying sample S2 was excluded from the calculation. Sediment samples taken from the DTD canal (S2, S4) and sediment sample S3 showed elevated concentrations of total sterols; the average levels of total sterol concentrations in the previous ones were about 10 to 150 times higher than those in other sediment samples (S1, S5–S10). Elevated concentrations of total sterols clearly indicated their origin which could be related to the untreated municipal sewage and smaller dilution capacity of the DTD canal and the Krivaja River in comparison to the Danube and Tisza rivers. It is worth mentioning that sampling location S1 had a significantly lower concentration of total sterols than the other sediment samples taken from the DTD canal, especially when comparing with sediment sample S2 sampled in Vrbas town, indicating that Vrbas town and its industry have a huge impact on the contamination. Vrbas town does not have a wastewater treatment plant, and this town is the regional center of meat and confectionery industries. Regarding the Danube River, the decreasing trend of total sterol concentrations was observed from Danube sediment sample S6 followed by S7 and S8 (with similar total sterols concentration) and the sediment sample taken in the vicinity of Novi Sad (S9).

In order to design measures for adequate control and reduction of environmental pollution, information about the origin of fecal contamination is needed (Kong et al. 2015). Therefore, three diagnostic indices were applied in this study (Table S8) in order to estimate the origin of sterols at investigated sites: the coprostanol/(cholesterol + cholestanol) index, the coprostanol/(coprostanol + cholestanol) index, and the epicoprostanol/coprostanol index. These diagnostic rations are often used as a diagnostic tool for human fecal contamination (Furtula et al. 2012; Matić-Bujagić et al. 2016). The ratio of coprostanol to cholesterol plus cholestanol > 0.2

(Fig. 4) indicates human fecal contamination (Furtula et al. 2012). In this study, values > 0.2 were determined at seven sampling sites indicating that the investigated sediments in the studied rivers were moderately contaminated by raw sewage (Quéménéur and Marty, 1994). The coprostanol/ (coprostanol + cholestanol) index (Fig. 4) revealed that 4 of 10 sediment samples (S5–S7 and S9) had a value of > 0.7 which is an indication of urban sewage pollution, while four sampling locations (S1, S2, S8, and S10) had index values between 0.3 and 0.7 which indicates difficult-to-confirm source of pollution. All the samples having a value of > 0.7 were taken from the Danube and Tisza rivers.

The ratio between epicoprostanol/coprostanol reveals whether the sewage was treated (> 0.8) or not (< 0.2) before discharge into the environment (e.g., rivers). Ratio values between 0.2 and 0.8 suggest two possible scenarios: uncertain if sediments are affected either by continuous discharge of untreated wastewater or by the release that occurred some time ago (Matić-Bujagić et al. 2016). Three sediment samples (S3, S8, and S9) showed occurrence of untreated sewage, while in three sediment samples (S2, S4, and S7) the epicoprostanol/ coprostanol index was between 0.2 and 0.8. The sterol ratios at locations S1, S5, S6, and S10 were higher than 0.8 which is related to partially treated (primary and secondary) sewage (Matić-Bujagić et al. 2016). Since in the Republic of Serbia only a fraction of wastewater is treated in any way (Schröder et al. 2016), it could be concluded that sampling locations S2, S4, and S7 are affected by untreated sewage discharged in the past.

Polycyclic aromatic hydrocarbons

Twenty-seven of 50 analyzed PAHs were quantified ranging from 43.5 μg/kg dry-wt (S9) to 1396 μg/kg dry-wt (S1), with an average concentration of 493 μg/kg dry-wt. Comparison of the composition profiles of two- to six-ring aromatic PAHs (except for perylene) in the investigated sediment samples revealed similarities in composition of PAHs among the sampling locations (Fig. S2). Namely, higher molecular PAHs (three-, four-, and five-ring) were the most abundant in sediment samples as higher molecular PAHs are less affected by degradation at elevated temperatures during the summer periods than lower molecular PAHs (Duong et al. 2014). The four- to five-ring PAHs were also predominant in sediment samples from the Tiber River, Italy (Montuori et al. 2016a). However, the most frequently observed PAHs at sampling locations S1 and S2 were naphthalene and its alkylated derivate 2,6-dimethylnaphthalene.

