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Comparative analysis of dioxin and dioxin-like compounds in sediments from different anthropogenic impact reservoirs

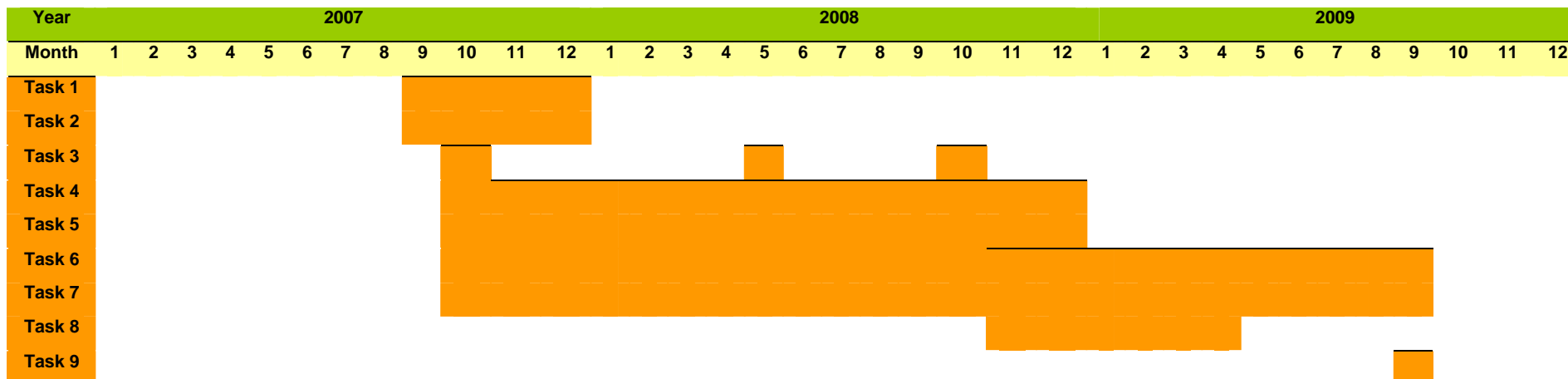
Results of the first year research concerning Sokołowka reservoirs

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1.1. Timetable of PhD

			Deliverables
Pilot activity	Task 1	Study area, maps, data and documentation about Sokołówka River	12.2007
	Task 2	Literature review	
Field research	Task 3	Collection of samples	10.2007; 05.2008; 10.2008
Chemometric analysis	Task 4	Measurement of the PCB, PCDD, and PCDF congener concentrations and profiles.	Reports: 12.2007; 12.2008
	Task 5	Analysis of the trophodynamic of selected PCB, PCDD, and PCDF congeners.	
Evaluation of the Sokołówka river status	Task 6	Assessment of the environmental status of Sokolowka river watershed based on chemometric analyses	Reports: 12.2007; 12.2008;
	Task 7	Evaluation of the river sediment toxicity based on TEQs.	
Dissertation	Task 8	Preparation of PhD thesis manuscript on the basis of obtained results	04.209
	Task 9	Qualify as a PhD	09.2009



1.2. Abstract

The transport pattern of the organochlorine pollutants along the river corridor is an important issue due to their accumulation in reservoirs bottom sediments and bioaccumulation in the food chain.

Polychlorinated dibenzo-para-dioxins (PCDDs) and dibenzo-para-furans (PCDFs) and polychlorinated biphenyls (PCBs) differ in their acnegenic, carcinogenic and teratogenic effects to humans and animals. Thus seventeen most toxic 2,3,7,8-substituted PCDD/DF and twelve PCB congeners were selected to determine sediment contamination of five urban reservoirs cascade situated on Sokołówka river.

Obtained data showed that the highest potential to accumulation of PCBs had the reservoirs situated at the end of river system. This situation can be linked with stormwater and roads runoff input during high river flow.

Adverse results were observed for PCDD/DF where minimum concentration was observed in the initial reservoir, maximum in middle reservoir, and decline at the end of the reservoirs' continuum. This situation can be related to the hydraulic transport and deposition of PCDD/DFs along the cascade system.

A number of large urban and industrial agglomerations located within reservoirs catchment as well as transformation and transfer along the reservoir food chain exert the possible sources of analyzed contaminations. Release of PCBs from technical oils and mixtures can be a significant source of PCDFs in the environment. As an additional source thermal processes, such as burning trash can result in the concentration of PCDDs and PCBs. Also use of pentachlorofenol results in significant release of analyzed contaminants.

1.3. Introduction

As a consequence of the rapid development of modern societies during the 20th century, a significant amount of organic chemicals has been dispersed into the environment. Many of them have been used as pesticides, insecticides, defoliants, industrial chemicals (PCBs) or produced as undesirable industrial by-products (dioxins and furans) [1]. A large proportion of them shows several metabolic and toxic activities including mutagenic, immunotoxic and carcinogenic effects. Among this group of substances, the organochlorine compounds including polychlorinated biphenyls (PCBs) and polychlorinated dioxins and furans (PCDD/DF), have received most attention with regard to their widespread use, persistence and bioaccumulation in the environment.

Polychlorinated biphenyls (PCBs) is an important group of substances manufactured in large amounts for numerous industrial applications between the 1930s and 1970s and dispersed in the environment mainly as a result of industrial utilization [2, 3].

The second group of organochlorine substances is polychlorinated dioxins and furans. They are manufactured as by-products of a range of processes, such as municipal waste incineration, metal smelting, chlorine bleaching in the pulp and paper industry, or vehicular emissions.

Due to their lipophilic character they can bioaccumulate in cells and pass up through the food chain, they are also able to remain in soils, sediments and waterbodies for several years. The environmental persistence of PCBs and PCDD/DF results primarily from the inability of natural aquatic and soil biota to metabolize these compounds at a considerable rate [4].

