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Spatial distribution, ecological risk and sources of polycyclic aromatic hydrocarbons (PAHs) in water and bottom sediments of the anthropogenic lymnic ecosystems under conditions of diversified anthropopressure

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Keywords: polycyclic aromatic hydrocarbons (PAHs), bottom sediments, ecological risk, catchment area, diagnostic ratios, anthropopressure.

Abstract: The research determined the concentrations of selected polycyclic aromatic hydrocarbons (PAHs) in water and sediments of Kłodnica River reservoirs and distribution depending on number of rings, ecotoxicological impact on studied ecosystems and possible sources of origin. Samples were subjected to qualitative and quantitative analysis by gas chromatography coupled with a GC-MS mass detector, using a ZB-5MS column and electron ionization. The sum of 16 PAHs in water ranged 0.111–0.301 µg/L (mean 0.200 µg/L) in Dzierżno Duże, 0.0410–0.784 µg/L (mean 0.303 µg/L) in Dzierżno Małe and 0.0920–1.52 µg/L (mean 0.596 µg/L) in Pławniowice. While in sediments respectively: 17.5–37.2 µg/g (mean 26.8 µg/g), 4.33–8.81 µg/g (6.43 µg/g) and 2.27–9.50 µg/g (5.30 µg/g). The concentration of PAHs in sediments of reservoirs, which spatial management of the catchment area accounts for over 90% of agricultural and forest land, was up to eight times lower than in sediments of the reservoir which is 69%, while built-up and transport areas are 24%. In sediments of Dzierżno Małe and Pławniowice PAHs with 5 and 6 rings dominate, while in Dzierżno Duże – 2 and 3 rings. Higher concentrations of PAHs with higher molecular weight, found in the bottom water layers, confirm the role of the sedimentation process in the transport of these compounds in reservoirs. Assessment of sediment quality, based on ecotoxicological criteria, showed that PAHs may cause toxic effects in Dzierżno Duże, while in Dzierżno Małe and Pławniowice can cause sporadic adverse effects. The likely source of PAHs in reservoirs is low emissions.

Introduction

The creation of anthropogenic lakes is one of the elements of reducing water deficit. In many cases depleted sand mine excavations are subjected to so-called water reclamation. Excavations are flooded by groundwater and nearby watercourses. The ecological and economic value of reservoirs depend on the quality of the water supplied. The exploitation of mineral deposits building aggregates or sand is carried out all over the world. Knowledge of the structure and method of managing the catchment areas supplying anthropogenic reservoirs is necessary to develop principles for the protection and exploitation of their water resources.

One of the parameters determining the quality of water and bottom sediments is the content of organic pollutants such as polycyclic aromatic hydrocarbons (PAHs). PAHs are among the priority substances and allow for the determination of the chemical status of water in water bodies but also in bottom sediments. This is an important assumption from the point of view of the obligations imposed on Poland by the European Union in the Water Framework Directive in achieving good water quality (Regulation of the Minister of Maritime Economy and Inland Navigation of October 11, 2019).

PAHs are introduced into water along various routes including atmospheric deposition, river runoff, domestic and industrial emissions as well as direct spillage of petroleum or petroleum products. There are also natural sources of PAHs such as forest fires, volcanic eruptions, natural leakage, diagenesis of organic matter, and synthesis by plants. Input from natural sources is generally low compared with that from anthropogenic sources (Kostecki et al. 2000, Kostecki and Czaplicka 2001, Lawal 2017, Wolska et al. 2012).

