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*Original Research*

# PCB and Heavy Metal Contamination in Bottom Sediments from Three Reservoirs of Different Catchment Characteristics

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## Abstract

This study shows a comparative analysis of occurrence and concentration of PCBs and heavy metals in bottom sediment samples collected from three different types of reservoirs: a small and highly urbanized catchment (Sokolowka Reservoir; SR), a large and diversified (agricultural/urban) catchment (Jeziorsko Reservoir; JR) and a small catchment of agricultural impact (Barycz Reservoir; BR).

Total PCB concentration ranged from 121.37 (JR) to 694.31 ng/kg d.w. (SR). Individual congeners were detected with values from 0.07 (PCB-169) to 327.34 ng/kg d.w. (PCB-118). The maximum total WHO-TEQ concentration was observed in reservoirs situated in the highly urbanized catchment (SR; 1.42 ng TEQ/kg d.w.), whereas the minimum concentration was noted in the diversified catchment reservoir (JR; 0.28 ng TEQ/kg d.w). The WHO-TEQ concentration of samples collected from a reservoir of the small and agriculture catchment was in the value of 0.40 ng TEQ/kg d.w.

The highest concentration of heavy metals was observed in SR sample and ranged form 0.41 for Cd to 607.16 mg/kg d.w. for Mn. The JR sample showed several times lower concentrations ranging between 0.04 for Se to 237.26 mg/kg d.w. for Mn, but the lowest values were noted for the BR sample (0.12 for Cd to 192.84 mg/kg d.w. for Mn).

Generally, the concentrations of PCBs and heavy metals were highest in the sample from the urban area (represented by Sokolowka Reservoir) and indicated the effect of urban catchment use on the pollutant distribution patterns.

**Keywords:** PCBs, heavy metals, reservoir bottom sediments, HRGC-HRMS

## Introduction

Polychlorinated biphenyls (PCBs) are a class of chlorinated, aromatic compounds which have 1 to 10 chlorines on a biphenyl structure. Due to their stable properties such as low dielectric constant, chemical inertness, non-flammability, high heat capacity, high electrical resistivity and low acute toxicity, they were found as ideal for industrial applications and thus were produced and used in many countries including: The United States, Russia, Japan, France, and Czechoslovakia. Global PCB use is evaluated as 1.2 to 1.5 million tons, but this value can be underestimated due to the

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true value because of illegal and unknown productions [1-3]. Although the production and use of PCBs was banned almost all over the world more than 25 years ago, they are still detected in many ecosystem compartments, especially in streambed and reservoir sediments [4-8].

Anthropogenic activity has also introduced a significant amount of heavy metals into aquatic environments. The main input of these chemicals is connected with untreated sewage release, washed-out from dumping grounds, settlement of atmospheric dust as well as use of the plant protection agents in agriculture. Great amounts of heavy metals are discharged by rivers and concentrated in bottom reservoir sediments, exerting ecotoxicological effects on water biota.

Sediments are the ultimate sink for PCBs and heavy metals. As in soils, sediment samples are matrices that accumulate liphoplilic substances and can receive inputs from various pathways, such as: atmosphere deposition, land runoff, industrial/wastewater treatment plant discharges and, due to their hydrophobic character, rapidly associate on sediments. It is estimated that 97% of released PCBs in a water column are retained in sediment [9], which serves as a storage compartment for the long-term release of sediment-associated PCBs and poses a threat to aquatic organisms [10-12]. Thus these compartments act as a sink for PCBs and heavy metals, and therefore are important in pollution studies and monitoring of ecosystem stress [13].

This study reports the concentration of PCBs and trace metals in bottom sediments collected from three different types of reservoirs and determines the role of the reservoir catchment characteristics on the sediment contamination.

## Material and Methods

### Study Areas

Three reservoirs (Fig. 1) were examined in this study. The reservoirs are located in the catchments of urban, mixed agriculture/urban and agriculture impact (Table 1).