Currently, many countries impose a strict control on the use and release of PCBs and PCDD/DF. In effect, their input into the environment has decreased significantly; nevertheless, a release of these substances from contaminated reservoirs such as lakes and coastal sediments still exists [5]. Recent surveys have shown that it is possible for large amounts of persistent organochlorines to be released into the atmosphere from contaminated sites and redistributed on a global scale [6]. Many of them decompose slowly and exert toxic effects on plants and animals, in consequence causing a large-scale environmental degradation. Despite many years of measuring levels in numerous environmental compartments, the quantitative information on emissions of PCBs and PCDD/DF remains limited and subject to significant uncertainties. The lack of complete and accurate emission data for PCBs and PCDD/DF is considered by many scientists a key knowledge gap in understanding of the overall environmental distribution and loss of these chemicals.

1.4. Material and methods

1.5. Study areas and Sampling

Sokołowka river (drainage area 45,4 km²) represents a highly urbanized and industrialized catchment contaminated with heavy metals and organic compounds due to the sewage and stormwater disposal. The river length from the spring to the estuary is 13.3 km, 13.0 km of which

remains on the territory of the City of Lodz. The main channel was channelised by concrete slabs, to straighten the course and deepen the bed for purpose of detention of storm waters [7, 8]. Sediment samples were collected by sediment core sampler from 5 reservoirs situated on Sokołowska River, twice: during spring and autumn period of 2007 (Fig.1). Samples were placed in amber containers and transported to the laboratory at the temperature of 4°C. They were subsequently freeze dried at -40°C, and homogenized. They were analyzed to determine concentrations of 12 PCB and 17 PCDD/DF congeners.

1.6. PCBs and PCDD/DF analysis

A 2 g of samples were spiked with isotopically labelled standard of known quantity to monitor the sampling efficiency and extracted by ASE (Automatic System Extraction) 200 Dionex. All ¹³C-labelled internal standards were delivered by Cambridge Isotopes Laboratories (USA). Extraction of PCB and PCDD/DF was conducted at 150 atm (11 Mpa) and the oven was heated to 175 °C with toluene.

After that, the removal of interferences from extracts was performed using a multilayer column packed with neutral silica and silica modified with 44% (w/w), 22% H₂SO₄, 3% KOH and 10% AgNO₃. Elution was performed with 200 ml of hexane. After this step the sample solvent volume was reduced to approximately 5mL by rotary evaporation and concentrated to 100 µl under a gentle stream of nitrogen. During concentration n-hexane was replaced by n-nonane and external standard was added.

Samples were analyzed by HRGC-HRMS: HP 6890N by Agilent Technologies equipped with a DB5-MS column (60 m x 0.25 mm i.d., film thickness 0.25 µm) in the splitless injection mode, coupled with a high resolution mass spectrometer AutoSpec Ultima using perfluorokerosene (PFK) as a calibration reference. The GC temperature program was 150°C for 2 min, 20°C/min to 200°C (0 min), 1°C/min to 220°C for 16 min and 3°C/min to 320°C for 3 min. The injector temperature was 270°C. The MS was operated with a mass resolution of 10 000, and the electron impact ionization energy was 34,8 eV with an ion source temperature of 250°C. Helium was used as a carrier gas at a flow rate 1.6 ml/min. Samples were quantified with an isotope dilution method.

1.7. Results

1.8. PCBs in sediments collected during spring period

Individual PCB congener concentrations as well as I-TEQ concentrations are given in Tables 1 and 2, and indicate that reservoirs are heterogeneous with values ranging from 0.00 to 2834,50 ng/kg of dry weight.

The maximum concentration of total PCBs was observed in the Teresy Reservoir (3741,3400 ng/kg) (Table 1). The dominant homologues observed at this site were congeners PCB-118 (2834,50 ng/kg dry weight), PCB-167 (399,7100 ng/kg dry weight), PCB-114 (154,8900 ng/kg dry weight) and PCB-123 (118,00 ng/kg dry weight). Nevertheless, the highest I-TEQ concentration was noted in the

Pabianka Reservoir (2,3280 ng/kg dry weight) and was mostly generated by PCB-126 congener concentration (21,9400 ng/kg) which possesses the highest TEF value (0,1) (Table 2). On the other hand, at this site were no PCB-114, PCB-169 and PCB-189 congeners were observed (Table 1).

From all congeners recommended by WHO, homologues PCB-77, 81, 126 and 169, called coplanar, possess more toxic properties than non-coplanar congeners (Table 3) (Sapozhnikowa et al., 2005). In this study, congener PCB-77 had the highest concentration at Pabianka Reservoir site (85,99 ng/kg) whereas at other sites this value was about 40 to 1,7 times lower. Congeners PCB-81 and PCB-126 were also the highest in samples collected from Pabianka Reservoir (187,65 ng/kg and 21,94 ng/kg dry weight, respectively) whereas congener PCB-169 was observed in none of the analyzed samples.

For all samples, PCB-118 congener had the highest frequency of occurrence which ranged from 75, 76 % for the Teresy Reservoir site, 72,07 % for the Zgierska Reservoir, 57,59 % for the Lower Pond to 30,36 % for the Pabianka Reservoir. In consequence, pentachlorobiphenyls were the predominant homologues in sediment form all of analyzed samples.

1.9. PCBs in sediments collected during autumn period

Individual PCB congener concentrations as well as I-TEQ concentrations from the sediment samples taken from the reservoirs are given in Tables 3 and 4. The values range from 0,00 to 92,89 ng/kg of dry weight.