Bottom sediments constitute an integral part of water ecosystems. Their physicochemical and biological conditions are formed for a long time and are rather stable. They accumulate pollutants such as phosphorous compounds, heavy metals or PAHs (Kostecki and Kowalski 2019, Smal et al. 2015, Tarkowska-Kukuryk 2013). PAHs are poorly soluble in water. The higher their weight is, the lower is their water solubility (Tobiszewski and Namieśnik 2012). They bind with organic particles suspended in water. Suspended and sedimented particulate-bound forms and aqueous phases are the most bioavailable fractions of PAHs metabolized by organisms (Olenycz et al. 2015, Moslen et al. 2019). They are bound to the sediment particles and do not easily undergo degradation processes. When the sediment ages, their concentration increases (Dong et al. 2015, Feng et al. 2016, Duodu et al. 2017, Kostecki and Czaplicka 2001, Kostecki et al. 2000).

Under the changeable hydrodynamic conditions (strong waving, resuspension) bottom sediments may become a source of secondary pollution for water masses also with PAHs. The two-way pollutant exchange between water and bottom sediments is one of the main elements for the matter circulation process in a water ecosystem. The bottom sediment analysis may constitute a valuable material for describing sources of the pollutant distribution in a reservoir as well as can form the basis for determining the possible secondary water pollution and provide decision support for ecological utilization of dredged sediment (Dong et al. 2015, Pohl et al. 2018, Liu et al. 2020).

Due to the harmful effects on the environment, PAHs can be divided into three groups: PAHs with 2 and 3 aromatic rings (the least harmful and undergoing degradation most easily), PAHs with 4 aromatic rings in the molecule (toxic for animal organisms) and PAHs with 5 and 6 aromatic rings (mutagenic and carcinogenic properties) (Kalinowski and Załęska-Radziwiłł 2009, Kostecki and Kowalski 2019).

The assessment of a hazard resulting from pollution of the environment by PAHs is often limited to the determination of their concentrations. However, knowledge of the emission sources, transport pathways and sites of deposition in the aquatic environment is important. The concentration ratios of selected hydrocarbons can indicate the source of emission and suggest the transport pathway prior to their final deposition in sediments. The origin of PAHs may also affect their ageing in the sediment which in consequence may alter their mobility. Therefore, knowledge of the spatial distribution of PAHs in the aquatic environment is important (Wolska et al. 2012).

The aim of the study was to determine the distribution, ecological risk and source of PAHs in bottom sediments and waters of the Hydrotechnical System of the Kłodnica River created in highly urbanized and industrialized area. The aim was to compare the extent of bottom sediment pollution and to indicate the impact of differential anthropopressure on this pollution by PAHs. An overview of the distribution of PAHs in water and bottom sediments of the reservoirs was presented. Based on ecotoxicological criteria the impact of these pollutants on bottom sediments was characterized. On this basis the risk assessment was determined.

Material and methods

Study area

The study was conducted for three reservoirs located in the Silesian Voivodeship: Dzierżno Duże (DD), Dzierżno Małe (DM) and Pławniowice (P) (Figure 1). The reservoirs were established in the exploited open pits of sand mines. They form the so-called Western Hydrotechnical System of the Upper Silesian Industrial Region also known as the Hydrotechnical System of the Kłodnica River and make a water reserve for the Gliwice Canal and an industrial water source. Additionally, they are recreational areas and play the nature-forming role. The basic parameters of the selected reservoirs are presented in Table 1 (Reclamation program for dam reservoirs in the Kłodnica River catchment area, 2016). In Figure 2 the spatial development forms of three neighboring catchment areas were compared.

Table 1. Basic parameters characteristic for the reservoirs in the Hydrotechnical System of Kłodnica River (Reclamation program for dam reservoirs in Kłodnica River catchment area, 2016)