The urban catchment is represented by Sokolowka Reservoir (SR) (drainage area 45.4 km$^2$) situated in a highly urbanized and industrialized area that is contaminated by heavy metals and organic compounds due to sewage and stormwater disposal. River length from the spring to the estuary is 13.4 km, with 13.0 km on the territory of the City

Table 1. Research area characteristics.

| | SR | JR | BR |
|---|---|---|---|
| **Catchment** | | | |
| Surface area [km$^2$] | 45.40 | 54,500 | 819.50 |
| Slop [‰] | 6 | | 5.07 |
| Meadows and pastures [%] | 0 | 14 | n.a |
| Forests and coppices [%] | >10 | 16.40 | 41.60 |
| Arable land and orchards [%] | 0 | 42 | 63 |
| Litology | Quatery formation:<br>- clay, gravel, sand, slit | Quatery formation:<br>-sand, mud, slit | Quatery formation:<br>-river valley: sands, gravels, chalky clay<br>-plateux: boulder clay, slit |
| **River** | | | |
| Q [m$^3$/s] | 0.17 | 127 | 2.08 |
| Q max [m$^3$/s] | 2.61 | 972 | 237 |
| Q min [m$^3$/s] | 0.02 | 21.2 | 0.14 |
| Lengh [km] | 13.4 | 808.2 | 81.1 |
| Slop [‰] | 0.55 | 0.16 | 1.06 |
| **Reservoir** | | | |
| Max depth [m] | 1.50 | 4.79 | 2.00 |
| Mean depth [m] | 1.00 | 4.10 | 1.78 |
| Capasity [m$^3$] | 10.8 | 202.80 mln | 49.8 |
| Surface area [m$^2$] | 10.8 | 42.3 | 28 |
| Retention time [days] | 6-7 | 8-42 | 1-2 |

n.a. – data not available

of Łódź. The main channel was shaped by concrete slabs, to straighten the course and deepen the bed for the purpose of stormwater detention. The total surface area of the studied reservoir is 10,800 $m^2$ and average depth is 1.0 m [14, 15].

The mixed agriculture/urban catchment is represented by Jeziorsko Reservoir (JR), located in the middle course of the unregulated Warta river (drainage area – 55.100 $km^2$) between the towns Skeczniew and Warta (18º 41' East 51º47' North). At its maximum capacity the reservoir covers 42,300 $m^2$ with a total capacity of 202.8 mln $m^3$ and average depth of 4.10 m. The catchment area has a well-developed settlement net. Densely built-up villages dominate. The catchement area is composed mainly of agricultural land. Arable lands cover approximately 42% of the land's surface, meadows and pastures approximately 14%. There are mainly small farms, often of an area up to 5 ha [16-23].

The agriculture catchment is represented by Barycz Reservoir (BR), situated in the middle course of the Grabia river (drainage area 821.2 $km^2$) – one of the less polluted rivers in central Poland. The reservoir's total capacity is 28,000 $m^2$, with average depth of 1.78 m. The main catchment structures are arable land and orchards, which cover 63% of the area. The reservoir was built for water retention and irrigation of agriculture [24].

## Sampling

Bottom sediment samples were collected by a sediment core sampler once in the spring of 2007 from three stations (upper, middle and lower part) in each reservoir. Samples were filled into amber containers and transported to the laboratory at of 4°C. The samples were homogenized, freeze dried at -40°C and mixed in proportion 1:1:1. They were analyzed to determine concentrations of 12 PCB congeners (PCB-77, PCB-81, PCB-126, PCB-169, PCB-105, PCB-114, PCB-118, PCB-123, PCB-156, PCB-157, PCB-167 and PCB-189), 9 trace metals (Ni, Cu, Mo, Co, Cd, Pb, Mn, As, Se) and organic matter.

## PCB Analysis

PCB extractions, clean-up and analysis were performed according to US EPA 1668 Method [25] and PN/EN 1948: 3 2002 Norm [26]. Briefly, 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 $^{13}$C-labelled internal standards were delivered by Cambridge Isotopes Laboratories (USA). Extraction of PCB was operated at 150 atm (11 Mpa) and the oven was heated to 175ºC with toluene.