The maximum concentration of total PCBs was observed in the Pabianka Reservoir (149,58 ng/kg) (Table 3) with dominant congeners: PCB-118 (92,89 ng/kg dry weight), PCB-77 (17,41 ng/kg dry weight), PCB-123 (16,64 ng/kg dry weight) and PCB-167 (8,49 ng/kg dry weight). In this reservoir the highest I-TEQ concentration was also observed (0,0064 ng/kg dry weight), mostly generated by PCB-118 (0,0028 ngTEQ/kg dry weight) and PCB-77 (0,0017 ngTEQ/kg dry weight) (Table 4).

As opposed to the results obtained during the spring period the most toxic congener PCB-126 was not observed, thus I-TEQ concentration of total PCBs in autumn period was about 364 times lower than in the spring period (Fig 1 and 2).

1.10. PCDD/DF in sediments collected during spring period

The concentration levels of selected PCDD/DF (tetra to octa) in sediment samples are depicted in Table 5. The toxicity level of selected congeners (I-TEQ) is shown in Table 6.

The total concentration of PCDD/DF ranged from 0,5119 in the Teresy Reservoir to 12,9993 ng/kg of dry weight in the Lower Pond. The toxicity measures as I-TEQ ranged from 0,0483 in Upper Pond to 0,2496 ngTEQ/kg of dry weight in the Zgierska Reservoir.

It is indicated that the PCDD/PCDF ratio shows a predominance of PCDD in all sediment samples and represents 73,22 % in Upper Pond, 55,32 % in Lower Pond, 78,72% in Zgierska Reservoir, 62,51% in Teresy Reservoir and 100% in Pabianka Reservoir. In three reservoirs: Upper

Pond, Lower Pond and Zgierska Reservoir the dominant homologue was OCDD; nevertheless, this congener was not observed in two other reservoirs.

1.11. PCDD/DF in sediments collected during autumn period

The concentration levels of selected PCDD/DF (tetra to octa) in sediment samples are depicted in Table 7. The toxicity of selected congeners (I-TEQ) is shown in Table 8.

The total concentration of PCDD/DF ranged from 22,9787 in the Upper Pond to 254,5629 ng/kg of dry weight in the Zgierska Reservoir. The toxicity measures as I-TEQ ranged from 0,5243 in the Pabianka Reservoir to 4,9351 ngTEQ/kg of dry weight in the Lower Pond due to a high amount of 12378-PeCDD congener. Also, a high I-TEQ concentration of sediment samples collected from the Zgierska Reservoir was created by homologue 23478-PeCDF of high TEF value.

The PCDD/PCDF ratio showed a predominance of PCDD in sediment samples collected from the Zgierska, Teresy and Pabianka Reservoirs (86,16%; 87,83% and 91,41%; respectively). Nevertheless, in the Upper and Lower Ponds the predominance of PCDF was observed (61,01 % and 88,75%; respectively). In opposition to data obtained in spring, homologue OCDD was observed in high concentration in the Zgierska, Teresy and Pabianka Reservoirs; whereas small concentration was noted in the Upper and Lower ponds (Fig 3 and 4).

1.12. Discussion

The results of various studies regarding PCBs and dioxins in urban catchments must be carefully analyzed in view of different methods of analysis. Analysis of these substances at nanogram level requires specific standardized methods and a great deal of attention during sampling.

Urban catchments are frequently contaminated by PCBs and dioxins. Major current sources of PCBs to urban rivers include sewage input and combined sanitary overflows, although re-suspension of contaminated bed sediments and direct urban run-off may also be major sources. It frequently happens that wastewater input by stormwater outlets contribute to a higher contamination in the river and in consequence in reservoirs sediments, because some recycled toilet paper and laundry detergents may contain small amounts of PCBs and dioxins. Thus point-sources pollution may cause considerable differences in the results.

Obtained data has shown that the highest potential of PCBs' accumulation is observed in the reservoirs situated at the end of river system, due to a high amount of suspended and organic matter. Many researchers agreed that in the aquatic environment, sediment with a high content of organic matter contains a higher concentration of PCBs [9-15].

Fluctuations in total PCBs concentration as well as I-TEQ concentration have shown a rapid decline from the spring to the autumn period. This situation can be linked with a flow increase due to heavily sand-loaded roads run-off (stormwater). As reported by Polkowska et al. [16], a dynamic increase in the number of motor vehicles creates new problems in the field of environmental protection. Atmospheric burdens and fluxes can greatly influence the total PCBs amount in the

environment and are considered a major input of PCBs to waterbodies. The atmosphere is the conduit through which PCBs as well as other POPs can move from atmospheric emission sources via deposition to terrestrial and aquatic ecosystems [17]. Thus road transportation creates a serious problem due to exhaust a burning gases and usual wear of car tear parts involving PCBs. For this reason the input of PCBs from stormwater can be transported trough the river and deposited at the end of the river system (in the Pabianka Reservoir). PCBs concentration rizes during storm events, when sediments loading increases considerably. Suspended sediment has a lower grain size compared to bed sediments, and therefore, the higher surface area may account for the higher concentration of PCBs. Therefore sediments mobilized during high-flow events can be the dominant source of PCBs.

Another reason of higher PCBs concentration in the Pabianka Reservoir is the input of contaminants from the Brzoza River which transports untreated domestic sewage, as well as outlets situated in the middle part of the Sokolowka River.

PCBs can move from sediment to water by means of desorption, bioturbation, gas convection and erosion, and then may be transported and enriched in the surface micro layer or transported to air. The lower chlorinated PCB's congeners are sorbed less strongly than the higher chlorinated isomers. The low solubility and the strong adsorption of PCBs on sediment particles limit their leaching in soil. Lower chlorinated PCBs tend to leach more than highly chlorinated PCBs.