Parameter	(DD)	(DM)	(P)
Maximum reservoir width	1.0 km	1.5 km	1.2 km
Maximum reservoir length	5.9 km	0.8 km	3.2 km
Shoreline length	16 km	4.2 km	8 km
Maximum reservoir depth	25 m	15 m	16 m
Mean reservoir depth	14.6 m	11 m	11 m
Mean flow rate	6.6 m^3/s	0.72 m^3/s	0.65 m^3/s
Average retention time	approx. 200 days	approx. 100 days	approx. 900 days
Supplying watercourse	Kłodnica River	Drama River	Toszecki Stream
Outflow	Gliwice Canal	Gliwice Canal	Gliwice Canal
Catchment area size	545.01 km^2	177.99 km^2	121.79 km^2
Spatial development forms in the catchment area	agricultural areas (42%), forest areas (27%), built-up areas (19%), transport areas (5%), wasteland (5%), flowing water and stagnant water (2%)	agricultural areas (75%), forest areas (15%), built-up areas (7%), transport areas (1%), wasteland (1%), flowing water and stagnant water (1%)	agricultural areas (69%), forest areas (24%), built-up areas (3%), transport areas (2%), flowing water and stagnant water (2%)

The reservoir catchment areas adjoin one another. Their total area is 844.27 km^2. Its majority is located in the most industrialized region of Poland. The three studied reservoirs of the Hydrotechnical System of the Kłodnica River have the total area of approximately 10 km^2. They store approximately 140 million m^3 of water. Each reservoir makes a kind of a specific river treatment plant for the water drained off from the catchment area. The Gliwice Canal is the receiver of the water. The catchment areas of the discussed reservoirs are located in the Silesian Upland macro-region which is a geographic area with a highly unnatural landscape that has been profoundly transformed due to anthropopressure (Reclamation program for dam reservoirs in the Kłodnica River catchment area, 2016).

Research methodology

Water was sampled from each reservoir of the Hydrotechnical System of the Kłodnica River at inflow to the reservoir and at the central zone (at the deepest part of the reservoir), a surface and bottom water layer was collected in the water column. The bottom sediment samples were collected with a Birge-Eckman sampler in the central zone of the reservoir also at the deepest part of the reservoir. The bottom sediment were sampled from the upper layer (approximately 5-cm thickness of the sediment core) and the bottom layer (between 20 and 25cm in thickness of the sediment core). All water and sediment samples were collected three times in August (3 samples for each measuring point) and the result was presented as an average value in order to compare the concentrations of selected PAHs between reservoirs during the period of summer stagnation.

PAHs were determined according to the previously presented methodology (Pohl et al. 2018). The bottom sediments were dried to the air-dry condition, ground and sieved through a sieve with 1-mm openings. An appropriate sample amount (3 g) was extracted in an ultrasound bath with a constant flow rate of the cooling water (2 × 30 min). Each time a new portion of dichloromethane (40 mL) was added. After each extraction stage, the obtained extract was decanted. On the other hand, the water samples (volume of 500 mL) underwent triple extraction by shaking with three 40 mL portions of dichloromethane. Afterwards, the procedure for both matrices was analogous. The extracts were 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 to 1 ml and filtered through a syringe filter made of polytetrafluoroethylene (PTFE). The sample prepared in this way underwent qualitative and quantitative analyses conducted with the gas chromatography-mass spectrometry method (GC-MS;