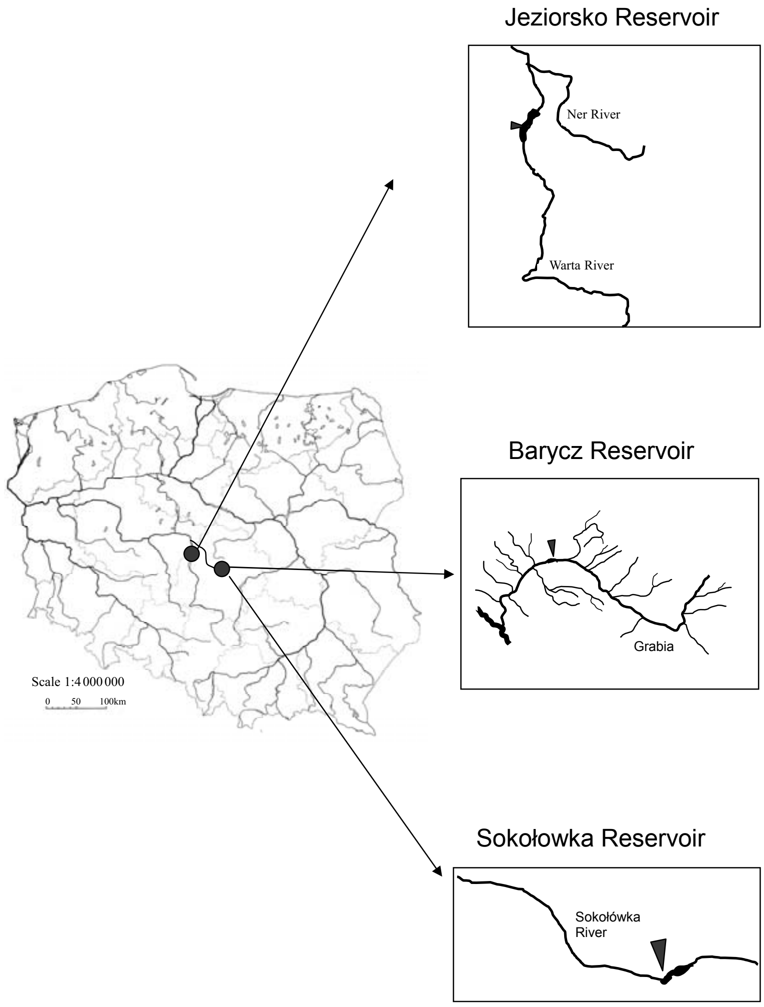


Fig. 1. Location of the sediment samples taking for the analysis.

Table 2. PCB congener's method detection limit [(MDL), pg/kg d.w.], relative standard deviation [(RSD), %] and recoveries [%].

| PCB congener | MDL [pg/kg] | RSD [%] | Recovery [%] |
|---|---|---|---|
| **77** | 0.037 | 3.01 | 105 |
| **81** | 0.106 | 4.49 | 94 |
| **126** | 0.044 | 1.76 | 102 |
| **169** | 0.038 | 2.35 | 102 |
| **105** | 0.143 | 6.96 | 101 |
| **114** | 0.026 | 2.37 | 93 |
| **118** | 0,074 | 3.85 | 102 |
| **123** | 0.111 | 4.20 | 96 |
| **156** | 0.063 | 2.87 | 98 |
| **157** | 0.066 | 2.4 | 93 |
| **167** | 0.042 | 3.64 | 104 |
| **189** | 0.110 | 6.96 | 101 |

Removal of interferences from extracts were conducted with the use of a multilayer column packed with neutral silica and silica modified with 44% (w/w), 22% $H_2SO_4$, 3% KOH and 10% $AgNO_3$. Elution was performed with 200 mL of hexane. After this step the sample solvent volume was reduced to approximately 5 mL by rotary evaporation and concentrated to 100 µL under a gentle stream of nitrogen. During the 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 to a high resolution mass spectrometer AutoSpec Ultima using perfluorokerosene (PFK) as a calibration reference. The GC temperature program was 150ºC for 2 min, 20ºC/min to 200ºC (0 min), 1ºC/min to 220ºC for 16 min and 3ºC/min to 320ºC 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 carrier gas at a flow rate of 1.6 mL/min. Samples were quantified with an isotope dilution method.

## Heavy Metals Analysis

The sediments were decomposed under pressure with a 3:1 mixture of $HCl/HNO_3$ in closed microwaves system MILESTONE 1200 MEGA. The determinations were performed by atomic absorption spectrometry in appropriate modes (flame system) with the use of a SOLAAR M6 (Unicam Atomic Absorption) spectrometer.

