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Characteristics, distribution, sources, and ecological risk of persistent organic pollutants (PAHs, PCBs) in the bottom sediments of a potamic ecosystem, in conditions of urban-industrial anthropopressure

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ABSTRACT

The impact of a strongly anthropogenic urban-industrial catchment on the pollution status of bottom sediments of a potamic ecosystem is presented, including the spatial and temporal distribution of selected persistent organic pollutants (polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs)). The study compares the pollution of bottom sediments of the Bytomka River at low and high water levels. The Bytomka River is characterized by a high proportion of industrial and municipal wastewater in the total water balance (80%–90%). At low water levels, the concentration ranged from 2.88 to 74.67 mg/kg d.w. (the sum of PAHs) and from below the method quantitation limit (MQL) to 26.13 µg/kg d.w. (the sum of PCBs), at high water levels from 3.90 to 116.53 mg/kg d.w. (the sum of PAHs) and from below MQL to 15.95 µg/kg d.w. (the sum of PCBs). It was found that the pollution of sediments with PAHs and PCBs is seasonally variable and depends on the water flow rate. High water levels are related to rainwater runoff from tarmacked surfaces and these periods are used to discharge increasing amounts of wastewater, which are sources of PAHs and PCBs. The analysis of characteristic ratios shows that air deposition associated with low emissions may also be one of the likely sources of PAHs in the river studied. According to the ecotoxicological indicators threshold effect concentration and probable effect concentration, concentrations of PAHs in the bottom sediments of the Bytomka River may have an adverse effect on plant and animal organisms living in these habitats. No impact of PCBs was found.

Keywords: Polycyclic aromatic hydrocarbons (PAHs); Polychlorinated biphenyls (PCBs); Bottom sediment; Water level; Water flow rate; Diagnostic ratios; Ecological risk

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1. Introduction

The concentration of urban agglomerations and industrial centers creates strong anthropopressure on the natural environment, in particular in relation to the surface, limestone, and potamic water ecosystems [1]. Watercourses in industrialized and densely populated areas are used, for better or worse, to collect discharges of treated municipal and industrial wastewater or rainwater [2].

Among the most troublesome pollutants that are harmful to aquatic ecosystems are persistent organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). These compounds are especially dangerous because of their persistence in the environment. The main feature of this group is resistance to degradation, both under physical, chemical, and biological conditions. At the same time, these pollutants can accumulate in organisms and be toxic to them. These pollutants

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enter into aquatic ecosystems mainly through industrial or municipal wastewater, rainwater, and snowmelt flowing down from nearby areas and in the form of deposition from the air [3,4]. PCBs and PAHs are characterized by low vapor pressure and solubility in water, and bind with organic particles suspended in water. Suspended and sedimented particulate-bound forms and aqueous phases are the most bioavailable fractions of PCBs and PAHs metabolized by organisms [5,6].

PCBs in the water environment originate solely from human activity [7]. Before their production and usage was banned in many countries in the 1970s, mixtures of different PCBs were used as insulating materials in capacitors and transformers, as hydraulic fluids for power transmission (mining, aviation), vacuum pump fluids, lubricants in gas turbines, cutting fluid lubricants, flame retardants, adhesives, additives for thermosetting plastics and copying papers, pesticides and preservatives, and impregnating additives to pesticides, paints and varnishes, and plasticizers for plastics [5,8,9].

In turn, PAHs can be generated from natural processes such as naturally exposed bitumen [10], as well as forest and prairie fires [11], but they are mostly emitted from anthropogenic sources [5,12–14]. Anthropogenic PAHs can be divided into the pyrogenic and petrogenic origin. Pyrogenic PAHs arise from the incomplete combustion of fossil fuels and biomass, petrogenic PAHs are associated with petroleum and slow maturation of organic matter [5,15]. Each of these processes creates a characteristic chemical pattern that makes it possible to identify the origin of PAHs [5]. The ratio between selected PAHs can be used to interpret the characteristics of specific PAH isomers based on their stability and the temperature at which the analyte was created [16].

The Bytomka River was selected for research as an example of a short watercourse with a large slope, canalized along its entire length. The catchment area is highly urbanized. The Bytomka River flows through three large cities: Bytom, Ruda Slaska, and Zabrze with a population of 168,000; 138,000; and 174,000, respectively [17]. These cities continuously discharge treated wastewater and rainwater into the river at an average rate of 1,111 and 4,600 m^3/d, respectively [18].

The paper describes the spatial variability of selected persistent organic pollutants (PAHs, PCBs) in the bottom sediments of the Bytomka River flowing through a highly urbanized and industrialized area. The differences in contamination of bottom sediments of a short-length and large-slope river ecosystem with PAHs and PCBs were measured at different water levels (low and high flow rate). Possible sources of contamination were determined. Then, the impact of these pollutants on bottom sediments is characterized based on ecotoxicological criteria.

2. Materials and methods

2.1. Research object

The length of the Bytomka River is about 20 km, and the catchment area about 150 km^2. The river is part of the Kłodnica River basin, located in the Odra River catchment area (southern Poland). The Bytomka River originates in Bytom (50°20′37.5″N, 18°53′46.7″E), at an altitude of 273.05 m a.s.l. It flows into the Kłodnica River at an altitude of 219.15 m a.s.l. (50°17′25.6″N, 18°42′44.3″E) [19,20].

The river has a very poor tributary network. It is fed mainly by mine waters, rainwater, and sewage discharges from industrial plants and wastewater treatment plants, amounting to an estimated 80%–90% of the average river flow. Throughout its course, the Bytomka River flows through a highly urbanized area and is canalized over its entire length. The catchment area is heavily transformed and deformed as a result of mining activities in this area. The catchment area consists of: strongly anthropogenic areas – 49%, agricultural land – 28%, forest and semi-natural areas – 22%, and water areas about 1% [20].

During low flow rates, suspended solids deposit as bottom sediments. During high flow rates, sediments are suspended and transported down the river. To determine the possible effect of water flow rate on the degree of pollution, samples of bottom sediments were collected during low water level (July) and high water level (September).

The bottom sediment samples were collected from the surface layer of the sediment (to a depth of 5 cm) with an Ekman-Birge sampler at eight sampling points along the entire length of the river (Fig. 1). Samples were taken twice at different water levels. Sediment samples were stored in a refrigerator at 4°C until the analysis. Geographical locations and depth of the sampling sites are shown in the table (Table 1).

2.2. Research methodology

Bottom sediments for PAH and PCB analysis were air-dried, ground, and passed through a sieve. PAHs were determined according to the previously presented methodology [21]. Three grams of dry sediment were extracted in an ultrasound bath with dichloromethane. The obtained extract was decanted and concentrated in a vacuum evaporator to the volume of 1 mL. The sample cleaning was conducted on glass chromatographic columns that contained aluminum oxide, silica gel, and anhydrous sodium sulfate. The extract was transferred onto a layer that had been previously washed. PAHs were leached out with dichloromethane. The eluate was concentrated and filtered through a syringe filter made of polytetrafluoroethylene (PTFE). The following compounds were determined: naphthalene (NP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FL), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (IcdP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP) with the gas chromatography-mass spectrometry method (GC-MS QP-2010 Plus Shimadzu, Japan). The ZB-5MS column (30 m × 0.25 mm × 0.25 μm) and electron ionization were used.

