Spatial distribution of PCDDs, PCDFs and dl-PCBs along the cascade of urban reservoirs

Magdalena Urbaniak, Marek Zieliński, Zbigniew Kaczkowski and Maciej Zalewski

ABSTRACT

The river environment is a highly complex system with a variety of processes continuously changing along its continuum (River Continuum Concept). Therefore identification of the threats that result from different elements of the river ecosystem is an intricate task, mainly because of the transportation and biological, geological and chemical processes occurring in such a system. The overall objective of the presented study was to examine the concentration and pattern of polychlorinated dibenzo-*para*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs) in the five urban, cascade reservoirs. The obtained data demonstrated an increasing total concentration of toxic PCDDs/PCDFs and dl-PCBs along the studied reservoirs starting from 266 ng/kg d.w. in the first pond up to 11,400 ng/kg d.w. in the last pond, wherein the highest World Health Organization – Toxic Equivalent (WHO-TEQ) concentration (18.9 ng TEQ/kg d.w.) was also recorded. The exception from this rule, with the lowest total and WHO-TEQ concentrations (182 ng/kg d.w. and 1.31 ng TEQ/kg d.w., respectively) was the middle newly constructed III reservoir, equipped with the sediment traps and sand separators at the stormwater outlets and ecotone zones around its catchment for enhancing the purification of inflowing stormwater. This situation may indicate the importance of such solutions for the reduction of PCDDs, PCDFs and dl-PCBs in the urban water ecosystems.

Key words | dl-PCB, PCDD, PCDF, spatial distribution, urban reservoir

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INTRODUCTION

Polychlorinated dibenzo-*para*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs) are groups of synthetic organic chemicals that can be found in many compartments of the environment, especially in organisms that are at the top of the food chain and may accumulate in significant amounts in these organisms. Their distribution in the environment is related to water and biogeochemical cycles. Moreover, toxicity, persistence and accumulation of PCDDs, PCDFs and dl-PCBs in the environment, and their biomagnification throughout the aquatic and terrestrial food chains affect these organisms, as the chemicals constitute a long-term health risk to humans and animals. The low volatility and low solubility of PCDDs, PCDFs and dl-PCBs in water predispose these substances to association with organic matter (Compilation of EU Dioxin Exposure & Health Data 1999). Therefore, the constructed reservoirs, where the flow velocity decreases and consequently the amount of suspended matter increases, create optimal conditions for the deposition of PCDDs, PCDFs and PCBs derived from various pathways such as atmospheric deposition, surface runoff, and industrial/wastewater treatment plant discharges. It is estimated that 97% of the released PCDDs, PCDFs and dl-PCBs in a water column are deposited in sediments (DiPinto *et al.* 1993), which serve as storage compartments for long-term release of the sediment-associated PCDDs, PCDFs and dl-PCBs, and therefore pose a threat to aquatic organisms (Knezovich *et al.* 1987).

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Thus, sediments in the reservoir act as a sink for most of the PCDDs/PCDFs and dl-PCBs, and are important in long-term pollution assessment studies and the monitoring of ecosystem stress (Thompson *et al.* 1996).

According to ecohydrology theory, strategy for reduction of the threat posed by PCDDs, PCDFs and dl-PCBs to aquatic ecosystems, and consequently to human health, should be based not only on reduction of their emission into the river environment (a gradual process based on clean technologies and policy) but mostly on: (1) understanding the role of reservoirs in the transport of PCDDs, PCDFs and dl-PCBs along the river continuum; (2) their accumulation in reservoir sediments and biotransformation into less or non-toxic compounds; and (3) development of tools and methods for enhancement of the ecosystem resilience against this impact. Both monitoring of the appearance and concentration of these contaminants in aquatic ecosystems, and the identification of the original processes that affect their concentration and risk for the water environment postulated by the first principle (I) of ecohydrology have been critical to regulation of the hydrological pattern and to reservoir construction that is aimed at enhancement of river resilience and the reservoir ecosystem advocated by the second principle (II) of ecohydrology (Zalewski *et al.* 1997; Zalewski 2000, 2006). Therefore in this study, in accordance with the first principle of ecohydrology, we examined the concentrations and patterns of PCDDs, PCDFs and dl-PCBs in sediments of five cascade reservoirs located along the urban Sokołówka River. The results were discussed to identify possible sources that contribute to contamination of the sediment by PCDDs, PCDFs and dl-PCBs and to determine the role of hydrological and biological processes in the obtained values.

MATERIALS AND METHODS

Study site

The Sokołówka River (drainage area of 45.40 km^2) is situated in the north-western part of the city of Łódź, Central Poland (Figure 1) and represents a highly urbanized and industrialized catchment area that is contaminated with organic compounds due to sewer and stormwater overflows. The main stretch of the river was channelized to straighten the course and deepen the bed for the purpose of stormwater retention. Two landscaped retention reservoirs were restored (ponds nos. III and IV) to improve the retention capacity of the urban landscape, and to reduce the stormwater flow peaks along the river length. These ponds, together with the pre-existing old ponds nos. I, II and V, were selected as a study area for the presented research.

The new multipurpose reservoirs fit within the river valley and create a picturesque landscape, nesting sites for birds and recreation areas. The ecohydrology theory postulates the use of such reservoirs as sites that are friendly both to the environment and to humans, and act as an element of the 'blue-green network' of the city of Łódź (Wagner & Zalewski 2009, 2011).

The studied reservoirs differ from each other in age, size, theoretical water residence time, light intensity and input flow. Nevertheless, all of these reservoirs can be regarded as small impoundments, with riverine character and short water retention time (Table 1).

Reservoir I

The first pond, situated in the Adam Mickiewicz Park, in the vicinity of a large housing development, has a surface area of 16,400 m^2 and a capacity of 22,500 m^3. The average water retention time is 8.7 days. The age of the reservoir was assessed as more than 100 years old (Jokiel & Maksymiuk 2002; Bieżanowski 2003; Kujawa & Kujawa 2003; Wagner *et al.* 2007). The deposited bottom sediments have been removed periodically from the reservoir, the last time in 2000.

Reservoir II

The second pond, also situated in the Adam Mickiewicz Park, covers an area of 11,000 m^2 with a capacity of 11,100 m^3 and an average water retention time of 3.9 days. The age of this reservoir, similarly to reservoir I, is more than 100 years old (Jokiel & Maksymiuk 2002; Bieżanowski 2003; Kujawa & Kujawa 2003; Wagner *et al.* 2007). Similarly to reservoir I, the deposited bottom sediments were removed in 2000.