Thus, to distinguish petrogenic and pyrogenic sources of PAHs in the presented study, the ratio of methylphenanthrenes (1-, 2-, 3-, and 9-methyphenanthrene) to phenanthrene (MP/P ratio) (Colombo et al. 1989; Zakaria et al. 2002) and the ratio of fluoranthene to fluoranthene plus pyrene (Fl/(Fl + Py)) were
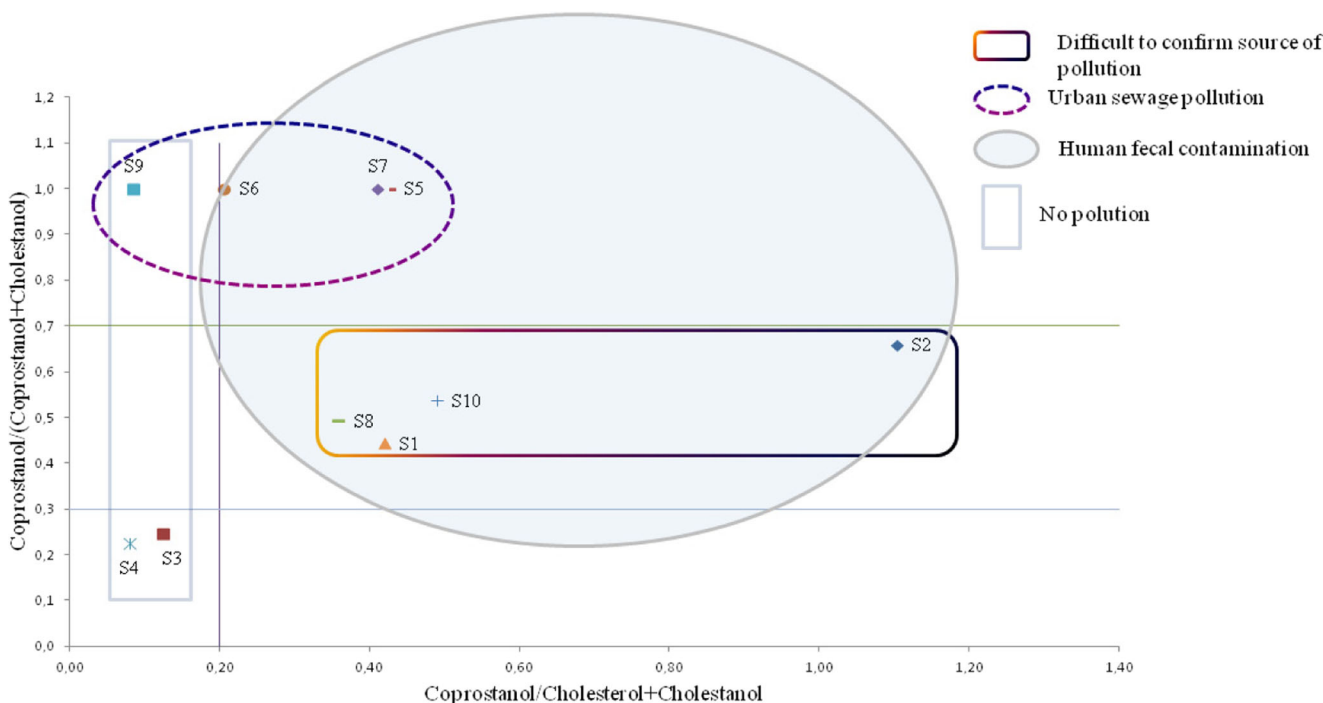
Fig. 4 Relationship between coprostanol/(cholesterol + cholestanol) and coprostanol/(coprostanol + cholestanol) ratios in studied sediment samples

used. Ratios of MP/P were less than 1 in all investigated sediment samples (Tables S10-1 and S10-2), suggesting the pyrogenic PAH inputs (Zakaria et al. 2002). The ratios of Fl/ (Fl + Py) were between 0.40 and 0.50 (S2, S4) indicating liquid fossil fuel (vehicle and crude oil) combustion (Yunker et al. 2002), while the values higher than 0.5 were found at all other locations indicating pyrogenic source, which is in argument with the MP/P ratio. Sampling location S4 is located near operating oil wells which was probably the reason for the petrogenic source of PAHs.