For PCB analysis, 1 g of dry sediment was extracted twice using ultrasound with acetone:hexane (1:1, v/v) mixture. The obtained extract was concentrated in a vacuum evaporator to the volume of 5 mL and 0.5 g of activated copper (to remove sulfur) was added and shaken for 6 h. The sample was purified on a florisil/Na_2SO_4 column. The column was conditioned with 5 mL hexane, and the

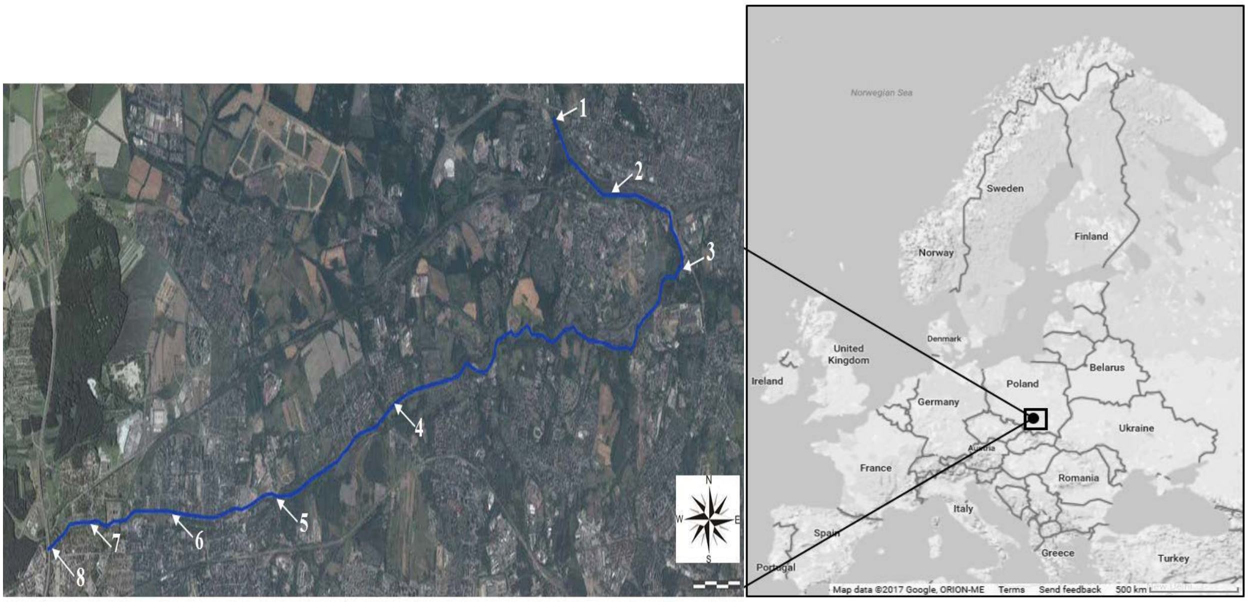


Fig. 1. Location of the study area and sampling sites in the Bytomka River, Poland.

Table 1
Geographical locations of the sampling sites

Sampling point	Latitude	Longitude	River kilometres
*S*1	50°20′37.5″N	18°53′46.7″E	0.0
*S*2	50°20′31.7″N	18°54′54.1″E	1.0
*S*3	50°20′07.1″N	18°55′11.9″E	3.0
*S*4	50°19′15.3″N	18°49′58.1″E	10.0
*S*5	50°18′41.7″N	18°47′54.8″E	13.0
*S*6	50°18′34.1″N	18°45′59.4″E	15.0
*S*7	50°18′30.0″N	18°44′27.0″E	17.0
*S*8	50°17′25.6″N	18°42′44.3″E	20.0

sample was eluted with 50 mL hexane. The sample was concentrated to 1 mL and analyzed for selected PCB congeners: 28, 52, 101, 138, 153, 180, and 209. The qualitative and quantitative analysis of the samples was performed by the gas chromatography-electron capture detector method (GC-ECD GC-2010 Shimadzu, Japan). The ZB-5MS column (30 m × 0.25 mm × 0.25 µm) was used for the analysis.

2.3. Quality assurance and quality control system

Based on the information contained in the work [22], the quality assurance and quality control (QA/QC) system was developed. For PAHs, analysis solutions were prepared in dichloromethane (Chempur, Poland). The stock standard solution was obtained by tenfold dilution, the certified PAHs standard (Sigma-Aldrich, United States), in dichloromethane. The stock deuterated standard solution was obtained by diluting the standard deuterated solution (200 µg/mL concentration) 10 times in dichloromethane. Working calibration solutions were prepared by diluting the stock solutions with dichloromethane. The calibration was done at five concentration levels. The calibration curve for bottom sediment samples ranged from 0.030 to 3.000 µg/ml.

In the case of PCBs, analysis solutions were prepared in hexane (Chempur Company). The PCB mix standard solution 7 (PCB No 28, 52, 101, 138, 153, 180, and 209) from Sigma-Aldrich (United States) was used as a certified standard. The stock standard solution with a concentration of 1 µg/mL was obtained by 10-fold dilution of the certified solution. Two calibration curves were prepared: 0.01–0.5 µg/mL and 0.001–0.01 µg/mL. Working calibration solutions for the curve 0.01–0.5 µg/mL were prepared by diluting the stock solutions with hexane. The calibration was done at five concentration levels. Working calibration solutions for the curve 0.001–0.01 µg/mL were prepared by diluting the standard with a concentration of 0.01 µg/mL. The calibration was also carried out at five concentration levels.

A standard solution derived from another series than the calibration standard was used to check the calibration. The quality control of the research was based on the analysis of blind samples and recovery with the working standard, parallel for each series of samples.

The limits of detection (LOD) were determined with the $S/N = 3$ method using consecutive dilution series. The limits of quantification (LOQ) were defined as three times the LOD. The method quantitation limit (MQL) was determined at 0.01 mg/kg for PAHs and 1.0 µg/kg for PCBs.

3. Results and discussion

3.1. Water flow rate

In July, the water level and the flow rate were low. The flow rate increased from 0.38 m^3/s at the highest position in the river profile (*S*1) to 2.66 m^3/s at the final position (*S*8). In September, the water level and the flow rate were high. The flow rate ranged from 0.83 m^3/s at the *S*1 site to 4.66 m^3/s at the *S*8 site. At the high water level, the amount of water carried in the stream bed was about two times higher than in the low state.