Table 3. Heavy metals method detection limit [(MDL), pg/kg d.w.], relative standard deviation [(RSD), %] and recoveries [%].

| Heavy metal | MDL [mg/kg] | RSD [%] | Recovery [%] |
|---|---|---|---|
| **Ni** | 0.08 | 11.44 | 96 |
| **Cu** | 0.04 | 3.54 | 99 |
| **Mo** | 0.1 | 8.89 | 105 |
| **Co** | 0.08 | 4.67 | 102 |
| **Cd** | 0.02 | 12.05 | 97 |
| **Pb** | 0.1 | 3.02 | 103 |
| **Mn** | 0.03 | 2.89 | 98 |
| **As** | 0.001 | 7.51 | 96 |
| **Se** | 0.002 | 8.23 | 101 |

## Organic Matter Analysis

Organic matter was determined by the gravimetrical method. Briefly, 10 g sediment samples were placed overnight in crucibles in a drying oven at 105ºC. Then sediments were weighted and dried in a muffle furnace at 500ºC overnight. The determination of organic matter content was calculated as:

$$M_{om}=(M_{105}-M_{500})/M_0$$

## Quality Assurance/Quality Control

The analytical method used was properly validated on the basis of internal reference materials and the analytical laboratory involved in 2005 successfully passed the accreditation procedure.

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. Analyte recoveries were determined by analyzing samples spiked with PCB standards. The recovery coefficient was taken into account for calculating the final concentrations of analytes. The PCBs and heavy metals method detection limit (MDL), relative standard deviation (RSD), and recoveries were presented in Tables 2 and 3.

## Statistics

Analysis of variance was performed using "Statistica" software for Windows. A Kruskal-Wallis ANOVA by Ranks and Mann-Whitney U tests were used to compare treatment levels.

## Results and Discussion

### PCB Concentrations

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

The results presented the concentration levels of the individual PCB congeners in sediment samples in a ng/kg dry-weight basis. Individual PCB concentrations as well as WHO-TEQ concentrations are given in Table 2 and Table 3, respectively, and revealed that studied reservoirs vary with values ranging from 0.07 to 327.34 ng/kg d.w. All PCB congeners were detected in the sediment samples, although 8 congeners had the highest values in the catchment of high urban impact (SR), 3 in the catchment of agricultural impact (BR) and 1 in mixed agriculture/urban catchment (JR) (Table 4).

The most abundant congeners were the mono-ortho PCB constituting 94.44%, 70.97% and 80.38% of the total amount of PCBs in SR, JR and BR sites, respectively (Fig. 2). From this group congeners PCB-105 and PCB-118 showed their predominance with values of 23.43%, 17.15%, 22.08% and 47.14%, 29.39% and 34.05% of total PCBs for SR, JR and BR, respectively (Fig. 3). From the non-ortho group, PCB-77 represented 2.96% in Sokolowka Reservoir, 1.45% in Jeziorsko Reservoir and 0.89% in Barycz Reservoir of the total amount of PCBs. Nevertheless, the percentage of this congener in comparison to the total amount of non-ortho PCBs, represented 53.26%, 5.00% and 4.55%. PCB-81 constituting 0.59%, 24.49% and 17.59% of the total PCBs and 10.52%, 84.35% and 89.63% of non-ortho PCBs in sediment samples collected from SR, JR, and BR sites. The obtained results also indicated that the most toxic congener, PCB-126, had the highest values in the SR site (36.03% of non-ortho PCBs) and lowest in the BR site (5.30% of non-ortho PCBs) as well as in the JR site (6.31% of non-ortho PCBs). The obtained results showed that non-ortho PCB congener nos. 77, 81, 126 and 169 were present in lower concentration compared to mono-ortho PCBs, and are comparable with results of Hong et al. [27] and Gardinali et al. [28].

In general, the highest PCB concentrations were observed at the SR site 694.30 ng/kg d.w. (Table 6) with predominance of PCB-118 (327.34 ng/kg d.w.), PCB-105 (162.69 ng/kg d.w.), PCB-167 (60.72 ng/kg d.w.) and PCB-123 (60.72 ng/kg d.w.) (Table 4). These results can be linked to the high content of organic matter detected at this site (Table 6) [29–35]. Medium PCBs pollution was observed in the BR sediment collected from the area of lowest human impact. Sediments collected from the reservoir of mixed catchment (JR) possess the lowest concentrations of selected PCBs, except the congener PCB-169 (Table 4). Total PCB concentration at this site was 121.37 ng/kg d.w. Nevertheless, the Kruskal-Wallis ANOVA by Ranks and Mann-Whitney U tests showed no significant differences between reservoir sediments.