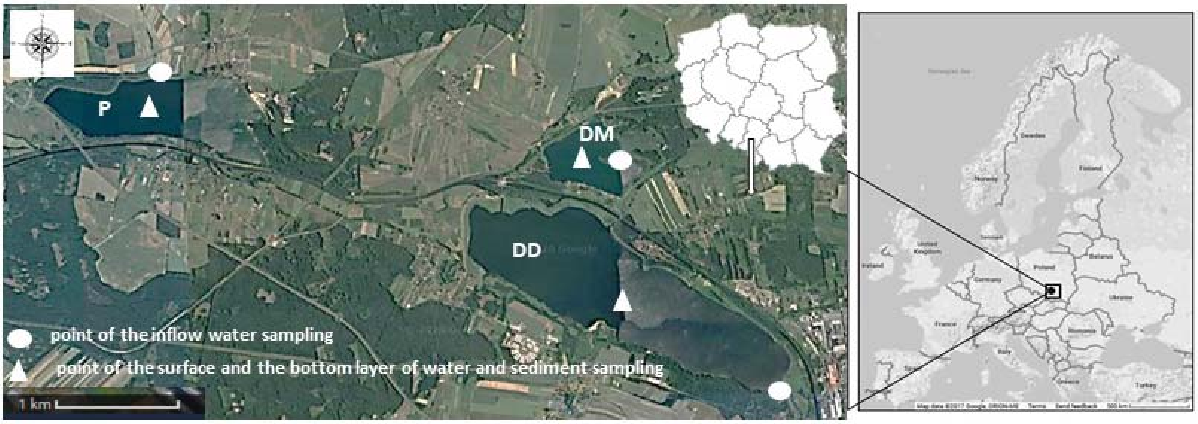

Fig. 1. Location of the study area and sampling sites in the Hydrotechnical System of Kłodnica River, Poland (https://www.google.pl/maps/@50.376089,18.5271938,11078m/data=!3m1!1e3)

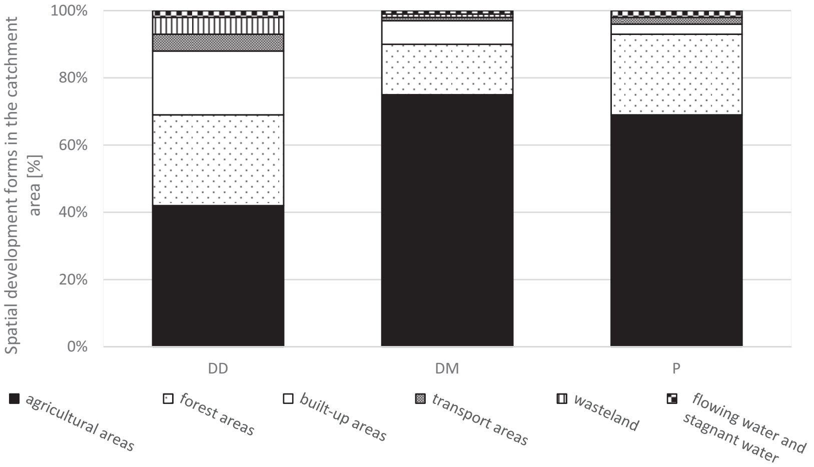

Fig. 2. Spatial development forms in the catchment area of the Hydrotechnical System of Kłodnica River

GC-MS QP-2010 Plus Shimadzu) using the ZB-5MS column (30 m × 0.25 mm × 0.25 μm) and electron ionization.

The following compounds were determined: naphthalene (NP), acenaphthylene (ACY), acenaphthene (ACE), fluorine (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), and benzo(g,h,i)perylene (BghiP) (US EPA, 1984).

Quality assurance and quality control system (QA/QC)

Based on the information contained in the work of Konieczka and Namieśnik (2010) the quality assurance and quality control systems were developed. The solutions of the analytes were prepared in dichloromethane (Chempur company). The stock standard solution, the stock deuterated standard solution and working calibration solutions were prepared. A standard solution derived from another series than calibration standard was used to check the calibration. The quality control of 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 used in the research (Table 2).

Results and discussion

PAHs in water

The highest value of the sum of 16 PAH concentrations at the inflow was determined for the Pławniowice reservoir (Toszecki Stream) – 0.389 μg/L. The sum at the inflow to Dzierżno Duże (the Kłodnica River) and to Dzierżno Małe (the Drama River) was 0.259 μg/L and 0.196 μg/L, respectively (Table 3).

The share of selected PAHs in the water of the watercourses supplying the reservoirs was varied (Figure 2, Figure 3). In the Kłodnica River water (Dzierżno Duże inflow) the highest share was observed for the 6-ring PAHs. The BghiP concentration at that point was 0.208 μg/L and made over 80% of the sum of all the determined PAHs. The Dzierżno Duże reservoir acts as a "natural" sedimentation reservoir and cleans the water of the heavily polluted Kłodnica River flowing into it. The Kłodnica River is a receiver of a significant amount of sewage, most of which goes to it through its tributaries (Nocoń et al. 2006). A larger share of PAHs with 5 and 6 rings in the water flowing into the reservoir may have toxic effects on this environment and organisms living in it.