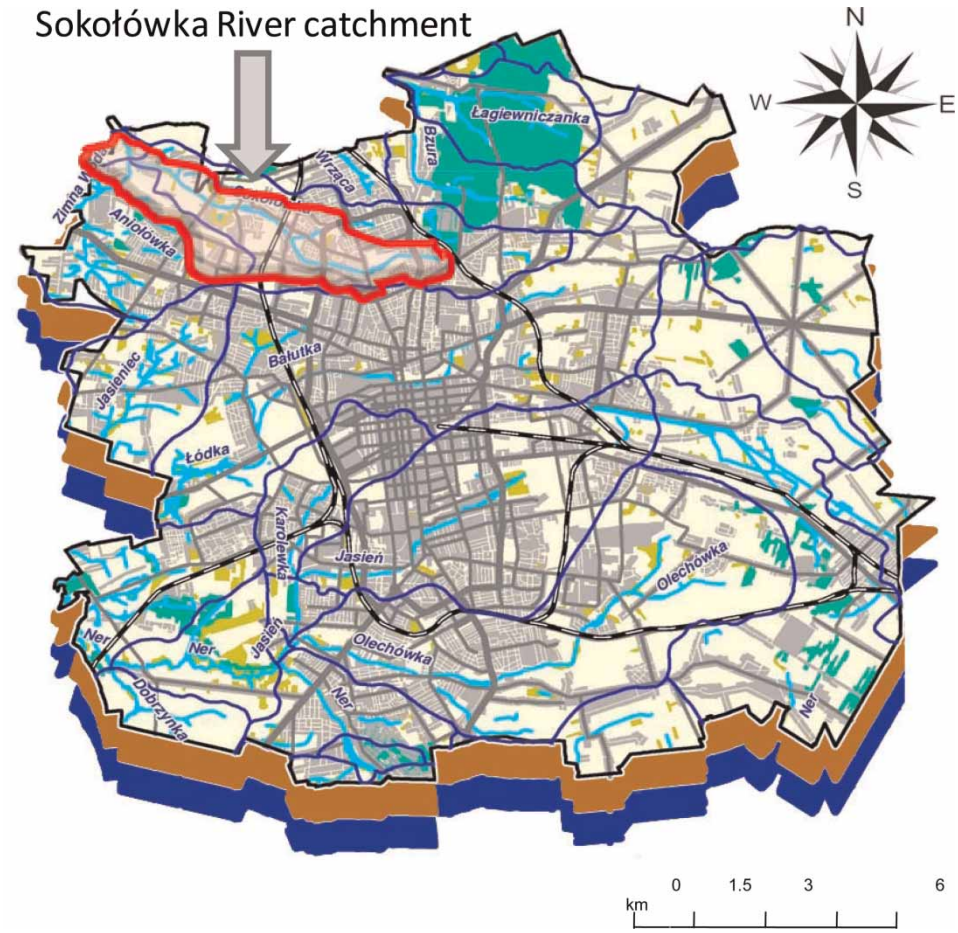

Figure 1 | Location of the Sokołówka River catchment against a background of the city of Łódź.

Reservoir III

The third reservoir located in the estate area was built in 2004 in a trough of an old fish pond (called Chachuły Pond) as a first element of the Sokołówka River valley renaturalization. The surface area of reservoir III is 18,600 m^2, its capacity is 24,000 m^3, and the mean water retention time was 7.7 days (Jokiel & Maksymiuk 2002; Bieżanowski 2003; Kujawa & Kujawa 2003; Wagner *et al*. 2007). The nearest catchment, as well as the littoral zone of the reservoir, has been planted with terrestrial and aquatic plants used for purification of inflowing stormwater and road runoff. Moreover, the outlets of stormwater canals were equipped with separators and sedimentation ponds for the reduction of organochemical compounds (Wagner & Zalewski 2009, 2011).

Reservoir IV

Pond IV is also a newly constructed pond, built in 2006, and situated in the estate area within a trough of the old Kondracki Pond. The reservoir was built laterally on the right riverbank. The surface area is 4,000 m^2 with the capacity of 4,100 m^3 (Jokiel & Maksymiuk 2002; Bieżanowski 2003; Kujawa & Kujawa 2003; Wagner *et al*. 2007).

Reservoir V

Reservoir V is located on the outskirts of the city, in the middle section of the river valley, which has maintained a semi-natural character. Additionally, the reservoir is a recipient of waters from a tributary of the Sokołówka River – the Brzoza River (Figure 1), which is also a stormwater receiver.

Table 1 | Characteristics of the Sokołówka River and its urban cascade reservoirs

	I	II	III	IV	V
River					
Average Q (m^3/s)	0.03	0.033	0.036	0.039	0.068
Q max (m^3/s)	0.68	0.75	0.81	0.92	1.48
Q min (m^3/s)	0.006	0.006	0.007	0.008	0.014
River catchment above the reservoir					
Surface area (km^2)	6.25	6.87	7.37	7.87	13.97
Forests (%)	11	11	19	19	19
Agricultural lands (%)	13	13	23	23	23
Urban lands (%)	60	60	47	47	47
Others (%)	16	16	11	11	11
Reservoir					
Construction time	XIX	XIX	2004	2006	XIX
Max surface area (m^2)	16,400	11,000	18,600	4,000	15,000
Min surface area (m^2)	n.a.	n.a.	14,000	n.a.	15,000
Max depth (m)	1.5	1.5	2.0	1.0	2.0
Average depth (m)	1.0	1.0	1.3	n.a.	1.3
Capacity (m^3)	22,500	11,100	24,000	4,100	20,000
Average Q (m^3/s)	0.03	0.033	0.036	0.039	0.068
Average retention time (days)	8.7	3.9	7.7	n.a.	3.4
The presence of macrophytes	–	–	+	–	–
The presence of separators and sedimentation ponds	–	–	+	–	–
Multimesh gillnet CPUE ($g/m^2/h$)	n.d.	n.d	5.00	14.1	6.80
Percentage of fish with a weight >100 g in cumulated catch (%)	n.d.	n.d.	17.5	62.5	20.0

CPUE, catch per unit effort; n.a., data not available; n.d., not determined.

The surface area of reservoir V is 15,000 m^2, the capacity is 20,000 m^3, and the average water retention time is 3.4 days (Jokiel & Maksymiuk 2002; Bieżanowski 2003; Kujawa & Kujawa 2003; Wagner *et al*. 2007). The deposited sediments have not been removed since its reconstruction in 1980.

Sampling

Bottom sediment samples (10–25 cm thickness) were collected by a sediment core sampler twice a year (spring and autumn) in 2007 and 2008 from three stations (upper, middle and lower part) in each reservoir (Figure 2). Samples were filled into amber containers and transported to the laboratory at 4 °C. After that, samples were homogenized, freeze dried at –40 °C and mixed in proportion 1:1:1 to obtain one representative sample for each reservoir.

PCDD/PCDF and dl-PCB extractions, clean-up and analysis

The 17 2,3,7,8-substituted PCDDs and PCDFs and 12 dl-PCBs congeners were extracted, purified and analysed according to US EPA 1613 Method (1994b), US EPA 1618 Method (1999), and PN-EN 1948 (2002). In short, 2 g of dry sediment samples were spiked with ^{13}C-labelled internal standard of a known quantity to monitor the sampling efficiency and extracted by ASE (Accelerated Solvent Extraction) 200 Dionex. Extraction was operated at 150 atm (11 Mpa) and the oven was heated to 175 °C with toluene.