Contaminated sediments can release some amounts of PCBs into the food web during water mixing [18]. On the other hand, sedimentation can greatly reduce PCBs concentration in water (and increase in sediments) by binding PCBs congeners to particulates. Thus higher sedimentation rates accompanied by sediment burial in eutrophic reservoirs have been suggested as a one of the mechanisms responsible for this negative relationship. Studies in 19 temperate lakes located in the southern part of Sweden\ demonstrated a negative relationship between lake trophy and PCBs concentration. The concentration of PCBs in aquatic organisms decreased with the trophic status of lakes, measured as a total phosphorus concentration or plankton biomass. Due to the greater amounts of settling organic matter the microbial degradation in shallow eutrophic lakes, it is insufficient to mineralize the entire pool of settling organic carbon. In consequence, liphophilic PCBs associated with a settling organic matter may not be released back to water but accumulate in the sediment [19]. On the other hand, the turnover of an organic matter in oligotrophic lakes is more efficient, thus the PCBs associated with settling particles are recycled back to water.

The PCBs deposited in sediments may be taken up directly from the sediment to the food chain by benthic organisms. Aquatic invertebrates assume an important role in the cycling of PCBs within and between ecosystems. Evans et al. [20] described that *Mysid crustaceans* from Lake Michigan have low assimilation efficiency for PCBs and high efficiency for faecal excretion of ingested PCBs which in consequence reach the sediments in PCBs. Additionally, *Mysid*, by vertically migrating in a water column, may transport PCBs into the surface region. Fox et al [21] reported a positive correlation between PCB levels in *Oligochaeta* and sediments. Also the uptake of PCBs from the sediments by larvae of *Chironomidae* was directly related to the concentration of PCBs in the

sediment. *Chironomidae* can also transfer PCBs from the aquatic to the terrestrial environment when larvae metamorphose into adults. The rate of this transport was estimated at 20 ug/m²/year of PCBs [22].

The second group of analyzed substances was polychlorinated dioxins and furans (PCDD/DF). The highest total PCDD/DF concentration was noted in the Zgierska Reservoir, and the highest I-TEQ concentration (toxicity) in the Lower Pond. These results suggest a considerable input of dioxins from untreated domestic sewage.

Different sources of PCDD/DF are characterized by different congener patterns. Sediments of Zgierska, Teresy and Pabianka were high in concentration of PCDD/DF, nevertheless the patterns of relative concentration were different.

Thermal processes, such as trash burning can also result in the production of a range of PCDDs. Also the use of pentachlorofenol results in a significant release of OCDD, which was observed in high amount in the Zgierska, Teresy and Pabianka Reservoirs.

The PCDFs occur as trace contaminants in technical PCBs mixtures, and therefore a release of PCBs can be a significant source of PCDFs in the environment. A relatively high percent of PCDF in the Upper and Lower Ponds (61,01 % and 88,75%; respectively) suggests that technical PCBs mixtures may be the possible sources. Also, the high concentration of TeCDF and PeTCDF in total PCDFs suggests the release from technical PCBs mixtures (e.g. Kanechlor). These results also indicate that high amount of PCBs detected during spring period could be degraded to PCDF, and in consequence a considerable increase of PCDF in the autumn period can be observed.

1.13. Other samples

In 2007 samples of fish and macrophytes from three reservoirs (Teresy, Zgierska and Pabianka) were collected. In Table 9 all fish samples (which are not analyzed yet) are summarized with their names, short samples descriptions and sampling dates. All samples were homogenized and freeze-dried.

1.14. References

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Table 1. Concentration of 12 PCB congeners (recommended by EPA 1668 Method) in sediment samples collected from Sokolowka river reservoirs during spring period 2007.

Congener	Lower Pond	Zgierska Reservoir	Teresy Reservoir	Pabianka Reservoir
PCB-77	2,4300	2,1500	49,2600	85,9900
PCB-81	9,6700	3,4600	110,5100	187,6500
PCB-105	11,3400	2,7900	57,4600	165,3700
PCB-114	9,5100	2,7200	154,8900	0,0000
PCB-118	168,2500	57,4700	2834,5000	787,7000
PCB-123	26,6300	8,0000	118,0000	143,0800
PCB-126	2,7000	0,5400	8,4500	21,9400
PCB-156	0,0000	1,4000	5,4600	20,6000

PCB-157	0,0000	0,7000	2,7300	10,3000
PCB-167	56,3400	0,0000	399,7100	1171,7200
PCB-169	0,0000	0,0000	0,0000	0,0000
PCB-189	5,2900	0,5300	0,3600	0,0000
total [ng/kg]	292,1500	79,7500	3741,3400	2594,3600

Table 2. I-TEQ concentration of 12 PCB congeners (EPA 1668) in sediment samples collected from Sokolowka river reservoirs during spring period 2007.

I-TEQ	TEF	Lower Pond	Zgierska Reservoir	Teresy Reservoir	Pabianka Reservoir
PCB-77	0,0001	0,000243	0,000215	0,004926	0,008599
PCB-81	0,0003	0,002900	0,001037	0,033153	0,056296
PCB-105	0,00003	0,000340	0,000084	0,001724	0,004961
PCB-114	0,00003	0,000285	0,000081	0,004647	0,000000
PCB-118	0,00003	0,005047	0,001724	0,085035	0,023631
PCB-123	0,00003	0,000799	0,000240	0,003540	0,004292
PCB-126	0,1	0,270127	0,053659	0,844745	2,193772
PCB-156	0,00003	0,000000	0,000042	0,000164	0,000618
PCB-157	0,00003	0,000000	0,000021	0,000082	0,000309
PCB-167	0,00003	0,001690	0,000000	0,011991	0,035152
PCB-169	0,03	0,000000	0,000000	0,000000	0,000000
PCB-189	0,00003	0,000159	0,000016	0,000011	0,000000
I-TEQ [ng/kg]		0,282	0,057	0,990	2,328

Table 3. Concentration of 12 PCB congeners (recommended by EPA 1668 Method) in sediment samples collected from Sokolowka river reservoirs during autumn period of 2007.