Compared with other river sediments in Europe, the concentrations of ∑PAHs (16 US EPA PAHs) in the sediment samples from Serbian rivers and canals (29.7–1047 μg/kg dry-wt) were similar to those found in the Danube River, Novi Sad, Serbia (975 μg/kg dry-wt) (Škrbić et al. 2005b); Marano and Grado Lagoon, Italy (50–1026 μg/kg dry-wt) (Acquavita et al. 2014); the Danube River, Hungary (8.3–1202 μg/kg dry-wt) (Nagy et al. 2014); and Durance River, France (57–1528 μg/kg dry-wt) (Kanzari et al. 2015). The concentrations were higher than those found in the Tiber River, Italy (4.5–652 μg/kg dry-wt, 13 analyzed PAHs) (Minissi et al. 1998) and the Tiber River, Italy (158–272 μg/kg dry-wt) (Patrolecco et al. 2010) and lower than those found in the Ammer River, Germany (112–22,900 μg/kg dry-wt) (Liu et al. 2013), Gulf of Trieste, Italy (214–4416 μg/kg dry-wt) (Bajt 2014), Huveaune River, France (572–4235 μg/kg dry-wt) (Kanzari et al. 2014), and Ría de Arousa, Spain (45–7901 μg/kg dry-wt) (Pérez-Fernández et al. 2015).

Among the total number of sediment sites (98) along the whole length of the Danube River sampled during the JDS1

study, 2 mg/kg concentration was exceeded in 17 samples only (JDS1, Summary of the Final Report Joint Danube Survey, 2002). The maximum concentration at 17 sample sites obtained for PAHs during the JDS1 study was considerably higher than the maximum level of 1135 and 1047 μg/kg detected during the JDS2 study (JDS2, Joint Danube Survey 2, 2008) and in the presented study, respectively. This might suggest a decrease in PAH levels in the Danube sediments since 2001. Comparing the result obtained for the middle Danube region obtained in this study with the results for the River Danube basin obtained during the JDS2 study (Table S11), it could be concluded that the maximum determined concentration and the average concentration of PAHs obtained were within the range.

Spatial distribution of persistent organic pollutants

Forty-seven of 90 PCBs analyzed were detected in the investigated sediment samples, ranging from 0.928 μg/kg dry-wt (S7) to 32.1 μg/kg dry-wt (S2) (Table S8). In the investigated sediment samples, the average $\sum PCB_6$ concentration (1.57 μg/kg dry-wt) was about four times lower than the average concentration of $\sum PCB_6$ (6.4 μg/kg dry-wt) in the JDS2 study (JDS2, Joint Danube Survey 2, 2008) (Table S11).

Further on, the cluster analysis was carried out on the investigated sites using composition ratios of four commercial formulations of Chlophen (Germany), Aroclor (USA), Sovol (Russia), and Chlorofen (Poland). These formulations are supposed to be used in Serbia, because exact data are not available. Takasuga et al. (2006) reported congener profiles of 24

major PCB congeners in formulations mentioned above, and according to these results and the congener profiles of 24 major PCB congeners of 47 quantified in the presented study, cluster analysis was carried out. Cluster analysis was performed using composition ratios of 24 congeners for PCB formulations and the investigated sites. The dendrogram obtained is shown in Fig. S3. According to the results of cluster analysis, all of the analyzed samples are classified into the same group of highly chlorinated PCB formulations.

Among the OCPs examined in this study, dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), and dieldrin were only detected (Table S8). DDTs exhibited the highest concentration followed by HCHs. The obtained concentration range for the sum of DDTs (0.455–61.2 µg/kg dry-wt) was comparable with the values (3.2–61.5 µg/kg dry-wt) reported by Torres et al. (2002) for sediment samples taken from the Amazon region in Brazil. The sites located on the Danube River before Novi Sad city (S7, S8) had a relatively high concentration of OCPs in comparison to the other sampling sites (Table S8). The total concentrations of the sum for the OCPs determined at sampling locations S7 and S8 were 17.1 and 61.6 µg/kg dry-wt, respectively, while the concentrations for other sampling sites were in the range of 0.564–7.86 µg/kg dry-wt. Obtained results (when the sampling locations S7 and S8 are excluded from calculations) are comparable with those found for sediments in the Tiber River, Italy (0.66–10.02 µg/kg dry-wt) (Montuori et al. 2016b), and the Arc River, France (0.02–7.15 µg/kg dry-wt) (Kanzari et al. 2012).