In the Drama River, which flows into Dzierżno Małe, the shares of particular hydrocarbons were more varied in comparison to the contents determined for the water flowing into the first reservoir. The highest percentage values were determined for PAHs with lower molecular weight (two-ring PAHs – 12.2%; three-ring PAHs – 49.0%) (Figure 3). This indicates a different source of PAH than in the above case. The Drama River is not as heavily polluted as the Kłodnica River, it leads relatively clean waters, but exceeding the standards for total phosphorus and phosphate levels does not allow it to be included in any class of water purity (Wikipedia, 03.07.2020). Also the catchment area consists mainly of agricultural and forest areas, because of all this the load of incoming pollutants including PAHs is lower and the PAHs distribution is different.

As already mentioned, the highest concentration of the sum of 16 PAHs at the inflow point was observed for the watercourse supplying Pławniowice (0.389 μg/L). The highest percentage in the PAH sum was determined for PAHs with higher molecular weight (five-ring PAHs – 51.4%; six-ring PAHs – 33.2%). The percentage of the two-ring and three-ring PAHs was insignificant (approximately 6.00%). The characteristics of water pollution in Toszecki Stream (inflow to Pławniowice) and the development of the catchment areas is more similar to the Drama River than the Kłodnica River, however, the sum of concentrations of PAHs was the highest of all at the inflow. This shows that the concentration of PAHs in water can be temporary and result from, e.g., sewage discharge. Therefore, the analysis of sources of origin of the tested compounds is better based on the concentrations obtained in the bottom sediment.

All the determined PAHs demonstrated values below the limit of quantification in the surface water layer of Dzierżno Duże. In the remaining reservoirs the sum of the 16 PAH concentrations in the epilimnion was 0.0460 μg/L in Dzierżno Małe and 0.106 μg/L in Pławniowice. In Dzierżno Małe only two compounds from the PAH group were determined, i.e., NP (0.0360 μg/L) and PHE (0.0100 μg/L). The remaining PAHs were below the level of quantification. For Pławniowice the analyzed sample composition was more diverse regarding the percentage of particular PAHs. The highest concentrations were observed for the six-ring PAHs (over 40.0%) (Figure 3). When compared to the results obtained for the inflow and

Table 2. Characteristics of the analytical procedure

Matrix	The limit of detection (LOD)	The limit of quantification (LOQ)	The method quantitation limit (MQL)	The obtained recovery values [%]	The relative standard deviation RSD [%]	Uncertainty of measurement [%]	Precision reproducibility range [%]
Water	0.00200 μg/L for benzo(a)piren	0.00600 μg/L for benzo(a)piren	0.00800 μg/L for benzo(a)piren	90–115	15	up to 20.0	0–20
	0.00300 μg/L for others PAHs	0.00800 μg/L for others PAHs	0.0100 μg/L for others PAHs				
Bottom sediments	**7.00 μg/kg**	**21.0 μg/kg**	**30.0 μg/kg**	**70–115**	**15**	**up to 30.0**	**0–25**

Table 3. PAHs concentration in the water samples of the studied reservoirs (unit: [µg/L])