Table 4. Concentration of 12 PCB congeners in bottom sediments collected form reservoirs of different catchment characteristics [ng/kg d.w.].

| Congener | SR | JR | BR |
|---|---|---|---|
| **PCB-77** | **20.57** | 1.60 | 3.12 |
| **PCB-81** | 4.06 | 30.02 | **61.56** |
| **PCB-126** | **13.91** | 2.19 | 3.64 |
| **PCB-169** | 0.07 | **1.49** | 0.36 |
| **PCB-105** | **162.69** | 20.91 | 77.28 |
| **PCB-114** | **26.23** | 1.24 | 9.28 |
| **PCB-118** | **327.34** | 35.70 | 119.21 |
| **PCB-123** | **57.18** | 7.69 | 19.97 |
| **PCB-156** | 1.80 | 8.88 | **33.46** |
| **PCB-157** | **17.34** | 4.44 | 8.20 |
| **PCB-167** | **60.72** | 4.94 | 11.48 |
| **PCB-189** | 2.40 | 2.26 | **2.50** |

Table 5. WHO-TEQ concentration of 12 PCB congeners in bottom sediments collected form reservoirs of different catchment characteristics [ngTEQ/kg d.w.].

| WHO-TEQ | *TEF [28]* | SR | JR | BR |
|---|---|---|---|---|
| **PCB-77** | 0.0001 | **0.0021** | 0.0002 | 0.0003 |
| **PCB-81** | 0.0003 | 0.0012 | 0.0090 | **0.0185** |
| **PCB-126** | 0.1 | **1.3915** | 0.2194 | 0.3637 |
| **PCB-169** | 0.03 | 0.0021 | **0.0446** | 0.0108 |
| **PCB-105** | 0.00003 | **0.0049** | 0.0006 | 0.0023 |
| **PCB-114** | 0.00003 | **0.0008** | 0.0000 | 0.0003 |
| **PCB-118** | 0.00003 | **0.0098** | 0.0011 | 0.0036 |
| **PCB-123** | 0.00003 | **0.0017** | 0.0002 | 0.0006 |
| **PCB-156** | 0.00003 | 0.0001 | 0.0003 | **0.0010** |
| **PCB-157** | 0.00003 | **0.0005** | 0.0001 | 0.0002 |
| **PCB-167** | 0.00003 | **0.0018** | 0.0001 | 0.0003 |
| **PCB-189** | 0.00003 | 0.0001 | 0.0001 | 0.0001 |

Table 6. Characteristic of bottom sediments collected form reservoirs of different catchment characteristics.

| | SR | JR | BR |
|---|---|---|---|
| **Total PCB [ng/kg, d.w.]** | 694.31 | 121.36 | 350.06 |
| **WHO-TEQ [ng TEQ/kg, d.w.]** | 1.42 | 0.27 | 0.40 |
| **Organic matter [%]** | 9.69 | 1.04 | 0.96 |

The toxic potency of PCB congeners in environmental samples was estimated by a WHO Toxic Equivalent (WHO-TEQ). To evaluate these values we used the toxic equivalence factors (TEFs) defined for PCBs that induce aryl hydrocarbon hydroxylase activity in a similar manner as 2,3,7,8-TCDD. The TEF values recommended by the WHO are summarized in Table 4 [36].

From all the 12 congeners recommended for the analysis by WHO, homologues PCB-77, 81, 126 and 169, called as coplanar, posses more toxic properties than non-coplanar congeners (Table 5) [33, 34]. The maximum total WHO-TEQ concentration was observed in the SR sample, then in the BR and JR samples (1.42, 0.36 and 0.22 ng TEQ/kg d.w., respectively) (Table 3). This high WHO-TEQ value was mostly generated by PCB-126 concentration (1.39 ng TEQ/kg d.w.), which possess the highest TEF value (0.1) (Tables 4, 5 and 7). The concentration of this homologue was 3.8 to 6.3 times higher in proportion to other samples. An adverse result was obtained for congener PCB-169, which possesses the lowest concentration at the SR site (0,0021 ng TEQ/kg d.w.) and highest at the JR site (0.0046 ng TEQ/kg d.w.) (Table 5). Congeners PCB-77 had the highest concentration in SR sample (0.0021 ng TEQ/kg of dry weight), whereas for other sites this value was about 7.0 to 10.5 times lower. Congener PCB-81 differs among the samples, but the highest concentration was observed in the BR sample.