Interfering material was removed using a multilayer silica column and a florisil column. Elution was performed with 200 mL of hexane and solvent volume was reduced to 5 mL by rotary evaporation and the sample was concentrated

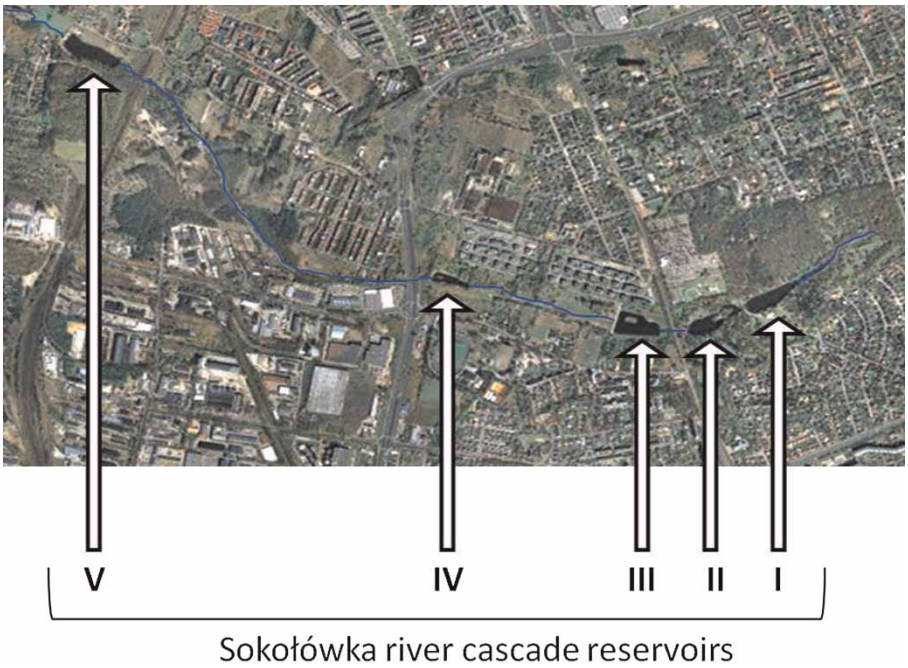

Figure 2 | Sampling sites along the Sokołówka cascade reservoirs. Numbers I–V indicate the reservoir numbers.

to 100 μL under a gentle stream of nitrogen, replacing n-hexane by n-nonane and adding external standards.

Samples were analysed by high resolution gas chromatography/high resolution mass spectrometry: HP 6890N Agilent Technologies (Santa Clara, USA) equipped with a DB5-MS column (60 m × 0.25 mm, i.d. film thickness 0.25 μm) in the splitless injection mode, coupled to a high resolution mass spectrometer Auto Spec Ultima (Milford, USA) using perfluorokerosene (PFK) as a calibration reference. Samples were quantified with the isotope dilution method.

PCDD/PCDF and dl-PCB quality assurance/quality control

The analytical method used for PCDD, PCDF and dl-PCB analysis was properly validated on the basis of internal reference materials; the analytical laboratory involved in 2005 and 2009 successfully passed the accreditation procedure.

All glassware and bottles used in the field and laboratory were cleaned with detergent, rinsed with ultra-pure water, followed by heating at 450 °C overnight. Before use, the glassware was rinsed with acetone and hexane.

Each analytical batch contained a method blank, a matrix spike and duplicate samples. A reagent blank was used to assess artifacts and precision was verified by duplicate analyses. Samples spikes were used as an additional check of accuracy. Recoveries of an analyte were determined by analysing samples spiked with PCDD/PCDF and dl-PCB standards. Recoveries of 13C-labelled PCDD, PCDF and dl-PCB congeners through the analytical procedure ranged from 74 to 146%. The recovery coefficient was taken into account for calculating the final concentrations of analytes. The effectiveness of the presented analytical method was evaluated by analysis based on the updated Standard Reference Material: *Certificate of Analysis for SRM 1939a, Polychlorinated Biphenyls (Congeners) in River Sediment A* (National Institute of Standards and Technology 1990). The precision, the limits of detection and the limit of quantification of the analysed PCDD, PCDF and dl-PCB congeners are presented in Table 2.

Statistics

The presented data were subjected to statistical analyses using 'Statistica' software for Windows. The non-parametric Friedman analysis of variance (ANOVA) test was used to detect differences in the treatments across the studied cascade reservoirs. The Wilcoxon matched pairs test was used

Table 2 | The basic parameters of the analytical method used

PCDD/PCDF	Precision (%)	Limit of Detection (LoD) (pg/kg)	Limit of Quantification (LoQ) (pg/kg)
2,3,7,8-TCDD	5.0	0.12	0.41
1,2,3,7,8-PeCDD	9.0	0.25	0.84
1,2,3,4,7,8-HxCDD	7.0	0.14	0.45
1,2,3,6,7,8-HxCDD	4.0	0.080	0.28
1,2,3,7,8,9-HxCDD	5.0	0.090	0.31
1,2,3,4,6,7,8-HpCDD	11	0.25	0.83
OCDD	6.0	0.13	0.42
2,3,7,8-TCDF	11	0.31	1.03
1,2,3,7,8-PeCDF	5.0	0.090	0.30
2,3,4,7,8-PeCDF	1.0	0.030	0.11
1,2,3,4,7,8-HxCDF	3.0	0.040	0.15
1,2,3,6,7,8-HxCDF	5.0	0.13	0.42
1,2,3,7,8,9-HxCDF	2.0	0.19	0.64
2,3,4,6,7,8-HxCDF	10	0.060	0.19
1,2,3,4,6,7,8-HpCDF	8.0	0.15	0.51
1,2,3,4,7,8,9-HpCDF	3.0	0.080	0.26
OCDF	6.0	0.12	0.38
PCB 77	3.0	0.050	0.12
PCB 81	4.5	0.11	0.35
PCB 126	1.8	0.040	0.15
PCB 169	2.4	0.040	0.13
PCB 105	7.0	0.14	0.48
PCB 118	3.9	0.070	0.25
PCB 123	4.2	0.11	0.37
PCB 156	2.9	0.060	0.21
PCB 157	2.4	0.070	0.22
PCB 167	3.6	0.040	0.21
PCB 189	7	0.11	0.37
PCB 114	2.4	0.030	0.13

to compare the obtained concentrations in two paired reservoirs. Significance was determined based on a probability level of $p \leq 0.05$.

RESULTS

The data obtained demonstrated that the 17 total 2,3,7,8-substituted PCDDs, PCDFs and 12 dl-PCB congeners increased along the studied cascade reservoirs from 266 ng/kg d.w. in reservoir I to 11,400 ng/kg d.w. in reservoir V with the exception of newly constructed reservoir III, in which the lowest value was recorded (183 ng/kg d.w.; Table 3).