Congener	Upper Pond	Lower Pond	Zgierska Reservoir	Teresy Reservoir	Pabianka Reservoir
PCB-77	2,7667	3,5135	3,5978	1,9175	17,4115
PCB-81	0,4752	0,4711	0,1386	0,4089	2,5446
PCB-105	2,8348	5,9301	3,6198	2,7887	3,3860
PCB-114	0,2460	0,0000	0,1195	0,0000	4,9621
PCB-118	39,0501	14,5597	5,2942	4,3716	92,8889
PCB-123	7,5452	2,7198	0,8143	0,7089	16,6402
PCB-126	0,0000	0,0000	0,0000	0,0000	0,0000
PCB-156	7,0630	4,4610	0,8463	0,0000	0,0000

PCB-157	0,4905	0,0000	0,0000	0,0161	3,2482
PCB-167	3,8269	2,0624	0,0000	0,2577	8,4995
PCB-169	0,0000	0,0000	0,0000	0,0000	0,0000
PCB-189	0,5182	0,6221	0,0000	0,0000	0,0000
total [ng/kg]	64,8165	34,3399	14,4306	10,4692	149,5809

Table 4. I-TEQ concentration of 12 PCB congeners (EPA 1668) in sediment samples collected from Sokolowka river reservoirs during autumn period of 2007.

Congener	TEF	Upper Pond	Lower Pond	Zgierska Reservoir	Teresy Reservoir	Pabianka Reservoir
PCB-77	0,0001	0,0003	0,0004	0,0004	0,0002	0,0017
PCB-81	0,0003	0,0001	0,0001	0,0000	0,0001	0,0008
PCB-105	0,0000	0,0001	0,0002	0,0001	0,0001	0,0001
PCB-114	0,0000	0,0000	0,0000	0,0000	0,0000	0,0001
PCB-118	0,0000	0,0012	0,0004	0,0002	0,0001	0,0028
PCB-123	0,0000	0,0002	0,0001	0,0000	0,0000	0,0005
PCB-126	0,1000	0,0000	0,0000	0,0000	0,0000	0,0000
PCB-156	0,0000	0,0002	0,0001	0,0000	0,0000	0,0000
PCB-157	0,0000	0,0000	0,0000	0,0000	0,0000	0,0001
PCB-167	0,0000	0,0001	0,0001	0,0000	0,0000	0,0003
PCB-169	0,0300	0,0000	0,0000	0,0000	0,0000	0,0000
PCB-189	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000
I-TEQ		0,0023	0,0014	0,0007	0,0006	0,0064

Table 5. Concentration of 17PCDD/DF congeners (recommended by EPA 1613) in sediment samples collected from Sokolowka river reservoirs during spring period of 2007.

Congener	Upper Pond	Lower Pond	Zgierska Reservoir	Teresy Reservoir	Pabianka Reservoir
2378-TCDD	0,0000	0,0000	0,0000	0,0000	0,0000
12378-PeCDD	0,0000	0,0600	0,0900	0,0000	0,1200
123478-HxCDD	0,0000	0,1200	0,2100	0,1600	0,1700
123678-HxCDD	0,1900	0,0000	0,1500	0,0900	0,0000
123789-HxCDD	0,0000	0,0600	0,2400	0,1500	0,1900
1234678-HpCDD	0,1115	0,3458	0,0000	0,0000	0,0599
OCDD	7,0258	6,6057	6,9879	0,0000	0,0000
2378-TCDF	0,1541	0,2565	0,6485	0,0000	0,0000

12378-PeCDF	0,2454	0,1258	0,0699	0,0000	0,0000
23478-PeCDF	0,0000	0,0988	0,0585	0,0000	0,0000
123478-HxCDF	0,0259	0,0522	0,0000	0,0000	0,0000
123678-HxCDF	0,0000	0,1225	0,0000	0,1119	0,0000
234678-HxCDF	0,0000	0,0000	0,0000	0,0000	0,0000
123789-HxCDF	0,0000	0,0987	0,0000	0,0000	0,0000
1234678-HpCDF	0,0000	4,2592	1,2986	0,0000	0,0000
1234789-HpCDF	0,0000	0,0000	0,0000	0,0000	0,0000
OCDF	2,2548	0,7942	0,0000	0,0000	0,0000
Total [ng/kg]	10,0076	12,9993	9,7532	0,5119	0,5399

Table 6. I-TEQ concentration of 17 PCDD/DF congeners (EPA 1613) in sediment samples collected from Sokolowka river reservoirs during spring period of 2007.

Congener	TEF	Upper Pond	Lower Pond	Zgierska Reservoir	Teresy Reservoir	Pabianka Reservoir
2378-TCDD	1,0000	0,0000	0,0000	0,0000	0,0000	0,0000
12378-PeCDD	1,0000	0,0000	0,0600	0,0900	0,0000	0,1200
123478-HxCDD	0,1000	0,0000	0,0120	0,0210	0,0160	0,0170
123678-HxCDD	0,1000	0,0190	0,0000	0,0150	0,0090	0,0000
123789-HxCDD	0,1000	0,0000	0,0060	0,0240	0,0150	0,0190
1234678-HpCDD	0,0100	0,0011	0,0035	0,0000	0,0000	0,0006
OCDD	0,0003	0,0021	0,0020	0,0021	0,0000	0,0000
2378-TCDF	0,1000	0,0154	0,0257	0,0648	0,0000	0,0000