3.2. PAHs in bottom sediment samples

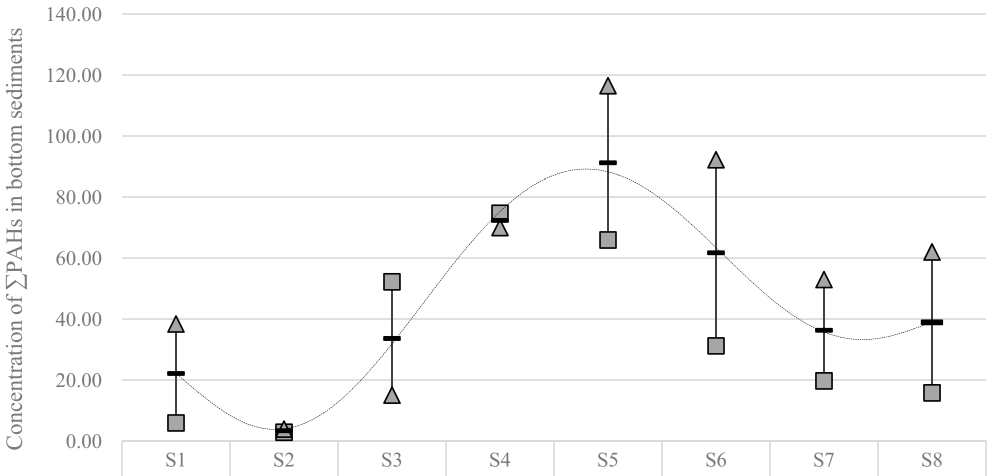
In bottom sediment samples, the sum of 16 PAHs ranged from 2.88 mg/kg d.w. (d.w. – dry weight) to 74.67 mg/kg d.w. in July and from 3.90 to 116.53 mg/kg d.w. in September (Fig. 2). For concentrations below the limit of quantification, the analyte concentration of 0 was used for the calculation. The dominant compounds from the studied PAH group include PHE, FLA, and PYR.

The lowest concentrations of all tested compounds in the low water level were recorded at the *S*2 sampling point. Whereas the highest concentrations were found at *S*3 (ACY – 0.50 mg/kg d.w.), *S*4 (NP – 3.38 mg/kg d.w., ACE – 1.74 mg/kg d.w., FL – 1.61 mg/kg d.w., PHE – 13.20 mg/kg d.w., ANT – 5.04 mg/kg d.w., FLA – 13.25 mg/kg d.w., PYR – 10.36 mg/kg d.w., BaA – 7.10 mg/kg d.w., CHR – 3.28 mg/kg d.w., BghiP – 2.76 mg/kg d.w.), and *S*5 (BbF – 3.61 mg/kg d.w., BkF – 2.40 mg/kg d.w., BaP – 4.42 mg/kg d.w., IcdP – 2.15 mg/kg d.w., DahA – 0.59 mg/kg d.w.) (Table 2).

When the water level was high, the lowest concentrations of selected PAHs were also recorded at the *S*2 sampling point. In turn, the highest concentrations were found at *S*5 (NP – 5.92 mg/kg d.w., ACY – 0.51 mg/kg d.w., ACE – 3.19 mg/kg d.w., FL – 5.18 mg/kg d.w., PHE – 32.86 mg/kg d.w., ANT – 6.05 mg/kg d.w., FLA – 14.47 mg/kg d.w., PYR – 14.69 mg/kg d.w., BaA – 8.87 mg/kg d.w., CHR – 4.03 mg/kg d.w., BbF – 4.70 mg/kg d.w., BkF – 3.06 mg/kg d.w., BaP – 6.04 mg/kg d.w., IcdP – 2.44 mg/kg d.w.), and *S*6 (DahA – 0.80 mg/kg d.w., BghiP – 3.86 mg/kg d.w.) (Table 2).

The observed increase in concentrations of tested analytes at *S*4 (10.0 km of the river course) and *S*5 (13.0 km of the river course) may be due to the fact that the coal waste dump Hałda Ruda in Zabrze, Poland is located in the vicinity of these sampling points [23]. Mining waste landfills from coal mining are often thermally active facilities, characterized by high interior and surface temperatures with gaps locally appearing on the surface. Gases are released from these crevices, which may include PAH compounds [24]. Mainly 2 and 3 ring PAHs enter the air, which is related to the volatility of PAHs [21]. Surface runoff from the Hałda Ruda dump could contribute to the introduction of many of these pollutants into the river, eventually accumulating in the bottom sediments of the Bytomka River. In September, during the high water level, the maximum values of concentrations of each analyte tested were higher compared to values obtained in July (low water level). This is especially evident in the case of PHE whose highest concentration was 2.5 times higher in September compared to July. During high water levels, surface runoff enters the river. This runoff, especially from impermeable surfaces (tarmacked surfaces), is one of the sources of bottom sediment pollution with PAH compounds. In addition, periods of high water levels are used to discharge an increased amount of wastewater, which increases the contamination of the watercourse with organic compounds, including PAHs.

Fig. 3 shows the composition pattern of PAHs in the Bytomka River sediments. The distribution is comparable along the entire course of the river, regardless of the water level. In July, 4-ring PAHs dominated along the entire course of the Bytomka River (percentage range 45.51%–55.90%). While in September, 3-ring (percentage range 21.39%–46.70%) and 4-ring (percentage range 34.02%–51.23%) PAHs dominated. The percentage of naphthalene was low and at a comparable level (0.37%–4.53% in July, 0.96%–5.08% in September), which is related to its properties (water solubility 31.7 mg/dm^3, $\log K_{ow}$ 3.30 [25]). The percentage of PAHs with a higher molecular weight was similar and amounted to 14.12%–22.03% in July and 11.43%–18.46% in



	S1	S2	S3	S4	S5	S6	S7	S8
■ July	5.93	2.88	52.20	74.67	65.90	31.19	19.71	15.80
▲ September	38.37	3.90	15.05	69.98	116.53	92.23	52.95	62.00
− average	22.15	3.39	33.63	72.33	91.22	61.71	36.33	38.90

Fig. 2. Sum of PAHs in sediment bottom samples (unit: (mg/kg d.w.)).

Table 2
PAHs concentration in bottom sediments (mg/kg d.w.)