Fig. 2 demonstrates the percentage composition of PCB homologues in the analyzed sediments. For all samples congener PCB-118 had the highest frequency of occurrence, ranging between 47.14% for the SR, 34.05% for the BR and 29.47% for the JR samples. In consequence, pentachlorobiphenyls were the predominant homologues in sediment form all of analyzed samples.

Obtained results presented low contamination levels by PCBs and corresponded with data presented by Covaci et al. [33] for the sediments of the Danube Delta, where the level of the sum of 7 ICES PCBs (PCB 28, 52, 101, 18, 138, 153 and 180) were < 2000 ng/kg d.w. In comparison, the PCB contamination of sediments collected from the Rhine Delta (The Netherlands) were up to 200,000 ng/kg d.w. Also, data of PCBs soil contamination in Poland presented by Falandysz [3] correspond with results obtained in the presented study. Nevertheless, it could be stated that no systematic measurements of PCB concentrations were undertaken in analyzed reservoirs. Thus data about the current PCB contamination status (especially by twelve PCB congeners recommended for the analysis by WHO) of this region are not available.

Table 7. Trace metals concentration in bottom sediments collected form reservoirs of different catchment characteristics [mg/kg d.w.].

| Concentration [mg/kg] | SR | JR | BR |
|---|---|---|---|
| **Ni** | **12.55** | 10.08 | 2.94 |
| **Cu** | **23.02** | 7.31 | 2.23 |
| **Mo** | **1.13** | 0.82 | 0.26 |
| **Co** | **5.13** | 2.26 | 0.76 |
| **Cd** | **0.41** | 0.34 | 0.12 |
| **Pb** | **19.32** | 9.13 | 2.85 |
| **Mn** | **607.16** | 237.26 | 192.84 |
| **As** | **2.62** | 1.33 | 0.87 |
| **Se** | **2.18** | 0.04 | 0.13 |

Presented results indicated that the average concentration of total PCBs in Sokolowka Reservoir was significantly higher compared to those in Jeziorsko and Barycz reservoirs. Due to the catchment, major current sources to urban rivers include sewage input and combined sanitary overflows, although re-suspension of contaminated bed sediments and direct urban runoff may also be significant sources.

These results may be due to the presence of the domestic and industrial wastewater discharges into the Sokolowka River. It frequently happens that wastewater input by storm water outlets contributes to 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. Thus point-source pollution may cause appreciable differences in the obtained results.

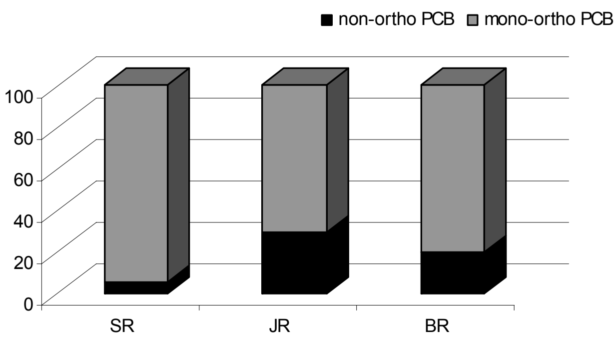


Fig. 2. Composition (%) of non-ortho and mono-ortho PCBs in sediments collected form reservoirs of different catchment characteristics.

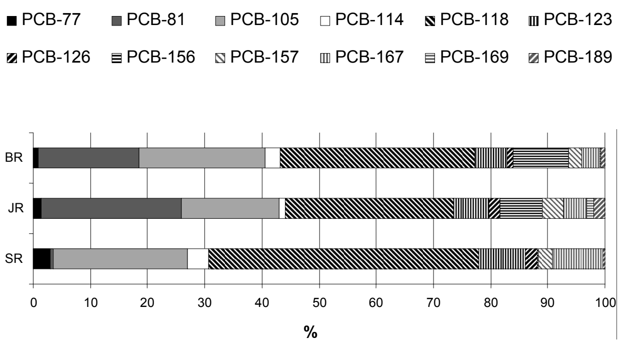


Fig. 3. Composition (%) of PCB congeners in bottom sediments collected from reservoirs of different catchment characteristics.