Spatial distribution of PCDDs and PCDFs along the cascade reservoirs of the Sokołówka River

Among all the analysed groups of toxins, a predominance of PCDDs was observed with the following values: 9.10, 58.2, 127, 303 and 10,400 ng/kg d.w. in I, II, III, IV and V, respectively, and accounted for 40.6, 70.2, 89.4, 81.5 and 98.4% of the total concentration of PCDDs/PCDFs. The significant increase in PCDD percentage contribution in the total PCDDs/PCDFs (of about 57.0%) along reservoirs was generated by the increasing concentration of the octachlorodibenzo-*p*-dioxin (OCDD) congener ranging from 19.3 to 93.2% (Tables 3 and 4).

The pattern of PCDDs differed between reservoirs, with the decreasing content of hexachlorodibenzo-*p*-dioxin (HxCDD) and heptachlorodibenzo-*p*-dioxin (HpCDD) congeners along the cascade. The decrease was observed especially for 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD and 1,2,3,4,6,7,8-HpCDD, whose contribution to the total PCDDs in reservoir I accounted for 12.4, 41.1 and 21.9%, respectively, whereas in other ponds it ranged from 0 to 9.79% (Table 4).

Table 3 | The results of statistical analysis using the Wilcoxon matched pairs test

Reservoirs compared	PCDDs/PCDFs and dl-PCBs	PCDDs	PCDFs	dl-PCBs
I and II	–	–	–	+
I and III	+	–	–	+
I and IV	–	–	–	–
I and V	+	+	–	–
II and III	+	–	+	+
II and IV	+	–	–	+
II and V	+	–	–	+
III and IV	+	–	+	+
III and V	+	–	–	+
IV and V	+	+	–	–

–, statistically not significant; +, statistically significant with p-value ≤ 0.05.

Table 4 | Spatial variation of PCDD, PCDF and dl-PCB concentrations along the cascade of urban reservoirs

	I (ng/kg d.w.)		II (ng/kg d.w.)		III (ng/kg d.w.)		IV (ng/kg d.w.)		V (ng/kg d.w.)	
Reservoir	**A**	**SD**	**A**	**SD**	**A**	**SD**	**A**	**SD**	**A**	**SD**
2378-TCDD	n.d.	n.d.	n.d.	n.d.	0.0800	0.150	n.d.	n.d.	n.d.	n.d.
12378-PeCDD	0.480	0.960	0.840	0.940	0.0700	0.130	0.210	0.430	0.0200	0.0400
123478-HxCDD	n.d.	n.d.	0.420	0.770	n.d.	n.d.	n.d.	n.d.	1.00	2.01
123678-HxCDD	1.13	2.14	n.d.	n.d.	0.780	0.570	0.310	0.620	6.86	13.7
123789-HxCDD	3.74	3.94	0.420	0.810	0.780	1.57	n.d.	n.d.	4.90	9.33
1234678-HpCDD	1.99	3.91	6.83	12.0	6.93	4.07	29.7	29.03	736	1,050
OCDD	1.76	3.51	49.7	95.0	118	66.6	273	245	9,680	13,500
Total PCDD	9.10	1.78	58.2	110	127	71.9	303	273	10,400	14,500
2378-TCDF	1.85	2.82	0.190	0.250	0.410	0.820	0.830	1.66	n.d.	n.d.
12378-PeCDF	1.78	2.51	0.460	0.830	0.960	1.170	0.840	1.37	n.d.	n.d.
23478-PeCDF	1.42	2.84	1.94	2.30	1.14	1.56	1.88	2.92	0.870	1.71
123478-HxCDF	1.85	3.68	1.75	2.03	1.15	0.820	1.35	2.30	7.19	14.2
123678-HxCDF	n.d.	n.d.	2.10	2.40	0.850	0.620	0.890	1.23	n.d.	n.d.
234678-HxCDF	3.81	5.66	6.60	4.87	1.61	1.17	3.02	5.78	50.03	56.7
123789-HxCDF	0.150	0.290	1.32	1.47	0.490	0.650	0.830	1.45	n.d.	n.d.
1234678-HpCDF	1.46	2.92	6.17	5.47	4.20	5.43	11.3	9.59	58.9	79.2
1234789-HpCDF	0.140	0.270	n.d.	n.d.	0.370	0.750	1.52	1.76	0.170	0.350
OCDF	0.840	1.08	4.20	6.37	3.76	3.08	46.5	50.4	47.3	93.9
Total PCDF	13.3	12.4	24.7	18.3	14.9	14.2	69.0	72.2	164	157
PCB-77	6.87	9.18	11.9	17.6	3.51	0.95	16.5	22.0	25.8	40.92
PCB-81	1.13	1.97	2.77	4.62	1.19	1.60	33.1	51.8	47.5	93.41
PCB-126	3.89	6.73	0.680	1.35	0.270	0.310	2.91	3.78	7.07	10.0
PCB-169	0.0200	0.0400	0.0300	0.0600	0.140	0.280	n.d.	n.d.	n.d.	n.d.
PCB-105	45.3	78.3	4.60	5.18	4.54	1.73	23.4	23.6	42.2	82.1
PCB-114	6.70	13.0	4.31	4.83	1.63	1.86	50.5	70.5	1.24	2.48
PCB-118	126.1	139.0	92.6	77.0	24.3	23.1	745	1390	291	332
PCB-123	20.4	25.2	13.4	12.9	2.87	3.44	29.9	58.7	39.9	69.2
PCB-156	2.96	3.00	1.12	2.23	0.560	0.690	1.37	2.73	5.15	10.3
PCB-157	4.64	8.48	0.500	0.990	0.460	0.560	0.690	1.36	3.39	4.86
PCB-167	22.8	27.4	15.3	27.4	0.910	1.09	100	200	295	584
PCB-189	2.68	3.25	3.50	3.11	0.490	0.350	0.0900	0.18	n.d.	n.d.
Total dl-PCB	243	306	151	127	40.9	28.1	1,000	1,820	758	1,220
Total PCDD, PCDF and dl-PCB	266	320	234	253	182	114	1,380	2,170	11,400	15,900
WHO-TEQ	2.64	2.92	2.94	2.28	1.31	1.28	2.38	2.31	18.9	15.8

A, average; SD, standard deviation; n.d., not detected.

The concentration of PCDFs ranged from 13.3 ng/kg d.w. in reservoir I, 24.7 ng/kg d.w. in II, 14.9 ng/kg d.w. in III, 69.0 ng/kg d.w. in IV to 164 ng/kg d.w. in the last (V) reservoir (Table 3).