Date of sampling	Compound	Sampling point								Minimum	Maximum	Average
		*S*1	*S*2	*S*3	*S*4	*S*5	*S*6	*S*7	*S*8			
July – low water level	NP	0.20	0.01	0.56	3.38	2.77	0.98	0.45	0.43	0.01	3.38	1.10
	ACY	<0.01	<0.01	0.50	0.44	0.38	0.20	0.11	0.10	<0.01	0.50	0.22
	ACE	0.06	0.02	0.45	1.74	1.34	0.50	0.31	0.20	0.02	1.74	0.58
	FL	0.06	0.02	0.41	1.61	1.28	0.40	0.30	0.22	0.02	1.61	0.54
	PHE	1.00	0.42	5.88	13.20	10.07	3.85	2.55	2.12	0.42	13.20	4.89
	ANT	0.21	0.10	2.29	5.04	3.79	1.17	0.81	0.76	0.10	5.04	1.77
	FLA	0.92	0.50	11.07	13.25	11.68	5.60	3.41	2.20	0.50	13.25	6.08
	PYR	0.88	0.47	9.44	10.36	9.20	4.86	3.08	2.76	0.47	10.36	5.13
	BaA	0.56	0.27	6.02	7.10	6.36	3.48	2.05	1.65	0.27	7.10	3.44
	CHR	0.36	0.16	2.65	3.28	3.17	1.74	1.12	0.87	0.16	3.28	1.67
	BbF	0.40	0.20	2.61	3.40	3.61	1.79	1.19	1.00	0.20	3.61	1.78
	BkF	0.25	0.16	2.23	2.35	2.40	1.24	0.82	0.71	0.16	2.40	1.27
	BaP	0.39	0.24	3.46	4.24	4.42	2.36	1.46	1.13	0.24	4.42	2.21
	IcdP	0.22	0.12	1.61	1.98	2.15	1.14	0.75	0.45	0.12	2.15	1.05
	DahA	0.07	0.03	0.48	0.55	0.59	0.32	0.23	0.18	0.03	0.59	0.31
	BghiP	0.36	0.16	2.55	2.76	2.70	1.55	1.08	1.02	0.16	2.76	1.52
	∑PAHs	5.93	2.88	52.20	74.67	65.90	31.19	19.71	15.80	2.88	74.67	33.54
September – high water level	NP	0.37	0.07	0.46	1.93	5.92	2.59	1.12	0.71	0.07	5.92	1.65
	ACY	0.01	<0.01	<0.01	0.15	0.51	0.35	0.25	0.35	<0.01	0.51	0.20
	ACE	0.19	0.03	0.11	0.94	3.19	1.30	0.54	0.28	0.03	3.19	0.82
	FL	0.55	0.29	0.46	2.17	5.18	2.98	1.25	1.01	0.29	5.18	1.74
	PHE	6.56	1.07	4.14	27.30	32.86	26.70	12.19	16.69	1.07	32.86	15.94
	ANT	0.91	0.08	0.37	2.12	6.05	3.54	1.84	2.08	0.08	6.05	2.12
	FLA	6.93	0.51	2.16	9.04	14.47	12.87	8.45	10.79	0.51	14.47	8.15
	PYR	6.18	0.51	1.86	8.14	14.69	11.48	7.31	8.54	0.51	14.69	7.34
	BaA	4.41	0.24	1.15	4.30	8.87	7.39	4.71	5.44	0.24	8.87	4.56
	CHR	2.14	0.15	0.68	2.32	4.03	3.69	2.39	2.54	0.15	4.03	2.24
	BbF	2.38	0.23	0.85	2.76	4.70	4.54	3.03	3.09	0.23	4.70	2.70
	BkF	1.49	0.14	0.53	1.66	3.06	2.75	1.85	1.96	0.14	3.06	1.68
	BaP	2.77	0.24	0.92	3.12	6.04	5.19	3.67	3.69	0.24	6.04	3.21
	IcdP	1.09	0.13	0.47	1.36	2.44	2.21	1.58	1.69	0.13	2.44	1.37
	DahA	0.44	0.04	0.14	0.46	0.77	0.80	0.44	0.57	0.04	0.80	0.46
	BghiP	1.97	0.18	0.75	2.20	3.74	3.86	2.32	2.58	0.18	3.86	2.20
	∑PAHs	38.37	3.90	15.05	69.98	116.53	92.23	52.95	62.00	3.90	116.53	56.38

September for 5-ring PAHs, and 6.34%–9.74% in July and 5.09%–8.07% in September for 6-ring.

During low flow rates, suspended solids deposit as bottom sediments, while during high flow rates, sediments are suspended and transported down the river. The distribution of PAHs indicates that during intensive rain, mostly 3-rings PAHs were discharged into the river and ultimately to the bottom sediments. These PAHs are the least harmful and undergo degradation most easily.

3.3. PCBs in bottom sediment samples

In the case of PCBs, the sum of the seven congeners ranged from a concentration below the limit of quantification to 26.13 µg/kg d.w. in July and to 15.95 µg/kg d.w. in September (Fig. 4). As in the case of PAH, at concentrations below the limit of quantification, the value 0 was used for calculations.

No congener number 52 was found in any of the bottom sediment samples collected in July (low water level). An increase in concentrations of most of the tested PCB congeners was found at the *S*4 sampling point (congeners: 101–10.57 µg/kg d.w., 153–3.87 µg/kg d.w., 138–2.13 µg/kg d.w., 180–5.55 µg/kg d.w., 209–4.01 µg/kg d.w.), and *S*5 (congeners: 101–3.75 µg/kg d.w., 153–3.30 µg/kg d.w., 138–5.83 µg/kg d.w., 180–6.52 µg/kg d.w.) (Table 3).

In September (high water level), the trend of concentration changes along the river course was different. An