In order to distinguish the origin of DDT (technical DDTs or dicofol), the ratio between o,p'-DDT and p,p'-DDT was used. Dicofol was extensively used in pre-harvest as acaricide after OCPs such as DDT had been banned. Because of similarity in structures between DDT and dicofol, they exhibit analogue concerns about persistence, bioaccumulation, and influence on human and animal health (Fujii et al. 2011). In technical DDTs, the ratio of o,p'-DDT to p,p'-DDT ranges from 0.2 to 0.3, while dicofol shows the ratio from 1.3 to 9.3 or higher than 9.3 (Qiu et al. 2005). The ratio o,p'-DDT/ p,p'-DDT was in the range of 0.5–3.9 with the exception of S1–S6 and S10. At the mentioned sampling locations, the concentrations of p,p'-DDT were lower than the detection limit for p,p'-DDT, while the concentrations of o,p'-DDT were higher than the detection limit for o,p'-DDT (Table S8) implicating that the ratio of o,p'-DDT/p,p'-DDT is higher than 1.3. This finding indicates that dicofol was the main source for all of the studied sediment samples. Additionally, in order to follow the chronology of input of DDT in the environment, the ratio of three major compounds (DDT, DDE, and DDD) was calculated. The ratio of DDE + DDD to total DDE, DDD, and DDT ((DDE + DDD)/∑DDTs) indicates old DDT residues (> 0.5) or recent input (< 0.5) (Hitch and Day 1992; Škrbić et al. 2007). In this study, all studied samples showed the ratio of DDE and DDD to ∑DDTs (Table S8) higher than 0.5,

clearly demonstrating that there have been no recent inputs of DDT in the studied areas. The observed concentration (0.045 µg/kg dry-wt) for p,p'-DDT at sampling location S9 (Novi Sad) in comparison with the concentration (6.31 µg/kg dry-wt) obtained during the study undertaken by Škrbić et al. (2007) at the same sampling location clearly demonstrated decrease of DDT concentration during the last 10-year period.

The total HCH concentration (∑HCHs) ranged from not detected (<LOQ) (S6, S8, and S9) to 1.03 µg/kg dry-wt (S3). The results obtained for HCHs at sampling location S9 are in agreement with the results obtained by Škrbić et al. (2007).

The ratio of α-/γ-HCH could be used to distinguish whether the origin of HCH-containing pesticides is from the technical HCH or from lindane (Iwata et al. 1993). The ratio of α-HCH to γ-HCH between 4.6 and 5.8 is characterized for technical HCHs while the ratio of α-HCH to γ-HCH is close to zero for lindane application (Zhang et al. 2004). The α-/γ-HCH values obtained in the presented study were all below 2.2 indicating possible lindane usage.

Domestic chemicals and emerging organic chemicals

Pharmaceuticals and personal care products (PPCPs), industrial chemicals, and others represent novel emergent compounds (Schröder et al. 2016) which comprise a large proportion of the total contaminant concentration (Fig. 3) obtained in the presented study. Emerging organic contaminants (EOCs) are defined as natural or synthetically occurring substances that are not commonly monitored in the environment, but that can induce known or suspected undesirable effects on humans and ecosystems (Stuart et al. 2012; Meffe and de Bustamante, 2014; Petrović et al. 2014; Schröder et al. 2016; Škrbić et al. 2016). Di-n-butyl phthalate (DBP), bis(2-ethylhexyl) phthalate (DEHP), and butylbenzylphthalate were quantified in investigated sediment samples, among them DBP and DEHP as two of the most used phthalate compounds (PHCs) in industrial production. DEHP was detected at two sampling locations in concentrations of 286 µg/kg dry-wt (S10) and 1429 µg/kg dry-wt (S2). During the JDS3 study, DEHP was detected in the concentration range of 1–6 mg/kg (1000–1500 km of the Danube flow; thus, in the Serbian part of the Danube River). DEHP was found in elevated concentrations at sampling location S2 confirming that this location has the highest contamination. Total PHC concentrations in positive samples ranged from 1.20 µg/kg dry-wt (S9) to 1429 µg/kg dry-wt (S2), with an average value of 657 µg/kg dry-wt. This later value is over five times lower than the sediments in Vietnam (3900 µg/kg dry-wt) (Duong et al., 2014) and comparable to alluvial sediments in Jiang Han, China (927 µg/kg dry-wt) (Liu et al. 2010). In the study undertaken by Wang et al. (2014), PHCs were detected in all 34 sediment samples analyzed in typical riverine sediments in southern Jiangsu