12378-PeCDF	0,0300	0,0074	0,0038	0,0021	0,0000	0,0000
23478-PeCDF	0,3000	0,0000	0,0296	0,0175	0,0000	0,0000
123478-HxCDF	0,1000	0,0026	0,0052	0,0000	0,0000	0,0000
123678-HxCDF	0,1000	0,0000	0,0123	0,0000	0,0112	0,0000
123789-HxCDF	0,1000	0,0000	0,0000	0,0000	0,0000	0,0000
234678-HxCDF	0,1000	0,0000	0,0099	0,0000	0,0000	0,0000
1234678-HpCDF	0,0100	0,0000	0,0426	0,0130	0,0000	0,0000
1234789-HpCDF	0,0100	0,0000	0,0000	0,0000	0,0000	0,0000
OCDF	0,0003	0,0007	0,0002	0,0000	0,0000	0,0000
I-TEQ [ng/kg]		0,0483	0,2127	0,2496	0,0512	0,1566

Table 7. Concentration of 17PCDD/DF congeners (recommended EPA 1613) in sediment samples collected from Sokolowka river reservoirs during autumn period of 2007.

Congener	Upper Pond	Lower Pond	Zgierska Reservoir	Teresy Reservoir	Pabianka Reservoir
2378-TCDD	0,0000	0,0000	0,3037	0,0000	0,0000
12378-PeCDD	0,0000	1,8100	0,0000	0,8591	0,0837
123478-HxCDD	0,0000	0,0000	0,0000	0,0000	0,0000
123678-HxCDD	0,0000	0,0000	1,3474	1,2397	0,0611
123789-HxCDD	1,1082	0,0000	3,1326	0,0000	0,6983
1234678-HpCDD	7,8486	2,2192	9,6459	2,2554	5,3655
OCDD	0,0019	0,0068	204,8994	71,1892	63,9005
2378-TCDF	1,2400	0,5123	1,6389	0,0000	0,0000

12378-PeCDF	1,4397	1,7060	2,6422	0,5132	0,0000
23478-PeCDF	0,0000	4,7133	3,4158	1,3656	0,0498
123478-HxCDF	0,0000	2,9637	1,9040	0,0000	0,2115
123678-HxCDF	0,0000	4,6885	1,4698	0,0000	0,0000
234678-HxCDF	3,2500	7,4609	3,2000	0,0000	2,2582
123789-HxCDF	0,5811	0,0000	0,5879	0,0000	0,0000
1234678-HpCDF	5,8398	7,4482	12,1854	5,2524	2,2583
1234789-HpCDF	0,5493	0,0000	0,0000	0,0000	0,6987
OCDF	1,1200	2,3486	8,1897	3,3500	1,1091
total [ng/kg]	22,9787	35,8776	254,5629	86,0246	76,6947

Table 8. I-TEQ concentration of 17 PCDD/DF congeners (EPA 1613) in sediment samples collected from Sokolowka river reservoirs during autumn period of 2007.

Congener	TEF	Upper Pond	Lower Pond	Zgierska Reservoir	Teresy Reservoir	Pabianka Reservoir
2378-TCDD	1,0000	0,0000	0,0000	0,3037	0,0000	0,0000
12378-PeCDD	1,0000	0,0000	1,8100	0,0000	0,8591	0,0837
123478-HxCDD	0,1000	0,0000	0,0000	0,0000	0,0000	0,0000
123678-HxCDD	0,1000	0,0000	0,0000	0,1347	0,1240	0,0061
123789-HxCDD	0,1000	0,1108	0,0000	0,3133	0,0000	0,0698
1234678-HpCDD	0,0100	0,0785	0,0222	0,0965	0,0226	0,0537
OCDD	0,0003	0,0000	0,0000	0,0615	0,0214	0,0192
2378-TCDF	0,1000	0,1240	0,0512	0,1639	0,0000	0,0000

12378-PeCDF	0,0300	0,0432	0,0512	0,0793	0,0154	0,0000
23478-PeCDF	0,3000	0,0000	1,4140	1,0247	0,4097	0,0149
123478-HxCDF	0,1000	0,0000	0,2964	0,1904	0,0000	0,0212
123678-HxCDF	0,1000	0,0000	0,4689	0,1470	0,0000	0,0000
234678-HxCDF	0,1000	0,3250	0,7461	0,3200	0,0000	0,2258
123789-HxCDF	0,1000	0,0581	0,0000	0,0588	0,0000	0,0000
1234678-HpCDF	0,0100	0,0584	0,0745	0,1219	0,0525	0,0226
1234789-HpCDF	0,0100	0,0055	0,0000	0,0000	0,0000	0,0070
OCDF	0,0003	0,0003	0,0007	0,0025	0,0010	0,0003
I-TEQ [ng/kg]		0,8038	4,9351	3,0181	1,5056	0,5243