The contribution of PCDF congeners varied along the cascade of reservoirs, starting from a high contribution of lower chlorinated congeners in the first reservoir (mainly tetrachlorodibenzofuran (TCDF) and pentachlorodibenzofuran (PeCDF) accounting respectively for 13.9 and 13.4% of the total amount of PCDFs) in favour of the highly chlorinated chemicals in the last ponds (mainly 1,2,3,4,6,7-heptachlorodibenzofuran (1,2,3,4,6,7-HpCDD) and octachlorodibenzofuran (OCDF)) contributed to 67.4 and 35.8% in ponds IV and V. The exception to this rule was 1,2,3,4,6,7,8-heptachlorodibenzofuran (1,2,3,4,6,7,8-HpCDF), which showed a 11.7% decrease between reservoirs III and IV. Moreover, 38.6% reduction of the OCDF congener contribution was observed between the last two ponds (Table 4).

Spatial distribution of dl-PCBs along the cascade reservoirs of the Sokołówka River

The dl-PCB concentrations decrease from reservoirs I–III, from 243 in I to 40.9 ng/kg d.w. in III (Table 1). Whereas, the next reservoir, no. IV, was characterized by a large increase in the total dl-PCBs up to 1,000 ng/kg d.w. The last reservoir (V) also demonstrated the elevated concentration of those compounds – 758 ng/kg d.w. (Table 4).

Dl-PCBs were classified into two categories as follows: the first category (non-ortho) consisted of four dl-PCB congeners (PCB-77, PCB-81, PCB-126 and PCB-169), whereas the second one (mono-ortho) included PCB-105, PCB-114, PCB-118, PCB-123, PCB-157, PCB-167 and PCB-189.

The most abundant congeners were mono-ortho PCB, which contributed to 95.1 and 87.5% of the total dl-PCB in reservoirs II and III, respectively. The high contribution of these congeners was generated by the accelerated concentration of PCB-118. The average contribution of this congener varied from 38.3 to 73.9% of the total dl-PCBs concentration (Table 4).

The concentrations of non-ortho PCB were within the range 11.9, 15.4, 5.11, 52.5 and 80.4 ng/kg d.w., contributing to 4.89, 10.2, 12.5, 5.23 and 10.6% of the total dl-PCB in reservoirs I–V, respectively (Table 4).

Spatial distribution of WHO-TEQ concentration along the cascade reservoirs of the Sokołówka River

The highest World Health Organization – Toxic Equivalent (WHO-TEQ) concentration, expressing the net toxicity of a complex mixture of all analysed PCDD/PCDF and dl-PCB congeners, amounted to 18.9 ng TEQ/kg d.w. and was recorded in the last reservoir (V). Other sites were characterized by having about six times lower toxicity, and varied between 1.31 and 2.94 ng TEQ/kg d.w. The lowest WHO-TEQ concentration was recorded in the newly constructed reservoir III (1.31 ng TEQ/kg d.w.; Table 4).

Statistical analysis

The comparison of PCDD congeners concentrations using the Friedman ANOVA test showed no statistically relevant differences among the reservoirs studied; the same result was observed for PCDF congeners. Opposite results were obtained for dl-PCB and WHO-TEQ concentrations with differences confirmed.

Statistical analysis using the Wilcoxon matched pairs test showed that, in case of all congeners, concentrations of almost all testing pairs of reservoirs were statistically different, with the exception of the two pairs: I and II and I and IV (Table 3). In the case of PCDD congeners the statistically relevant differences were obtained for the following pairs: I and V, and IV and V (Table 3). Also in the case of PCDF congeners only two pairs showed statistically significant differences (II and III; III and IV). The dl-PCB congeners concentrations were different in case of seven pairs of reservoirs (Table 3). Among all the tested reservoir pairs the most similar were: I and IV, and I and II, as for the first pair there were no statistically relevant differences and for the second pair significant differences were noted only for dl-PCB. The two pairs of reservoirs II and III, and III and IV differed the most as relevant differences were obtained in three out of the four cases.

DISCUSSION

The concentrations of total PCDDs, PCDFs and dl-PCBs and WHO-TEQ obtained in the reservoirs studied (Table 5) were in the range of the concentrations recorded in other water ecosystems worldwide (Table 6). Differences between the presented levels may result from the variety of PCDD, PCDF and dl-PCB sources, including atmospheric deposition, industrial and domestic effluents, stormwater, spills and others.

In our study, the highest accumulation of PCDDs, PCDFs and dl-PCBs was recorded in the reservoirs situated at the end of the river system (reservoirs IV and V). Moreover, all samples contained very high concentrations of OCDD and OCDF, and relatively high concentrations of HpCDDs and HpCDFs (Tables 4 and 5). This situation

Table 5 | Spatial variation in the pattern of PCDDs (the contribution in the total of 2,3,7,8-substituted PCDDs), PCDFs (the contribution in the total of 2,3,7,8-substituted PCDFs) and dl-PCB congeners (the contribution in the total of dl-PCBs) along the cascade of urban reservoirs

	I (%)		II (%)		III (%)		IV (%)		V (%)	
Reservoir	A	SD	A	SD	A	SD	A	SD	A	SD
2378-TCDD	0	0	0	0	0.0600	0	0	0.070	0	0
12378-PeCDD	5.28	25.0	1.44	8.26	0.0500	22.1	0.0700	0.180	0	0.570
123478-HxCDD	0	2.49	0.730	0	0	0.790	0	0	0.0100	0
123678-HxCDD	12.4	2.43	0	18.3	0.61	0	0.100	0.460	0.0700	0.820
123789-HxCDD	41.1	2.45	0.730	44.7	0.62	49.9	0	0.710	0.0500	0
1234678-HpCDD	21.9	3.74	11.7	43.5	5.47	25.2	9.79	1.49	7.05	3.99
OCDD	19.3	53.6	85.4	47.9	93.2	51.7	90.0	1.61	92.8	2.65
2378-TCDF	13.9	5.88	0.78	47.7	2.74	2.08	1.20	2.33	0	1.08
12378-PeCDF	13.4	1.76	1.85	7.30	6.44	2.53	1.22	6.63	0	2.31
23478-PeCDF	10.7	17.5	7.84	9.32	7.64	6.63	2.72	5.61	0.530	6.14
123478-HxCDF	13.9	5.84	7.06	11.9	7.70	4.89	1.96	6.02	4.37	4.02
123678-HxCDF	0	5.88	8.50	0	5.66	6.58	1.29	4.19	0	6.23
234678-HxCDF	28.7	45.1	26.7	19.2	10.8	35.9	4.38	3.51	30.4	3.85
123789-HxCDF	1.09	5.88	5.33	2.07	3.27	8.13	1.20	5.06	0	1.98
1234678-HpCDF	11.0	47.7	25.0	20.8	28.1	30.6	16.4	14.9	35.8	17.5
1234789-HpCDF	1.04	0.590	0	1.96	2.50	0	2.20	5.77	0.110	1.47
OCDF	6.35	24.9	17.0	40.9	25.2	12.4	67.4	16.1	28.76	24.7
PCB-77	2.82	2.79	7.93	6.86	8.60	9.29	1.64	7.42	3.40	5.49
PCB-81	0.470	0.390	1.84	1.36	2.91	1.94	3.28	2.59	6.26	3.43
PCB-126	1.60	0.960	0.450	0.460	0.660	0.640	0.290	0.620	0.930	1.07
PCB-169	0.0100	0.0100	0.0200	0.110	0.340	0.670	0	0	0	0
PCB-105	18.6	8.55	3.05	7.79	11.1	10.2	2.32	10.32	5.56	3.01
PCB-114	2.75	1.73	2.86	1.69	3.99	4.06	5.01	8.65	0.16	1.66
PCB-118	51.8	8.13	61.4	13.48	59.5	15.0	73.9	15.5	38.3	31.9
PCB-123	8.38	3.57	8.87	2.85	7.03	3.17	2.96	3.08	5.26	5.32
PCB-156	1.21	5.32	0.740	6.50	1.38	2.77	0.140	0.0700	0.680	0.400
PCB-157	1.90	1.08	0.330	1.88	1.13	1.31	0.0700	0.0700	0.450	1.04
PCB-167	9.36	4.64	10.2	8.20	2.22	3.65	9.94	4.96	38.9	21.8
PCB-189	1.10	1.81	2.32	0.61	1.20	1.06	0.0100	0	0	0