An additional source is road transportation, which creates a serious problem due to exhausted gases and the wear and tear of car parts involving PCBs. For this reason the input of PCBs from storm water can be transported to the river and deposited in the reservoir. PCB concentrations increase during storm events, when sediment loads increase considerably. Thus suspended sediment, which has a lower grain size compared to bed sediments, occurs, and therefore the higher surface area may account for the higher concentrations of PCBs, and therefore sediments mobilized during high flow events can be the dominant source of PCBs.

### Heavy Metals Concentrations

Bottom sediments consist of a complex mixture of organic and inorganic components [34]. Thus levels of heavy metals in this matrix depend on various environmental parameters such as sediment texture, clay and organic matter content as well as on anthropogenic impact [35, 36]. Dube et al. [41] suggested that the fate of heavy metals in the environment is more dependent on physicochemical properties of matrices (e.g. sil, sediment, water ect.) than on the properties of metals.

The concentration of heavy metals in the SR, the JR and the BR samples are listed in Table 7. The highest concentrations of heavy metals (Ni, Cu, Mo, Co, Cd, Pb, Mn, As and Se) were observed in the SR sample and the lowest in the BR sample, except the Se, which had the lowest value in the JR sample (Table 7). This result can be linked to the high content of organic matter that readily adsorbs heavy metals (Table 6). As an additional reason for these results, human sources can be listed. The Sokolowka catchment has been under stress from a variety of anthropogenic impacts for several decades so that the high concentration of heavy metals suggests man-derived inputs [21, 22, 39]. Anthropogenic activity introduced a significant amount of heavy metals into the environment, especially due to sewage input, mining activities, copper production, dump lixiviation, and the use of coal and pesticides, as well as residential, commercial, industrial and road runoff [44-46].

It should be stated that the contamination level in all analyzed samples was low. Nevertheless, the obtained results corresponded with the concentration presented in other Polish studies [41, 45, 46]. As an example, Szarek-Gwiazda et al. [47] reported a similar concentration of Cd (1.4 and 1.1 mg/kg d.w for upper and lower part of the reservoir, respectively), Pb (27 and 23 mg/kg d.w. for upper and lower parts of reservoir, respectively), and Mn (481 and 221 mg/kg d.w. for upper and lower parts of reservoir, respectively) in the bottom sediments collected from Dobczyce Reservoir. Additionally, the above-mentioned researchers used the index of geoaccumulation ($I_{geo}$) and individual contamination factor (ICF) to determine the ecosystem pollution level, and they stated that the reservoir sediments were polluted to a low degree by Cd and relatively unpolluted by Pb and Mn. Study of Solecki and Chibowski [41] placed on Piaseczno Lake, Muśluchowskie Lake and Zembrzycki Reservoir showed parallel results, eg. mean concentration of 24 samples analyzed for Cu, Pb and Mn was in order 24.00-32.00 mg/kg d.w. for Cu, 24.00-29.00 mg/kg d.w. for Pb and 176.50-186.50 mg/kg d.w. for Mn, whereas concentrations obtained in our study showed the following values: 23.02, 19.32 and 607.16 mg/kg d.w. for SR, 7.31, 9.13 and 237.26 mg/kg d.w for JR sample and 2.23, 2.85 and 192.84 mg/kg for BR sample for Cu, Pb and Mn, respectively.

## Conclusions

Ecosystem characteristics can greatly modify contamination rate in freshwater reservoirs. As an example the catchment area exerting pollutant concentration in the reservoir as well as large catchment/reservoir ratio can be given [48, 49].

Obtained results, in reference to catchments, rivers and reservoir characteristics (Table 1) showed that the smallest reservoir (Sokolowka Reservoir) situated in a highly urbanized catchment, had the highest potential for PCB and heavy metal accumulation. On the other hand, the largest catchment (Jeziorsko Reservoir) possesses the lowest concentration of total PCBs. The BR was reported as the reservoir of medium PCB contamination and the lowest heavy metal contamination.

This study showed that the urban site had a higher concentration of PCBs and trace elements due to their association with organic matter in mixed runoff from residential, commercial and industrial land uses as well as from road runoff.

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