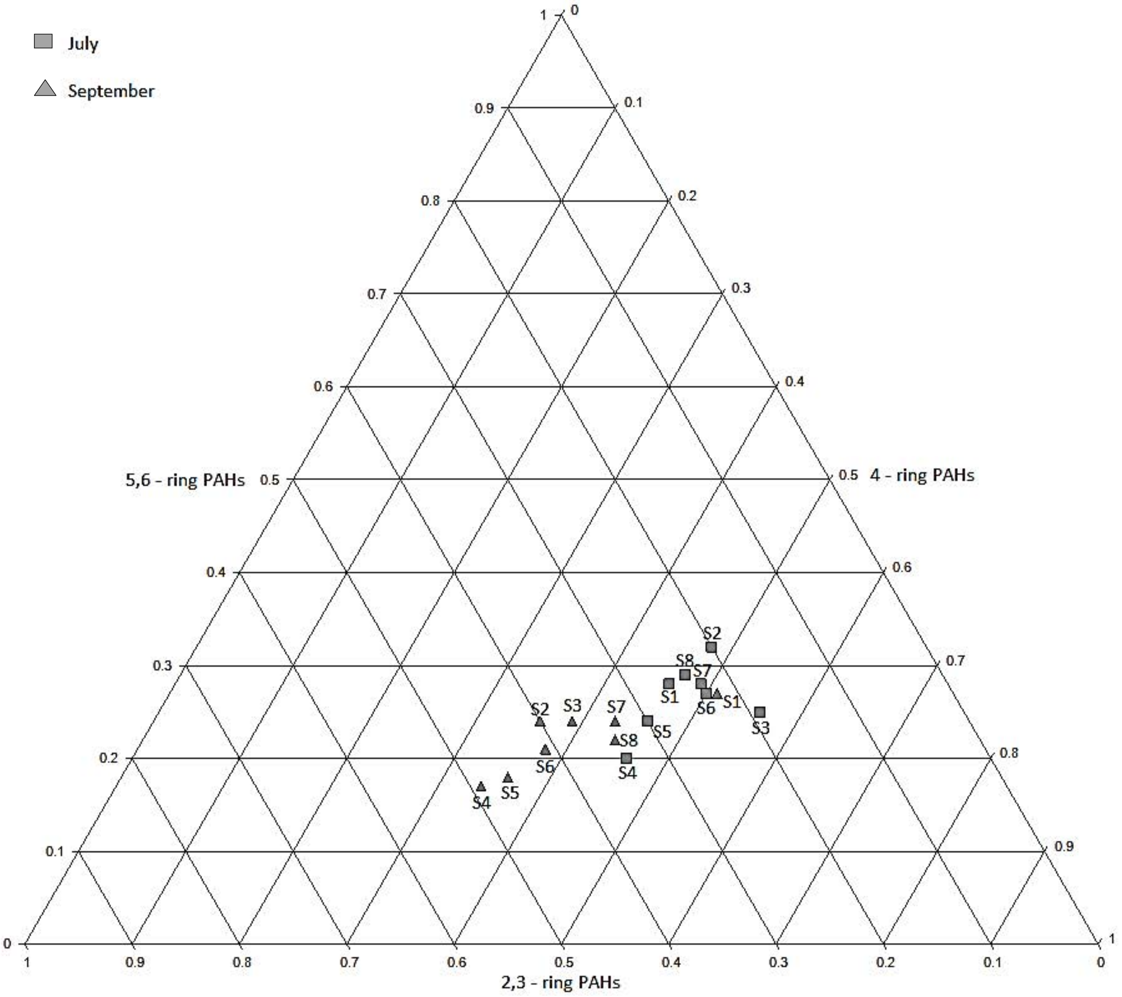
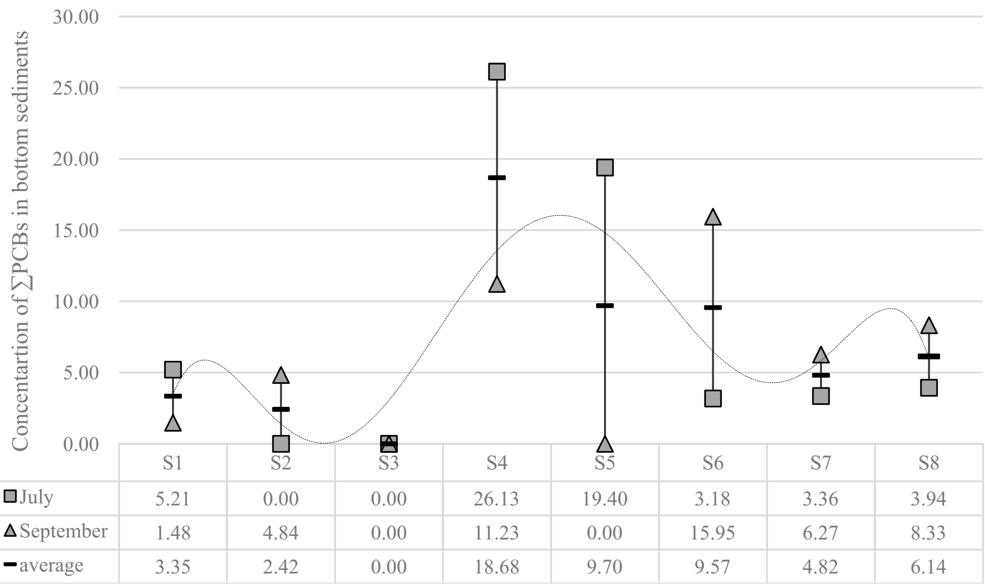


Fig. 3. Composition pattern of PAHs in bottom sediments of the Bytomka River.



	S1	S2	S3	S4	S5	S6	S7	S8
■July	5.21	0.00	0.00	26.13	19.40	3.18	3.36	3.94
▲September	1.48	4.84	0.00	11.23	0.00	15.95	6.27	8.33
−average	3.35	2.42	0.00	18.68	9.70	9.57	4.82	6.14

Fig. 4. Sum of PCBs in bottom sediment samples (unit: (mg/kg d.w.)).

Table 3
PCBs concentration in bottom sediments (μg/kg d.w.)

Date of sampling	Compound	Sampling point								Minimum	Maximum	Average
		*S*1	*S*2	*S*3	*S*4	*S*5	*S*6	*S*7	*S*8			
July – low water level	PCB 28	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	3.36	<1.00	<1.00	3.36	0.42
	PCB 52	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	–
	PCB 101	<1.00	<1.00	<1.00	10.57	3.75	<1.00	<1.00	1.07	<1.00	45.47	7.61
	PCB 118	1.50	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	1.50	0.19
	PCB 153	<1.00	<1.00	<1.00	3.87	3.30	1.18	<1.00	<1.00	<1.00	3.87	1.04
	PCB 138	3.71	<1.00	<1.00	2.13	5.83	2.00	<1.00	1.46	<1.00	5.83	1.89
	PCB 180	<1.00	<1.00	<1.00	5.55	6.52	<1.00	<1.00	1.41	<1.00	6.52	1.69
	PCB 209	<1.00	<1.00	<1.00	4.01	<1.00	<1.00	<1.00	<1.00	<1.00	4.01	0.50
	∑ PCB	5.21	<1.00	<1.00	26.13	19.40	3.18	3.36	3.94	<1.00	26.13	7.65
September – high water level	PCB 28	<1.00	2.05	<1.00	<1.00	<1.00	1.24	<1.00	<1.00	<1.00	2.05	0.41
	PCB 52	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	–
	PCB 101	<1.00	<1.00	<1.00	1.24	<1.00	3.05	<1.00	2.11	<1.00	3.05	0.80
	PCB 118	<1.00	<1.00	<1.00	2.10	<1.00	2.46	2.05	1.76	<1.00	2.46	1.05
	PCB 153	<1.00	1.11	<1.00	1.85	<1.00	2.09	1.00	1.00	<1.00	2.09	0.88
	PCB 138	<1.00	<1.00	<1.00	3.3	<1.00	3.94	1.87	1.91	<1.00	3.94	1.38
	PCB 180	1.48	1.68	<1.00	2.74	<1.00	3.17	1.35	1.55	<1.00	3.17	1.50
	PCB 209	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	–
	∑ PCB	1.48	4.84	<1.00	11.23	<1.00	15.95	6.27	8.33	<1.00	15.95	6.01

increase in value was recorded at the *S*2 sampling point (congeners: 28–2.05 μg/kg d.w., 153–1.11 μg/kg d.w., 180–1.68 μg/kg d.w.), *S*4 (congeners: 101–1.24 μg/kg d.w., 118–2.10 μg/kg d.w., 153–1.85 μg/kg d.w., 138–3.30 μg/kg d.w., 180–2.74 μg/kg d.w.), and *S*6 (congeners: 28–1.24 μg/kg d.w., 101–3.05 μg/kg d.w., 118–2.46 μg/kg d.w., 153–2.09 μg/kg d.w., 138–3.94 μg/kg d.w., 180–3.17 μg/kg d.w.). At the *S*3 and *S*5 sampling points, none of the analyzed congeners was recorded.

The distribution of PCB homologs varied throughout the course of the river. Local maxima of PCB concentrations, both during low and high water level, were located in the center of cities. The distribution of homologs were generally centered at the penta-, hexa-, and hepta- chlorinated congeners. Only in one sample the presence of decachlorobiphenyl was reported (*S*4 July – 15.35%). PCBs are a group of compounds characterized by low electrical conductivity, high thermal conductivity, high flash point, low vapor pressure, low solubility in water, and high solubility in lipids. These properties have contributed to their usefulness in technological processes and large-scale production in the last century [26]. The presence of multiple industry in the Bytomka River catchment area most likely had an impact on the distribution of homologues in the studied ecosystem.