Province, China, and the total concentrations of the six priority control PHCs in sediments ranged from 2.3 to 80.1 mg/kg with a mean concentration of 13.2 ± 14.7 mg/kg. The maximum total PHC concentration (1429 µg/kg dry-wt) obtained in the presented study was lower than the total minimum concentration (2.3 mg/kg) obtained in the previously mentioned study. Also, DEHP and DBP were the dominant PHCs in the study undertaken by Wang et al. (2014). The Priority Substance data sheet for protection of benthic organisms (EQS, Environmental Quality Standards, Substance Data Sheet, 2005) provides a proposal for specific quality standards in sediment to be 100 mg DEHP/kg sediment. All sampling sites investigated in the presented study showed concentrations far below this specific standard.

Further on, at all the studied sites, additionally 17 domestic and 10 industrial chemicals were observed, including disinfectants (phenol, 3- and 4-methylphenol), fatty acid methyl esters (methyl dodecanoate, methyl myristate, methyl palmitate), cosmetics/solvents (anthraquinone), chemicals that leach from tires (e.g., 2-methoxyphenol), and intermediates in organic synthesis (2,4-dimethylphenol, bisphenol A) (Table S8). Among 17 domestic compounds, benzyl alcohol (16.7–185 µg/kg dry-wt), octanol (2.34–40.6 µg/kg dry-wt), and phenylethyl alcohol (0.887–12.8 µg/kg dry-wt) were detected with frequency of 100%. 2-Phenoxy ethanol was also detected in all analyzed sediment samples. Squalene, which has application in numerous vaccine and drug delivery emulsions, was observed in all analyzed sediment samples (Table S8). Chemicals that leach from tires come into the environment by abrasion of the tires with roadway surfaces and, lately, as a result of roadway runoff, are distributed to soil and sediment. Over the service life of a tire, approximately 12% of the mass is released to the environment. Different vulcanization agents and antioxidants are used during manufacture of tires, and those additives among others represent potentially environmental problems (Unice et al. 2012; Unice et al. 2015). In the presented study, four compounds (4-hydroxy-3.5-dimethoxy-benzaldehyde, 2(3H)-benzothiazolone, 2-phenoxy-ethanol, and 2-methoxyphenol) that potentially can leach from tires were quantified in the concentration range from 27.6 to 703 µg/kg dry-wt. The obtained results were in the range with the results reported by Kadokami et al. (2013) for sediment samples in Dokai Bay, Japan (76 to 792 µg/kg dry-wt). 3- and 4-Methylphenol, which belong to the group of cresols, were detected at the elevated concentrations in the range of 1.47–684 µg/kg dry-wt with frequency of occurrence of 90%. Cresol isomers are used as precursors or synthetic intermediates in the production of pesticides, disinfectants, preservatives, and explosives while as antioxidants they were used to stabilize lubricating oil, motor fuels, rubber, polymers, elastomers, and food (Sanders et al. 2009). Chemicals used as intermediate in organic synthesis were detected with frequency less than 30%

except for 3- and 4-tert-butylphenol (100%) and carbazole (60%). For example, 3- and 4-tert-butylphenol were observed in all sediment samples, with an average concentration of 17.6 µg/kg dry-wt. Bisphenol A, used in the chemical industry as plasticizer in the production of polycarbonate and epoxy resin and as antioxidant in cosmetics, was detected at three locations in the concentration range from 3.68 µg/kg dry-wt (S5) to 17.0 µg/kg dry-wt (S8). Bisphenol A was also analyzed in sediments during the JDS3 study (JDS3, Joint Danube Survey 3, 2015) and was not detected in any of the analyzed sediment samples (LOQ was 10 µg/kg). It was confirmed that bisphenol A has estrogenic potential even at low concentrations (Duong et al. 2015).