Fig. 1

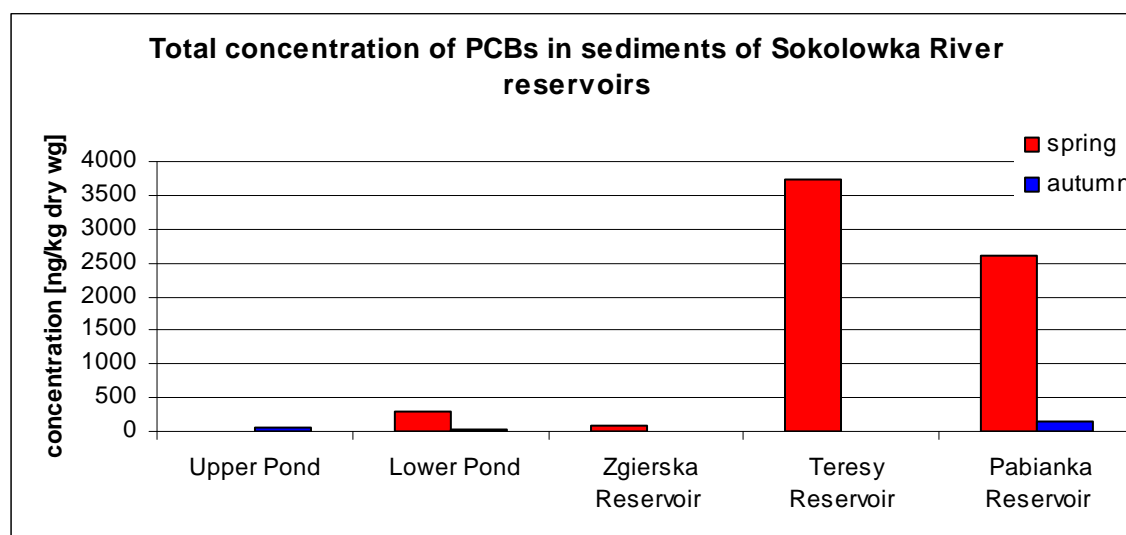


Fig 2.

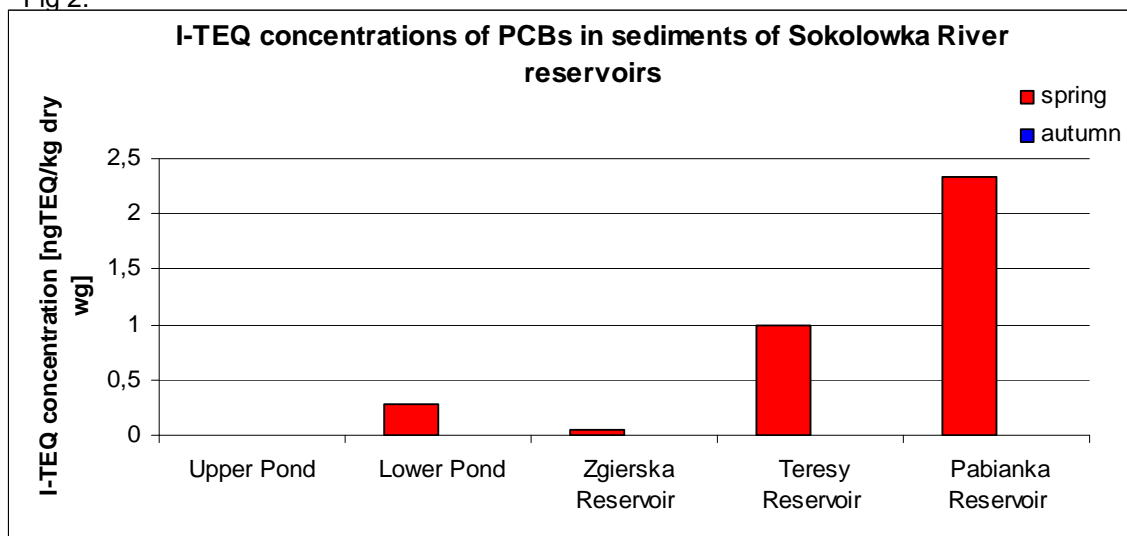


Fig. 3.

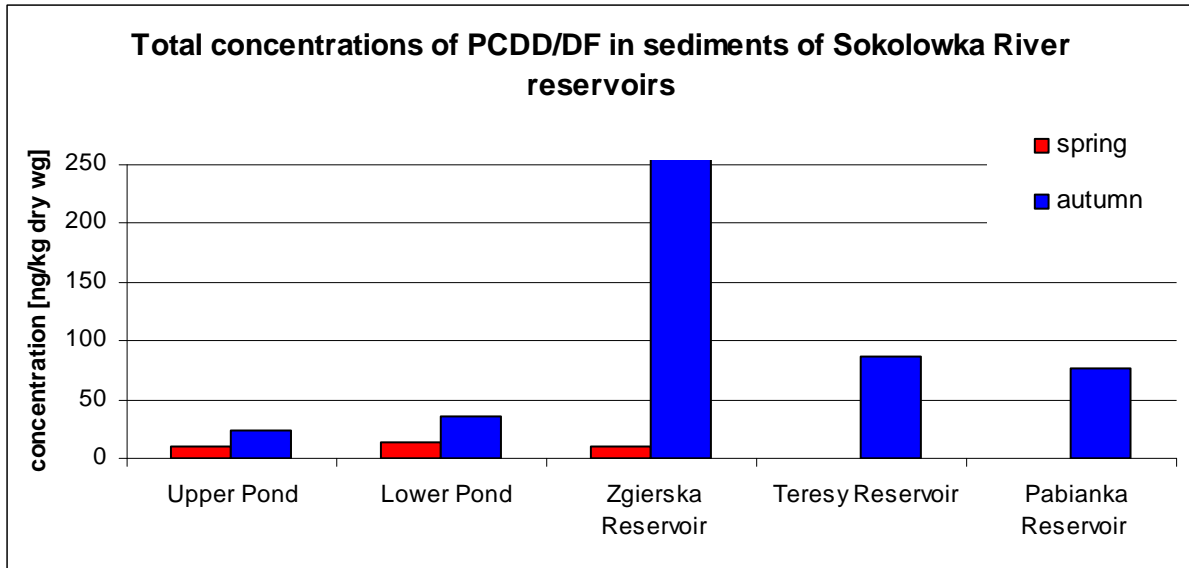


Fig. 4.