A, average; SD, standard deviation.

Table 6 | Levels of PCDDs, PCDFs, dl-PCBs and WHO-TEQ concentrations measured in reservoirs, lakes and river sediments located in different parts of the world, with urban/industrial catchment characteristics

Country	Site	Compound	Concentration	References
Germany	Small dam reservoirs	Σ PCDDs and PCDFs	19,000–20,000 ng/kg d.w.	Koh *et al.* (2004)
Holland	Ren River	Σ dl-PCBs	200,000 ng/kg d.w.	Rose & McKay (1996)
Great Britain; Great Britain	Shallow lake; small dam reservoir	Σ PCDDs and PCDFs; WHO-TEQ concentration; Σ PCDDs and PCDFs; WHO-TEQ concentration	590 ng/kg d.w; 6 ng TEQ/kg d.w.; 2,000 ng/kg d.w.; 92 ng TEQ/kg d.w.	Rose & McKay (1996); Kannan *et al.* (2001)
USA	Detroit River	Σ PCDDs and PCDFs; WHO-TEQ concentration	69 ng/kg d.w.; 3.99 ng TEQ/kg d.w.	Kannan *et al.* (2001)
USA	Lower Rouge River	Σ PCDDs and PCDFs; WHO-TEQ concentration	1,415 ng/kg d.w; 62 ng TEQ/kg d.w.	Kannan *et al.* (2001)
USA	Tittabawssee River	Σ PCDDs; Σ PCDFs	59–120 ng/kg d.w; 2,400–53,600 ng/kg d.w.	Hilscherova *et al.* (2003)
USA	Lake Ontario	Σ PCDDs and PCDFs	728.6–2,712 ng/kg d.w.	Marvin *et al.* (2002)
USA	Lake Erie	Σ PCDDs and PCDFs	778.8 ng/kg d.w.	Marvin *et al.* (2002)
USA	Housatonic River	Σ PCDDs, PCDFs and dl-PCBs	160–5,400 ng/kg d.w. (max. 82,000 ng/kg d.w.)	Eitzner (1993)
Korea	Masan Bay	Σ PCDDs and PCDFs	102–6,493 ng/kg d.w	Eitzner (1993)
Northern Taiwan	Small dam reservoir	WHO-TEQ concentration	0.95–14.4 ng TEQ/kg d.w.	Chi *et al.* (2007)
South Africa	Rivers	Σ PCDDs; Σ PCDFs; Σ dl-PCBs; WHO-TEQ concentration	2.8–170 ng/kg d.w; 0.86–13 ng/kg d.w; 130–1,300 ng/kg d.w; 0.2–1.4 ng TEQ/kg d.w.	Nieuwoudt *et al.* (2009)

can be linked to the input of PCDDs, PCDFs and dl-PCBs from the range of sources mentioned above, including the input of wastewater and stormwater as well as hydraulic transportation along the reservoirs that can affect their final spatial distribution in the cascade reservoirs studied.

Input of wastewater

The results showed the strong predominance of PCDDs in the total PCDD/PCDF concentration (accounted for up to 98.4%), generated mainly by the increased concentration of the OCDD congener. These findings demonstrate the serious effects caused by illegal disposal of untreated wastewater into the Sokołówka River from human settlements, which was confirmed in the field observations (Urbaniak *et al.* 2010). The similarity between PCDD/PCDF profiles in wastewater influent (Oleszek-Kudlak *et al.* 2005) and studied reservoir sediments (Table 5) suggests the influence of this source on the noted concentrations. According to Oleszek-Kudlak *et al.* (2005), the PCDD/PCDF profiles in wastewater influent to the Municipal Wastewater Treatment Plant in Zabrze, Poland, were characterized by the elevated contribution of 1,2,3,4,6,7,8-HpCDD (28.5%) and OCDD (69.5%) to the total of seven toxic PCDD congeners and increased contribution of 1,2,3,3,6,7,8-HpCDF (23.5%) and OCDF (55.9%) to the total of toxic PCDF congeners. In our study, the contribution of those congeners varied between 5.47 and 21.9% for 1,2,3,4,6,7,8-HpCDD, between 19.3 and 93.2% for OCDD, between 11.0 and 35.8% for 1,2,3,3,6,7,8-HpCDF and between 6.35 and 67.4% for OCDF (Table 5). Moreover, the results of McLachlan *et al.* (1996) demonstrated that all of the higher chlorinated congeners and a large part of the lower chlorinated ones in sludge from Stuttgart-Busnau originated from household wastewater of which the main source was laundry (Horstmann *et al.* 1993), as washing of contaminated clothing results in the increased amount of PCDD/PCDF in washing wastewater. Additionally, Rappe *et al.* (1990) reported that some amounts of PCDD/PCDF were also found in detergents. It was also demonstrated that some PCDDs/PCDFs can be transported from clothing to the skin surface and then removed during showering, providing the secondary source of these contaminants in the household wastewater (McLachlan *et al.* 1996). This finding agrees well with results presented by Huntley *et al.* (1997) who analysed the concentrations of PCDDs, PCDFs and coplanar PCBs in the surface sediments adjacent to four combined sewer overflows (CSOs) that discharged to the Lower Passaic River. According to Huntley *et al.* (1997), the obtained results with the elevated contribution of OCDD and 1,2,3,4,6,7,8-HpCDD in the total of seven PCDDs (ranging from 34.7 to 85.7% and from 7.31 to 36.5%, respectively) indicated that CSOs are significant mechanisms for boosting the sediment with PCDDs/PCDFs. The high conductivity of the riverine and the reservoir water demonstrated in our earlier study by Urbaniak *et al.* (2012), as well as the results of weekly monitoring of the Sokołówka River conducted since 2006, where conductivity intermittently exceeds 4,500 μS/cm, suggest that there is illegal input of domestic sewage.