3.4. Ecotoxicological analysis of the tested bottom sediments

The assessment of quality of bottom sediments of the Bytomka River was carried out on the basis of ecotoxicological criteria: threshold effect concentration (TEC) and probable effect concentration (PEC). TEC determines the concentration of compounds below which no toxic effects on organisms are observed; PEC determines concentrations above which toxic effects on organisms are often observed. While the concentrations at levels between the TEC and PEC values will cause sporadic adverse effects. Bottom sediments are considered to be toxic to aquatic organisms even only one chemical compound is found to exceed the PEC threshold content [27–29]. Table 4 summarize the classification of bottom sediments sampling along the entire length of the Bytomka River during low and high water level.

The results obtained indicate that bottom sediments collected from the Bytomka River may have toxic effects on aquatic organisms of the studied ecosystem. At most sites, PAH concentrations exceeded PEC values (Σ PAHs in July: *S*3 – 52.20 mg/kg d.w., *S*4 – 74.67 mg/kg d.w., *S*5 – 65.90 mg/kg d.w., *S*6 – 31.19 mg/kg d.w., Σ PAHs in September: *S*1 – 38.37 mg/kg d.w., *S*4 – 69.98 mg/kg d.w., *S*5 – 116.53 mg/kg d.w., *S*6 – 92.23 mg/kg d.w., *S*7 – 52.95 mg/kg d.w., *S*8 – 62.00 mg/kg d.w.). At the sampling points *S*4, *S*5, and *S*6, in both months the values exceeded concentration above which toxic effects on organisms are often observed, except for FL at the *S*6 station. In September, at high water levels, PAH concentrations were above the PEC value in a larger number of sampling points. Concentrations higher than PEC were recorded at *S*1 (except NP), *S*7 and *S*8 (for all analyzed PAHs). This indicates surface runoff and the likely discharges of wastewater during high water levels as one of the sources of pollution of bottom sediments with PAH compounds.

In the case of PCBs, a sum of concentrations of selected congeners at subsequent sampling points did not exceed the TEC value, so there is no toxic effect on organisms in the studied ecosystem.

Table 4
Classification of bottom sediments of the Bytomka River in terms of contamination by selected PAHs and PCBs

Date	Compound	Unit	Literature values*		Sampling points, bottom sediment classification according to ecotoxicological criteria							
			TEC	PEC	*S*1	*S*2	*S*3	*S*4	*S*5	*S*6	*S*7	*S*8
July – low water level	NP	(mg/kg d.w.)	0.176	0.561	0.20^{b}	0.01^{a}	0.56^{b}	**3.38**^{c}	**2.77**^{c}	**0.98**^{c}	0.45^{b}	0.43^{b}
	FL	(mg/kg d.w.)	0.077	0.536	0.06^{a}	0.02^{a}	0.41^{b}	**1.61**^{c}	**1.28**^{c}	0.40^{b}	0.30^{b}	0.22^{b}
	PHE	(mg/kg d.w.)	0.204	1.170	1.00^{b}	0.42^{b}	**5.88**^{c}	**13.20**^{c}	**10.07**^{c}	**3.85**^{c}	**2.55**^{c}	**2.12**^{c}
	ANT	(mg/kg d.w.)	0.057	0.845	0.21^{b}	0.10^{b}	**2.29**^{c}	**5.04**^{c}	**3.79**^{c}	**1.17**^{c}	0.81^{b}	0.76^{b}
	FLA	(mg/kg d.w.)	0.423	2.230	0.92^{b}	0.50^{b}	**11.07**^{c}	**13.25**^{c}	**11.68**^{c}	**5.60**^{c}	**3.41**^{c}	2.20^{b}
	PYR	(mg/kg d.w.)	0.195	1.520	0.88^{b}	0.47^{b}	**9.44**^{c}	**10.36**^{c}	**9.20**^{c}	**4.86**^{c}	**3.08**^{c}	**2.76**^{c}
	BaA	(mg/kg d.w.)	0.108	1.050	0.56^{b}	0.27^{b}	**6.02**^{c}	**7.10**^{c}	**6.36**^{c}	**3.48**^{c}	**2.05**^{c}	**1.65**^{c}
	CHR	(mg/kg d.w.)	0.166	1.290	0.36^{b}	0.16^{a}	**2.65**^{c}	**3.28**^{c}	**3.17**^{c}	**1.74**^{c}	1.12^{b}	0.87^{b}
	BaP	(mg/kg d.w.)	0.150	1.450	0.39^{b}	0.24^{b}	**3.46**^{c}	**4.24**^{c}	**4.42**^{c}	**2.36**^{c}	**1.46**^{c}	1.13^{b}
	∑ PAHs	(mg/kg d.w.)	1.610	22.800	5.93^{b}	2.88^{b}	**52.20**^{c}	**74.67**^{c}	**65.90**^{c}	**31.19**^{c}	19.71^{b}	15.80^{b}
	∑ PCB	(μg/kg d.w.)	59.80	676.00	5.21^{a}	<1.00^{a}	<1.00^{a}	26.13^{a}	19.40^{a}	3.18^{a}	3.36^{a}	3.94^{a}
September – high water level	NP	(mg/kg d.w.)	0.176	0.561	0.37^{b}	0.07^{a}	**0.46**^{b}	**1.93**^{c}	**5.92**^{c}	**2.59**^{c}	**1.12**^{c}	**0.71**^{c}
	FL	(mg/kg d.w.)	0.077	0.536	**0.55**^{c}	0.29^{b}	**0.46**^{c}	**2.17**^{c}	**5.18**^{c}	**2.98**^{c}	**1.25**^{c}	**1.01**^{c}
	PHE	(mg/kg d.w.)	0.204	1.170	**6.56**^{c}	1.07^{b}	4.14^{c}	**27.30**^{c}	**32.86**^{c}	**26.70**^{c}	**12.19**^{c}	**16.69**^{c}
	ANT	(mg/kg d.w.)	0.057	0.845	**0.91**^{c}	0.08^{b}	0.37^{b}	**2.12**^{c}	**6.05**^{c}	**3.54**^{c}	**1.84**^{c}	**2.08**^{c}
	FLA	(mg/kg d.w.)	0.423	2.230	**6.93**^{c}	0.51^{b}	2.16^{b}	**9.04**^{c}	**14.47**^{c}	**12.87**^{c}	**8.45**^{c}	**10.79**^{c}
	PYR	(mg/kg d.w.)	0.195	1.520	**6.18**^{c}	0.51^{b}	**1.86**^{c}	**8.14**^{c}	**14.69**^{c}	**11.48**^{c}	**7.31**^{c}	**8.54**^{c}
	BaA	(mg/kg d.w.)	0.108	1.050	**4.41**^{c}	0.24^{b}	**1.15**^{c}	**4.30**^{c}	**8.87**^{c}	**7.39**^{c}	**4.71**^{c}	**5.44**^{c}
	CHR	(mg/kg d.w.)	0.166	1.290	**2.14**^{c}	0.15^{a}	0.68^{b}	**2.32**^{c}	**4.03**^{c}	**3.69**^{c}	**2.39**^{c}	**2.54**^{c}
	BaP	(mg/kg d.w.)	0.150	1.450	**2.77**^{c}	0.24^{b}	0.92^{b}	**3.12**^{c}	**6.04**^{c}	**5.19**^{c}	**3.67**^{c}	**3.69**^{c}
	∑ PAHs	(mg/kg d.w.)	1.610	22.800	**38.37**^{c}	3.90^{b}	15.05^{b}	**69.98**^{c}	**116.53**^{c}	**92.23**^{c}	**52.95**^{c}	**62.00**^{c}
	∑ PCB	(μg/kg d.w.)	59.80	676.00	1.48^{a}	4.84^{a}	<1.00^{a}	11.23^{a}	<1.00^{a}	15.95^{a}	6.27^{a}	**8.33**^{a}