Compound	Inflow			Surface			Bottom			Environmental quality*	
	Range	***Mean***	***SD***	***Range***	***Mean***	***SD***	***Range***	***Mean***	***SD***	***AA-EQS***	***MAC-EQS***
DZIERŻNO DUŻE											
NP	–	< MQL	–	–	< MQL	–	–	< MQL	–	2	130
ACY	–	< MQL	–	–	< MQL	–	0.0320–0.0480	0.0400	0.00653		
ACE	–	< MQL	–	–	< MQL	–	0.0260–0.0400	0.0330	0.00572		
FL	–	< MQL	–	–	< MQL	–	–	< MQL	–		
PHE	0.0130–0.0190	0.0160	0.00245	–	< MQL	–	0.053–0.0790	0.0660	0.0106		
ANT	–	< MQL	–	–	< MQL	–	–	< MQL	–	0.1	0.1
FLA	0.0200–0.0300	0.0250	0.00408	–	< MQL	–	–	< MQL	–		
PYR	–	< MQL	–	–	< MQL	–	–	< MQL	–		
BaA	–	< MQL	–	–	< MQL	–	–	< MQL	–		
CHR	–	< MQL	–	–	< MQL	–	–	< MQL	–		
BbF	0.0100–0.0120	0.0107	0.000943	–	< MQL	–	–	< MQL	–	–	0.017
BkF	–	< MQL	–	–	< MQL	–	–	< MQL	–	–	0.017
BaP	–	< MQL	–	–	< MQL	–	–	< MQL	–	$1.7 \cdot 10^{-4}$	0.27
IcdP	–	< MQL	–	–	< MQL	–	–	< MQL	–		
DahA	–	< MQL	–	–	< MQL	–	–	< MQL	–		
BghiP	0.170–0.246	0.208	0.0310	–	< MQL	–	–	< MQL	–	–	$8.2 \cdot 10^{-3}$
∑PAHs	0.219–0.301	0.260	0.0335	–	–	–	0.111–0.167	0.139	0.0229		
∑2.3 rings PAH	0.0130–0.0190	0.0160	0.00245	–	–	–	0.111–0.167	0.139	0.0229		
∑4 rings PAH	0.0200–0.0300	0.0250	0.00408	–	–	–	–	–	–		
∑5.6 rings PAH	0.180–0.258	0.219	0.0318	–	–	–	–	–	–		
DZIERŻNO MAŁE											
NP	0.0190–0.0290	0.0240	0.00408	0.0290–0.0430	0.0360	0.00572	0.0260–0.0380	0.0320	0.00490	2	130
ACY	–	< MQL	–	–	< MQL	–	–	< MQL	–		
ACE	0.0450–0.0670	0.0560	0.00898	–	< MQL	–	–	< MQL	–		
FL	0.00900–0.0130	0.0110	0.00163	–	< MQL	–	–	< MQL	–		
PHE	0.0230–0.0350	0.0290	0.00490	0.0100–0.0120	0.0107	0.00094	0.0250–0.037	0.0310	0.00490		
ANT	–	< MQL	–	–	< MQL	–	–	< MQL	–	0.1	0.1
FLA	0.0160–0.0240	0.0200	0.00327	–	< MQL	–	0.0230–0.0350	0.0290	0.00490		
PYR	0.0100–0.0120	0.0107	0.000943	–	< MQL	–	0.0170–0.0250	0.0210	0.00327		
BaA	–	< MQL	–	–	< MQL	–	–	< MQL	–		