Risk assessment

The presence of phenanthrene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, and benzo(a)pyrene at sampling location S1 and phenanthrene, fluoranthene, and pyrene at sampling location S2, both located in the DTD canal of the urban sites of Vrbas town, exceeded the threshold effect level (TEL) for mentioned PAHs (Table S12) (MacDonald et al. 2003). For the other quantified PAHs (individual compounds and sum of PAHs), obtained concentrations were significantly lower than the targeted values for TELs and probable effect levels (PELs). The $\sum TEQ_{7carPAHs}$ and $\sum TEQ_{US\ EPA\ PAHs}$ obtained for sediment samples were in the range from 3.59 µg TEQ/kg (S9) to 103 µg TEQ/kg (S1) and from 3.62 to 104 µg TEQ/kg (Table S12), respectively. The range of $\sum TEQ_{7carPAHs}$ in the presented study was comparable with the range (7.05–174.4 µg TEQ/kg for $\sum TEQ_{7carPAHs}$) reported by Montuori et al. (2016a) for sediments sampled in the Tiber River and its estuary, Italy, and the range (3.240–154.6 µg TEQ/kg for $\sum TEQ_{6carPAHs}$ (without DahA)) reported by Sarria-Villa et al. (2016) for sediment sampled in the Cauca River, Columbia. Among the seven carcinogenic PAHs, BaP accounts between 63% (S2) and 72% (S1) of the $\sum TEQ_{7carPAHs}$. BbF accounts between 7.2% (S4) and 11% (S9), while DahA accounts between 4.2% (S2) and 8.8% (S3) of the $\sum TEQ_{7carPAHs}$, InP accounts in the range between 3.4% (S1) and 13% (S2), while Chr, BaA, and BkF account less than 6% of the total contribution to the $\sum TEQ_{7carPAHs}$. The obtained result for the $\sum TEQ_{US\ EPA\ PAHs}$ (3.62 µg TEQ/kg) at sampling location S9 (Novi Sad) was compared with the result for $\sum TEQ_{US\ EPA\ PAHs}$ (131 µg TEQ/kg) reported by Škrbić et al. (2005b) for the sediment sample from the same sampling location sampled in 2001. The result reveals significantly higher concentration reported in the previous study (Škrbić et al. 2005b) which could be explained as a result of the destruction of the Oil Refinery located in the vicinity of Novi Sad during the NATO intervention in 1999 when a huge amount of oil was released into the Danube River.

Table 2   Result of PCA for targeted compounds in sediment samples

Variable	PC1	PC2	PC3
Disinfectant	0.681	0.285	0.535
Intermediate in organic synthesis	*0.760*	0.213	− 0.150
Pesticide	0.175	0.222	− *0.893*
Leaching from tire	0.414	*0.805*	− 0.154
Personal care products	0.518	0.372	0.625
Phytosterol	0.207	*0.967*	0.02
Cholesterol	0.159	*0.928*	0.211
Plasticizer	0.549	0.471	0.207
Zoosterol	0.570	*0.762*	0.174
PAHs	*0.950*	− 0.048	0.023
Fatty acid methyl esters	− 0.239	*0.842*	− 0.287
PCBs	*0.851*	0.137	0.052
Eigenvalues	6.0	2.4	1.4
%Variance explained	50	20	12
%Cumulative variance	50	70	82

Values higher than 0.700 are marked italicize and they represent how good the correlation is between the components and the original variables

Comparing the total sum of identified PCBs in this study with the SQGs (MacDonald et al. 2003), it was shown that none of the sediment samples contained a level higher than the TEL (34.1 µg/kg dry-wt) and ERL (50 µg/kg dry-wt) targeted values for all 90 PCB congeners (Table S12). In comparison with Germany legislation which sets the target value of 20 µg/kg for each of the individual PCBs (28, 52, 101, 138, 153, 180) in sediments (Bergemann et al. 2008), none of the individual indicator congeners exceeded this target value. Regarding the TEQ evaluated for dioxin-like PCBs, six