The highest total and WHO-TEQ concentrations were recorded in the reservoirs with strong anthropogenic influence. This situation applies mainly to reservoirs IV and V located in the basin with the highest percentage of urbanized and industrialized areas (47% in the middle and 60% in the lower section of the Sokołówka River catchment). Furthermore, very high concentrations in the downstream reservoir (V) of the longest time of sediment accumulation (since 1980), which also contains water of the small tributary (Brzoza River) used to drain a 30,000 inhabitants residential estate of the city, and served as part of the municipal stormwater and sewage system, may imply a contribution of untreated sewage from the surrounding housing estates and industrial areas (Urbaniak *et al.* 2008, 2009, 2010). The highest time of sediment storage in the V reservoir (circa 30 years; Table 1), in which a variety of micropollutants from the catchment has been accumulated, may also indicate the impact of textile industry that operated intensively in Łódź until the end of the 1990s. The use of pigments and dyes in the textile processing may have discharged some amounts of PCDDs/PCDFs to the sewer system and subsequently to the rivers, due to the fact that the sewer system of Łódź collects domestic and industrial wastewater and stormwater and that the rivers are frequently used as wastewater receivers. Allock & Jones (1997) and Bostian *et al.* (2004) reported that pigments such as chloranil or dyes produced on the basis of chloranil may contain from 300 to 2,900 and from 2 to 200 μg TEQ/kg of dioxins, respectively, with the predominance of OCDD

congener ranged from 77 to 100% of the total of the seven PCDD studies, a finding that was similar to that of our study in which OCDD predominance (up to 93%) was also observed (Table 4).

The disposal of domestic sewage and industrial effluents from the neighbouring factory into reservoir IV (confirmed during field visits) and the extended water retention time of this reservoir related to its location on the right river bank, caused the accelerated growth of phytoplankton (Urbaniak *et al.* 2010). The exchange of pollutants between the deposited sediments and the water column due to foraging of benthivorous fish such as crucian (*Carassius carassius*) and Prussian carps (*Carassius gibelio*), tench (*Tinca tinca*) and roach (*Rutilus rutilus*) can lead to an increased concentration of pollutants in the water column. In reservoir IV not only was twice as much fish biomass noted as catch per unit effort (CPUE; Puertas & Bodmer 2004) but also the proportion of larger specimens, which are more effective in sediment resuspension, was clearly higher than that found in the III and IV impoundments (Table 1). This finding means that the highest rate of sediment and water mixing, boosting the water column in sediment-associated pollutants, should be observed in IV reservoir and could generate the higher PCDD/PCDF and dl-PCB concentration in the water. Our earlier study confirmed this effect (Urbaniak *et al.* 2012). Also coupled with the fact that the IV pond is the most shallow (maximum 1 m) among all the studied reservoirs, these events could stimulate this process. This effect can cause the accelerated accumulation of PCDDs/PCDFs and dl-PCBs on the surface of growing phytoplankton. Larrson *et al.* (1998), Berglund *et al.* (2001) and Roessink *et al.* (2008) suggested that PCBs associated with the phytoplankton cells can be removed from the water column due to sedimentation process and deposited in sediments. Our previous research focused on the investigation of transport and deposition drivers for 17 toxic PCDD/PCDF congeners in the Sokołówka cascade reservoirs, and demonstrated a positive strong correlation between WHO-TEQ concentrations in water and chlorophyll *a* content ($R = 0.90$, $p = 0.04$; Urbaniak *et al.* 2012). The same study demonstrated the elevated concentrations of the total toxic PCDD/PCDF congeners in the water samples of reservoir IV during summer when intensive growth of phytoplankton was observed (1,350 pg/L) compared with the winter sampling time with no phytoplankton present (28.4 pg/L; Urbaniak *et al.* 2012). Similar results were obtained for WHO-TEQ concentrations: 73.5 pg TEQ/L in summer and 0.009 pg TEQ/L in winter. Also of note was that the peak of benthivorous fish foraging occurred at this time, leading to increased resuspension of sediments for the summer season. Based on the above findings we concluded that the discharges of domestic sewage and industrial effluents, the extended retention time and small depth as well as the high fish density in the IV reservoir led to the association of discharged and resuspended from sediments PCDD/PCDF and dl-PCB on the surface of phytoplankton cells. The further sedimentation of phytoplankton blooms can be an important mechanism that boosts the levels of PCDDs/PCDFs and dl-PCBs in sediments in this reservoir (Urbaniak *et al.* 2010).

Input of stormwater

The removal of natural vegetation and its replacement with impervious cover, which consequently creates high flow peaks and increased volumes of runoff, are regarded as one of the major problems in the urban territory (Walker *et al.* 1999). The pollution of stormwater runoff affects the quality of the urban aquatic ecosystem. As reported by McLachlan *et al.* (1996), about 32% of the total amount of PCDDs/PCDFs and dl-PCBs entering the municipal wastewater treatment plants in Germany originates from the surface runoff. The results from Stockholm indicated that this amount is actually 20%. In addition, Marsalek *et al.* (2006) reported that the total annual precipitation in large industrialized cities is generally 5–10% higher than that in the surrounding areas, and for individual storms, the increase in precipitation can be as high as 30%. Therefore, varying meteorological changes during the research time, including seasons of drought (April, May, September in 2007 and 2008) and intensive storms (e.g. up to 38 mm rainfall/day in August 2008; http://www.tutiempo.net/en/Climate/LUBLINEK/121055.htm), may have influenced the scouring of PCDDs/PCDFs and dl-PCBs from the stormwater catchment and their transport down the cascade. This situation indicates that stormwater might be the second possible source of PCDDs/PCDFs and dl-PCBs in the urban cascade reservoirs, as the congener profile dominated by OCDD was also found

in urban stormwater (Naf *et al.* 1990), street runoff and stormwater sediments (Horstmann & McLachlan 1995).

The highest average concentrations of analysed PCDDs, PCDFs and dl-PCBs in the sediments of the studied reservoirs were observed in samples collected in the downstream reservoirs – in the IV reservoir (1,380 ng/kg d.w.) and the V reservoir (11,400 ng/kg d.w.), characterized by the largest total catchment area of 7.87 and 14.0 km^2, respectively, from which the higher proportion of atmospherically deposited PCDD/PCDF and dl-PCB can be flushed into the river ecosystem. Within the total Sokołówka catchment the urbanized, residential and industrial areas cover 47% of the middle and 60% of the upper catchment. The urbanized areas cover 3.46 km^2 of the catchment of the reservoir I, 3.69 km^2 of the reservoir II, 3.75 km^2 of the reservoir III, 4.12 km^2 of the reservoir IV and 6.56 km^2 of the catchment of the reservoir V. The above data indicate that reservoir V, which possesses the largest surface of the urbanized catchment (6.56 km^2), generates the highest amount of analysed pollutants (Table 4). Also, the highest WHO-TEQ concentration of 18.9 ng TEQ/kg d.w. is reported for this reservoir. Additionally, it can be emphasized that the two-fold increase in the urbanized catchment area (from 3.64 km^2 for the reservoir I to 6.56 km^2 for the reservoir V) was followed by an approximately seven-fold increase in WHO-TEQ concentration (2.64–18.9 ng TEQ/kg d.w.).