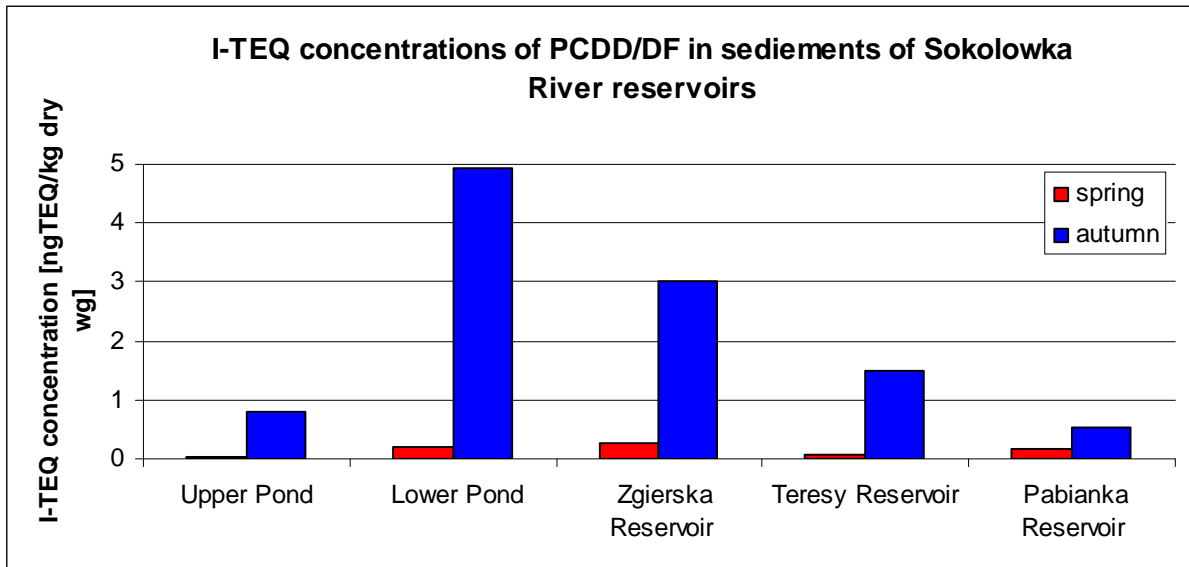


Table 9. Sampling information of fish collected in 2007.

Site/ collection date	Nr of samples	Species	LT	LC	Wight	Sex	Sample code
Zgierska Reservoir 12.11.2007	P1	Rutilus rutilus 1	16,4	13,4	55	F	Sok-Zb.Z.P1.07
		Rutilus rutilus 2	16,2	13,1	48,0	F	
		Rutilus rutilus 3	15,3	12,8	41	n.d	
		Rutilus rutilus 4	15,4	12,5	38	F	
		Rutilus rutilus 5	10,5	8,4	12	nd	
Teresy Reservoir 12.11.2007	P1	Rutilus rutilus 19	14	11,5	31	F	Sok-Zb.T.P1.07
		Rutilus rutilus 20	15,8	12,7	43		
		Rutilus rutilus 21	14,4	11,5	30		
		Rutilus rutilus 25	16,6	13,4	54		
		Rutilus rutilus 31	15,5	12,6	44		
	P2	Rutilus rutilus 22	18,6	15	81	F	Sok-Zb.T.P2.07
		Rutilus rutilus 26	19,2	15,5	82		
		Rutilus rutilus 27	19,1	15,1	92		
	P3	Rutilus rutilus 6	16,1	13	49		Sok-Zb.T.P3.07
		Rutilus rutilus 10	15,4	12,2	39		
		Rutilus rutilus 18	13,6	10,9	26		
		Rutilus rutilus 32	14,4	11,4	31		
	P4	Rutilus rutilus 33	13,6	10,9	26		Sok-Zb.T.P4.07
		Rutilus rutilus 4	14,4	11,7	31		
		Rutilus rutilus 5	14,6	11,8	36	F	
		Rutilus rutilus 7	15,3	12,6	41	F	
		Rutilus rutilus 8	14,4	11,8	34		
	P5	Rutilus rutilus 9	15,4	12,5	41		Sok-Zb.T.P5.07
		Rutilus rutilus 2	15,3	12,2	40		
		Rutilus rutilus 13	14,9	12	36		
		Rutilus rutilus 14	15	11,9	37		
		Rutilus rutilus 16	14,4	11,5	32		
	P6	Rutilus rutilus 17	14,9	12	37		Sok-Zb.T.P6.07
		Rutilus rutilus 23	20,7	16,8	119	F	
		Rutilus rutilus 24	19,3	15,8	87		
	P7	Rutilus rutilus 30	21	17,3	112		Sok-Zb.T.P7.07
		Rutilus rutilus 3	15,9	12,8	45		
		Rutilus rutilus 11	15,9	12,8	41		
		Rutilus rutilus 12	16,4	13,1	53		
	P8	Rutilus rutilus 15	15,3	12,2	43		Sok-Zb.T.P8.07
		Rutilus rutilus 1	24,1	19,5	188		
Pabianka Reservoir 12.11.2007	P1	Rutilus rutilus 1	17,2	13,3	49		Sok-Zb.P.P1.07
		Rutilus rutilus 2	16,6	13,4	50		
		Rutilus rutilus 3	16,5	13,4	50	F	
		Rutilus rutilus 4	16,5	13,2	52		

	P2	Rutilus rutilus 5	16,3	13,1	50		Sok-Zb.P.P2.07
		Rutilus rutilus 6	15,6	12,1	50	F	
		Rutilus rutilus 7	16,2	13,0	48	F	
		Rutilus rutilus 8	15,4	12,3	37		
		Rutilus rutilus 9	16,3	13,2	48	F	
	P3	Rutilus rutilus 10	14,8	11,8	34		Sok-Zb.P.P3.07
		Rutilus rutilus 11	15,0	12,0	36		
		Rutilus rutilus 12	14,9	11,9	34		
		Rutilus rutilus 13	15,2	12,3	42		
		Rutilus rutilus 14	16,4	13,3	47		
	O1	Perca Fluviatilis 1	32,0	28,5	528		Sok-Zb.P.O1.07
	K1	Carassius carassius 1	17,0	14,0	109		Sok-Zb.P.K1.07