dioxin-like PCBs (Table S12) were quantified in the presented study and the $\sum TEQ_{PCB}$ was within the range from 0.001×10^{-3} µg TEQ/kg (S7) to 2.10×10^{-3} µg TEQ/kg (S3). The obtained results were lower than those reported by Montuori et al. (2016b) (0.0006–0.37 µg TEQ/kg) for Tiber River and its estuary, Italy, and Syed et al. (2014) (0.03–2.22 µg TEQ/kg) for Ravi River, Pakistan. It is important to point out that the total sum of the dioxin-like PCBs showed the maximum concentrations at sampling locations S1 and S2, 0.68 and 0.55 µg/kg dry-wt, respectively, while the highest $\sum TEQ_{PCB}$ was estimated at sampling location S3 (Tables S8 and S12). At the mentioned location, dioxin-like PCB 126 was quantified and due to their higher TEF (0.1) in comparison to the other quantified dioxin-like PCBs (TEF was in the range of 0.0001–0.00003), the estimated $\sum TEQ_{PCB}$ showed the highest value. Regarding the OCPs at sampling locations S2, S3, S7, and S8 concentrations of DDE (sum of *o,p′* and *p,p′* isomers) exceeded TEL- and ERL-targeted values while at sampling location S8, the concentration of DDE was higher than the PEL-targeted value. Additionally, DDD (sum of *o,p′* and *p,p′* isomers) exceeded the TEL and ERL target values at sampling location S8 (Table S12).

Multivariate statistical analysis

The 143 quantified compounds of 940 investigated were divided into 12 groups (Table 2) according to their chemical similarities and usage (such as pesticides, intermediate, PCBs) in order to evaluate the spatial variation of these 12 groups (parameters) throughout the application of cluster analysis (Fig. 5). The information about the classification of

Fig. 5 Dendrogram of hierarchical cluster analysis for investigated locations

substances into certain groups is given in Table S13. The results significantly separated small rivers (Krivaja (S3) and Begej (S10)) and the DTD canal (S2, S4) on the one side and huge rivers (e.g., the Danube and Tisza Rivers) (S5–S9) on the other side. It is worth mentioning that high concentrations observed at sampling location S2 distinguish this location from the other sampling locations at the DTD canal and small rivers. Sediment sample S1 was taken before Vrbas town and was separated in groups with rivers, clearly demonstrating that Vrbas town and its industry have huge influence on pollution of the DTD canal. Values higher than 0.700 are marked italicize and they represent how good the correlation is between the components and the original variables.

Principal component analysis applied on the same data used for CA showed three principal components (PC) with eigenvalues higher than 1.0 (Table 2), which explains 82% of the total variance of the data. Loading values > 0.700 (correlation of chemical groups) are italicized throughout Table 2 as they represent how good the correlation is between the components and the original variables. PC1 explained 50% of total variance and was positively correlated with high loading value with three parameters including PAHs, intermediates in synthesis of organic compounds, and PCBs. According to the obtained correlations between mentioned chemical groups, it could be concluded that they have similar pollution sources. These compounds are mainly related to industrial wastewater. PC2 accounting for 20% of total variance showed correlation with fatty acid methyl esters, phytosterols, cholesterol, zoosterols, and compounds that leach from tire. Mentioned compounds are associated with sewage source and runoff from traffic. An important contribution for PC3 was pesticides accounting for 12% of total variance; these chemicals were mainly related to agricultural runoff and their use in agriculture.

Conclusion

Results obtained in the presented study revealed a widespread occurrence of different semi-volatile pollutants. The sediment samples in the Danube River and its tributaries are moderately polluted with 143 organic micro-pollutants. Among them, sterols were quantified at elevated concentrations suggesting that the water systems in Serbia are under the pressure of untreated wastewater because of absence of wastewater treatment plants. Additionally, direct discharge of untreated household wastewater to river recipient may be the possible source of PPCP pollution. All the sampling sites were more or less impacted by anthropogenic activities making the distribution of each chemical class varied among sampling locations. Throughout the application of chemometric tools such as hierarchical cluster analysis and principle component analysis, huge data set was interpreted in a more clear way, e.g., getting

the information about similar sources of pollution for certain groups of chemical contaminants. The comparison of PAH, OCP, and PCB concentrations with sediment quality guidelines revealed contaminations with PAHs and OCPs for several investigated locations. From the obtained results, it was confirmed that the screening method for 940 semi-volatile compounds applied for the first time for the study of sediment samples in Serbia is a very useful way to obtain an overview of sediment contamination. However, all the presented results cannot be obtained easily by conventional target analysis.

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