*[28,29]; ^{a}substance concentration < TEC (non-contaminated sediment, no toxic effect); ^{b}TEC < substance concentration < PEC (sediment contamination may cause sporadic adverse effects); ^{c}substance concentration > PEC (contaminated sediment, concentration of the compound may cause a toxic effect).

3.5. Source apportionment of PAHs

Characteristic ratios can provide information about the anthropogenic sources of PAHs [30,31]. This is based on the assumption that the ratio of selected PAHs is characteristic for a given emission source [12,14]. Fig. 5 presents average values of selected indicators for bottom sediment samples obtained in the authors' research. The analysis of diagnostic ratios shows that their values are similar to the values of indicators determining air quality for low emissions (combustion of solid fuels, i.e., coal and wood). Considering that the Bytomka River catchment is under strong anthropopressure and the area is highly urbanized, this type of deposition from the air may be one of the likely sources of PAHs in the watercourse studied.

4. Conclusion

The problem of discharging wastewater and surface runoffs into short watercourses is relevant to regions with highly developed industry and high population density all over the world. The conducted research provided comparative material for the problem of contamination of bottom sediments of short-length and large-slope river ecosystems with organic substances, in the conditions of industrialized and urbanized catchments. The specificity of short watercourses with a small but strongly anthropogenized catchment is the strong dynamics of changes in water levels. Attention was paid to the role of low and high water levels (flow rate) in the aspect of the pollution loads. Contamination of bottom sediments of the Bytomka River with persistent organic compounds (PAHs and PCBs) was variable and changed depending on the water flow rate. In the conditions of an anthropogenized catchment, in heavily industrialized areas, high water levels in the watercourse are related to the rainwater runoff from tarmacked surfaces, which are sources of PAHs and PCBs. Moreover, periods of high water levels in short streams, with a large drop, are used for discharges of increased amounts of wastewater, which prevents their dilution, worsens the self-purification processes, and causes the displacement of bottom sediments. It is indicated that the use of high water levels for discharges of wastewater is a harmful practice from the point of view of contamination of the watercourse with organic compounds, including PAHs and PCBs. The analysis of characteristic ratios shows that air deposition associated with low emissions may also be one of the likely sources of PAHs in the studied river.

The quality of bottom sediments was assessed on the basis of PEC and TEC ecotoxicological indicators.

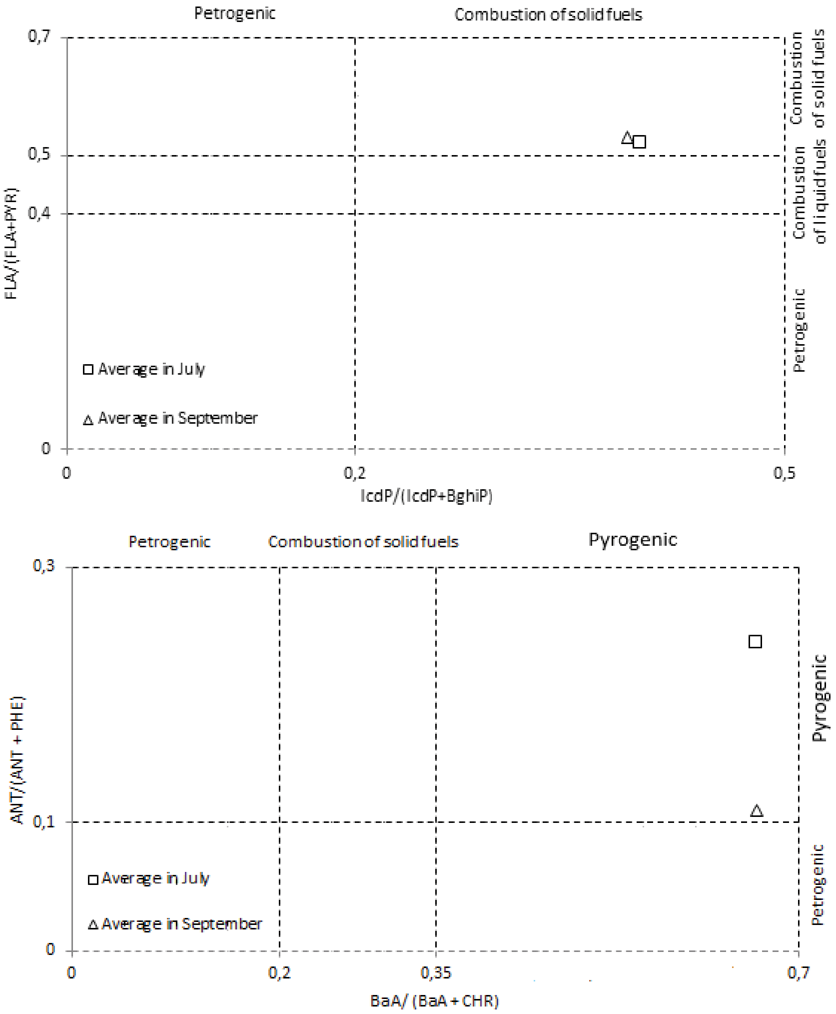


Fig. 5. Graphic interpretation of the PAH sources based on the selected diagnostic ratios.

The concentration of PAHs in sediments of the Bytomka River may cause toxic effects on aquatic organisms of the studied ecosystem. Moreover, at high water levels, PAH concentrations were above the PEC value in a larger number of sampling points. In the case of PCBs, the concentrations did not exceed the value of the TEC index, therefore, it can be assumed that the toxic effect of these substances on aquatic organisms should not occur.

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References

[1] E. Olkowska, B. Kudłak, S. Tsakovski, M. Ruman, V. Simeonov, Z. Polkowska, Assessment of the water quality of Kłodnica River catchment using self-organizing maps, Sci. Total Environ., 476–477 (2014) 477–484.