It should be also noted that the Sokołówka River receives the stormwater from the three kinds of stormwater catchments: residential (single-family houses); mixed residential/industrial; and apartmental (blocks of flats; Urbaniak & Zalewski 2012). According to Urbaniak & Zalewski (2012), the largest area of streets and parking (23% of the catchment area) noted for mixed residential/industrial catchment resulted in the highest WHO-TEQ concentration of the stormwater samples (27.5 pg TEQ/L). The residential and apartmental catchments characterized by lower percentage of streets and parking area of respectively 16 and 13% had correspondingly lower TEQ values (25.6 and 23.2 pg TEQ/L, respectively; Urbaniak & Zalewski 2012). This finding implies that rainfall and consequently the high runoff can scour PCDDs/PCDFs deposited in the stormwater catchment due to road transport (Mullis *et al.* 1996) – due to car exhaust gases and the normal wear and tear of vehicle parts that contain PCDDs/PCDFs (Ngabe *et al.* 2000; Polkowska *et al.* 2001; Kim *et al.* 2003; Helmreich *et al.* 2010). In the case of the Sokołówka catchment, its spatial organization indicates that car traffic can influence the contamination of its reservoirs with PCDDs/PCDFs and dl-PCBs. The current organization of the city funnels the major traffic both within the centre and between the centre and the city outskirts through the two main streets located between reservoirs II and III (Zgierska Street) and between reservoirs IV and V (Włókniarzy Avenue). This situation can generate PCDD/PCDF and dl-PCB pollution in road runoff and thus can affect river and reservoir contamination. The largest amounts of PCDD/PCDF emitted from a diesel engine are due to high chlorinated congeners, with the dominant fraction being 1,2,3,4,6,7,8-HpCDD/HpCDF and OCDD/OCDF and a higher proportion of PCDF than PCDD (Hagenmaier *et al.* 1990; Geueke *et al.* 1999; Ryan & Gullet 2000; Kim *et al.* 2003). For the study described here, the contribution of HpCDD and HpCDF to the total of PCDDs and the total of PCDFs varied between 5.47 and 21.9%, and from 11.0 to 35.8%, respectively. Moreover, our previous results from the Sokołówka River demonstrated that the riverine water samples collected near the busy Zgierska Street (located between reservoirs II and III) had elevated the concentration of toxic PCDD/PCDF to 12.53 pg/L, whereas other samples collected far from the roads and streets were characterized by concentrations ranging from 0 to 0.88 pg/L (Urbaniak *et al.* 2012). Despite the input of PCDD/PCDF from the street runoff, reservoir III was characterized as having the lowest value of total PCDDs/PCDFs and dl-PCBs, and WHO-TEQ concentrations, which amounted to 182 ng/kg d.w. and 1.31 ng TEQ/kg d.w., respectively. Analysis using the Wilcoxon matched pairs test revealed statistically significant differences ($p \leq 0.05$) between this pond and reservoir II (pair II and III) and IV (pair III and IV) in three out of four cases: (1) for all 29 PCDD, PCDF and dl-PCB congeners; (2) for PCDF congeners; and (3) for dl-PCB congeners (Table 3). Also for the other pairs, taking into account reservoir III (I and III; III and V), statistically significant differences were noted (Table 3). From the point of view of comparing the level of contamination, the most interesting differences are those noted for reservoirs III and IV, as they are newly constructed ponds of similar age, built in the middle of the Sokołówka River catchment

under comparable conditions. Hence the concentration of analysed compounds in those reservoirs should be similar. The obtained differences, beside the findings described in the previous section for IV reservoir, may be also related to the sediment traps and sand separators constructed at the stormwater outlets, used also as illegal sewage discharges into reservoir III. The inflowing stormwater and road runoff may also be partially purified in the land-water ecotone (Naiman & Decamps 1990; Schiemer *et al.* 1995) constructed in the nearest catchment and in the littoral zone of this reservoir. Such structures may capture and immobilize some of the discharged PCDDs/PCDFs and dl-PCBs, and thus may contribute to the reduction in their concentrations in the reservoir sediments (Macek *et al.* 2000; Susarla *et al.* 2002; Chaudhry *et al.* 2005; Yateem *et al.* 2007).

The housing area, including residential and apartment catchments, covers more than 59% of the upper and 21% of the middle section of the Sokołówka catchment. At the same time, the sediment samples from reservoir I located in the upper part of the Sokołówka catchment, contained a large portion of lower chlorinated tetrachlorodibenzofuran (TCDF) and PeCDD/PeCDF congeners (5.28% for 1,2,3,7,8-PeCDD and 13.9% for 2,3,7,8-TCDF and 13.4% for 1,2,3,7,8-PeCDF) in a typical 'burning profile' (Table 5). According to the US EPA (1994a), the emission of PCDDs/PCDFs due to house heating, its further deposition on the catchment surface and surface runoff may also contribute to the final PCDD/PCDF and dl-PCB concentration. In the case of Poland, Grochowalski & Chrząszcz (1997) reported, based on the study conducted in Krakow, that the domestic stove stack emitted about 100 ng/m^3 PCDD/PCDF. Pfeiffer *et al.* (2000) reported the PCDD/PCDF emissions for experimental oil-fired and gas-fired boilers in the range of 0.002–0.0142 ng I-TEQ/m^3 and the flue gas from wood-fired furnaces ranging from 0.014 to 0.076 ng I-TEQ/m^3. US EPA (1994a) accounted the emission from domestic burning of about 60% of the total PCDD/PCDF emission to the atmosphere in the USA.

CONCLUSIONS

In shallow, turbid, hypertrophic reservoirs located on small, urban rivers, the fate of PCDDs/PCDFs and dl-PCBs is mostly determined by the allochthonous matter (discharged as sewage and scouring from the catchment surface) transported down the cascade during intensive storm events. The presented study on the distribution of PCDDs/PCDFs and dl-PCBs along the cascade of reservoirs showed that there was increasing pollution levels, with the highest pollution values in the last reservoir in the cascade – also the biggest and the oldest reservoir. The middle reservoir III, with the lowest total and WHO-TEQ concentrations, was the exception to this rule. It was equipped with sediment traps and sand separators at the stormwater outlets and ecotone zones around the reservoir catchment to enhance the purification of inflowing storm-waters. The above results implicate the role of hydrological and biological processes towards the reduction of the micropollutant concentrations in the water ecosystems.

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