[2] V. Masindi, K.L. Muedi, Environmental Contamination by Heavy Metals, H. Saleh, R. Aglan, Eds., Heavy Metals, Intech Open, 2018, pp. 115–133. Available at: https://www.intechopen.com/books/heavy-metals/environmental-contamination-by-heavy-metals

[3] M. Kostecki, M. Czaplicka, A. Węglarz, Organic compounds (BTEXs, PAHs) in the battom sediments of dam-reservouir Dzierżno Duże (Upper Silesia), Arch. Environ. Prot., 26 (2000) 95–108.

[4] M. Kostecki, M. Czaplicka, Polycyclic aromatic hydrocarbons as part of contamination of sediments Gliwice Canal, Arch. Environ. Prot., 3 (2001) 119–135.

[5] M. Olenycz, A. Sokołowski, A. Niewińska, M. Wołowicz, J. Namieśnik, H. Hummel, J. Jansen, Comparison of PCBs and PAHs levels in European coastal waters using mussels from the *Mytilus edulis* complex as biomonitors, Oceanologia, 57 (2015) 196–211.

[6] M. Moslen, C.A. Miebaka, N. Boisa, Bioaccumulation of polycyclic aromatic hydrocarbon (PAH) in a bivalve (*Arca senilis* – blood cockles) and health risk assessment, Toxicol. Rep., 6 (2019) 990–997.

[7] J. Sanchez, M. Sole, J. Albaiges, A comparison of distribution of PCB congeners and other chlorinated compounds in fishes from coastal areas and remote lakes, Int. J. Environ. Anal. Chem., 50 (1993) 269–284.

[8] M. Andersson, R.T. Ottsen, T. Volden, Building materials as source of PCB pollution in Bergen, Norway, Sci. Total Environ., 325 (2004) 139–144.

[9] M. Rodziewicz, A. Kaczmarczyk, E. Niemirycz, Polychlorinated biphenyls in the sediments of the Odra River and its tributaries, Pol. J. Environ. Stud., 13 (2004) 203–208.

[10] J.P. Giesy, J.C. Anderson, S.B. Wiseman, Alberta oil sands development, Proc. Natl. Acad. Sci. U.S.A., 107 (2010) 951–952.

[11] C.A. Menzie, B.B. Potocki, J. Santodonato, Exposure to carcinogenic PAHs in the environment, Environ. Sci. Technol., 26 (1992) 1278–1284.

[12] P. Bigus, M. Tobiszewski, J. Namieśnik, Historical records of organic pollutants in sediment cores, Mar. Pollut. Bull., 78 (2014) 26–42.

[13] M. Mostert, G. Ayoko, S. Kokot, Application of chemometrics to analysis of soil pollutants, Trends Analyt. Chem., 29 (2010) 430–435.

[14] M. Tobiszewski, J. Namieśnik, PAH diagnostic ratios for the identification of pollution emission sources, Environ. Pollut., 162 (2012) 110–119.

[15] J. Balmer, H. Hung, Y. Yu, R. Letcher, D. Muir, Sources and environmental fate of pyrogenic polycyclic aromatic hydrocarbons (PAHs) in the Arctic, Emerg. Contam., 5 (2019) 128–142.

[16] C. Brewster, V. Sharma, L. Cizmas, T. McDonald, Occurrence, distribution and composition of aliphatic and polycyclic aromatic hydrocarbons in sediment cores from the Lower Fox River, Wisconsin, US, Environ. Sci. Pollut. Res., 25 (2018) 4974–4988.

[17] Available at: https://www.google.com/search?client=firefox-b-d&ei=-eFUXpj5I4uSkwXYq5zoDQ&q=Zabrze+population&oq=Zabrze+population&gs_l=psy-ab.3..0i19.29248.29248..30079...0.2..0.115.115.0j1......0....2j1..gws-wiz.......0i71.N-kw5X-cbRA&ved=0ahUKEwjY2eqoq-znAhULyaQKHdgVB90Q4dUDCAo&uact=5 (accessed February 25, 2020).

[18] Report on the Implementation of the National Program for Urban Wastewater Treatment, Poland, 2015.

[19] E. Cempiel, A. Czajkowska, K. Nowińska, M. Pozzi, Manifestations of Anthropopressure in the Bytomka River Catchment Area, Silesian University of Technology Publisher, Gliwice, 2014.

[20] D. Absalon, M. Matysik, In: L. Hejduk, E. Kaznowksa, Hydrology of Urbanized Catchments, Monographs of the Water Management Committee of the Polish Academy of Sciences, 2016, pp. 175–185.

[21] A. Pohl, M. Kostecki, I. Jureczko, M. Czaplicka, B. Łozowski, Polycyclic aromatic hydrocarbons in water and bottom sediments of a shallow, lowland dammed reservoir (on the example of the reservoir Blachownia, South Poland), Arch. Environ. Prot., 44 (2018) 10–23.

[22] P. Konieczka, J. Namieśnik, Estimating uncertainty in analytical procedures based on chromatographic techniques, J. Chromatogr. A, 1217 (2010) 882–891.

[23] M. Jabłońska-Czapla, S. Szopa, C. Rosik-Dulewska, Impact of mining dump on the accumulation and mobility of metals in the Bytomka River sediments, Arch. Environ. Prot., 40 (2014) 3–19.

[24] P. Kuna-Gwoździewicz, Polycyclic aromatic hydrocarbons in the gases of exhalation zones of a thermally selected active landfill for mining coal, J. Sustainable Min., 12 (2013) 7–12.

[25] M. Włodarczyk-Makuła, E. Wiśniowska, Evaluation of degradation possibility of PAHs by miroorganisms obtained from reject waters, Proc. ECOpole, 12 (2018) 599–610.

[26] S. Debela, I. Sheriffa, J. Wu, Q. Hua, Y. Zhang, A. Dibaba, Occurrences, distribution of PCBs in urban soil and management of old transformers dumpsite in Addis Ababa, Ethiopia, Sci. Afr., 8 (2020), doi: 10.1016/j.sciaf.2020.e00329.

[27] Y. He, W. Meng, J. Xu, Y. Zhang, C. Guo, Spatial distribution and potential toxicity of polycyclic aromatic hydrocarbons in sediments from Liaohe River Basin, China, Environ. Monit. Assess., 188 (2016) 1–10.

[28] D.D. MacDonald, C.G. Ingersoll, T.A. Berger, Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems, Arch. Environ. Contam. Toxicol., 39 (2000) 20–31.

[29] T. Solberg, J. Tiefenthaler Jr., G. O'Brien, H.F. Behnke, H.D. Poulson, J.P. Ela, S.D. Willett, Consensus-Based Sediment Quality Guidelines, Recommendations for Use & Application Interim Guidance, Developed by the Contaminated Sediment Standing Team, Wisconsin Department of Natural Resources, USA, 2003.

[30] F. Liu, J. Liua, Q. Chena, B. Wanga, Z. Caob, Pollution characteristics, ecological risk and sources of polycyclic aromatic hydrocarbons (PAHs) in surface sediment from Tuhai-Majia River system, China, Procedia Environ. Sci., 13 (2012) 1301–1314.

[31] X. Duan, Y. Li, X. Li, P. Yin, Historical records and the sources of polycyclic aromatic hydrocarbons in the East China Sea, China Geol., 4 (2018) 505–511.