CHR	–	< MQL	–	–	< MQL	–	–	< MQL	–		
BbF	0.0100–0.0130	0.0113	0.00125	–	< MQL	–	0.137–0.199	0.168	0.0253	–	0.017
BkF	–	< MQL	–	–	< MQL	–	0.0790–0.111	0.095	0.0131	–	0.017
BaP	–	< MQL	–	–	< MQL	–	0.0880–0.126	0.107	0.0155	$1.7 \cdot 10^{-4}$	0.27
IcdP	0.0290–0.0410	0.0350	0.00490	–	< MQL	–	0.128–0.178	0.153	0.0204		
DahA	–	< MQL	–	–	< MQL	–	–	< MQL	–		
BghiP	–	< MQL	–	–	< MQL	–	0.0250–0.035	0.0300	0.00408	–	$8.2 \cdot 10^{-3}$
∑PAHs	0.161–0.234	0.197	0.0298	0.0410–0.0530	0.0470	0.00490	0.548–0.784	0.666	0.0963		
∑2.3 rings PAH	0.0960–0.144	0.120	0.0196	0.0410–0.0530	0.0470	0.00490	0.0510–0.0750	0.0630	0.00980		
∑4 rings PAH	0.0260–0.0360	0.0307	0.00411	–	–	–	0.0400–0.0600	0.0500	0.00816		
∑5.6 rings PAH	0.0390–0.0540	0.0463	0.00613	–	–	–	0.457–0.649	0.553	0.0784		
PŁAWNIOWICE											
NP	0.0110–0.0170	0.0140	0.00245	0.0210–0.0310	0.0260	0.00408	0.0110–0.0170	0.0140	0.00245	2	130
ACY	–	< MQL	–	–	< MQL	–	–	< MQL	–		
ACE	–	< MQL	–	–	< MQL	–	0.0100–0.0130	0.0113	0.00125		
FL	–	< MQL	–	–	< MQL	–	0.0100–0.0130	0.0113	0.00125		
PHE	0.0100–0.0120	0.0107	0.000940	0.0100–0.0140	0.0120	0.00163	0.0140–0.0220	0.0180	0.00327		
ANT	–	< MQL	–	–	< MQL	–	–	< MQL	–	0.1	0.1
FLA	0.0160–0.0240	0.0200	0.00327	–	< MQL	–	0.0290–0.0430	0.0360	0.00572		
PYR	0.0130–0.0190	0.0160	0.00245	–	< MQL	–	0.0200–0.0300	0.0250	0.00408		
BaA	–	< MQL	–	–	< MQL	–	0.0130–0.0190	0.0160	0.00245		
CHR	–	< MQL	–	–	< MQL	–	0.0100–0.0130	0.0113	0.00125		
BbF	0.0690–0.101	0.0850	0.0131	0.0110–0.0150	0.0130	0.00163	0.319–0.463	0.391	0.0588	–	0.017
BkF	0.0440–0.0620	0.0530	0.00735	0.0100–0.0120	0.0107	0.000940	0.146–0.204	0.175	0.0237	–	0.017
BaP	0.0510–0.0730	0.0620	0.00898	–	< MQL	–	0.209–0.301	0.255	0.0376	$1.7 \cdot 10^{-4}$	0.27
IcdP	0.0690–0.0970	0.0830	0.0114	0.0380–0.0520	0.0450	0.00572	0.208–0.290	0.249	0.0335		
DahA	–	< MQL	–	–	< MQL	–	0.0230–0.0350	0.0290	0.00490		
BghiP	0.0380–0.0540	0.0460	0.00653	–	< MQL	–	0.0370–0.0530	0.0450	0.00653	–	$8.2 \cdot 10^{-3}$
∑PAHs	0.321–0.459	0.390	0.0563	0.0920–0.122	0.107	0.0123	1.06–1.52	1.29	0.187		
∑2.3 rings PAH	0.0210–0.029	0.0250	0.00330	0.0310–0.045	0.0380	0.00570	0.0450–0.0650	0.0550	0.00820		
∑4 rings PAH	0.0290–0.0430	0.0360	0.00572	–	–	–	0.0720–0.105	0.0883	0.0135		
∑5.6 rings PAH	0.271–0.387	0.329	0.0474	0.0610–0.0770	0.0690	0.00650	0.942–1.35	1.14	0.165		

< MQL – PAH concentration below the method quantitation limit

* environmental quality standards for priority substances for natural watercourses and lakes, including artificial surface water bodies and heavily modified surface water bodies

AA-EQS – annual average environmental quality standards

MAC-EQS – maximum allowable concentration environmental quality standards bottom layer samples, the lowest concentrations of the PAH sum were determined in the surface water layer of the discussed reservoirs. Differences in PAH concentrations between the surface and bottom layers of water may be related to the sorption process on the suspension or plankton organism biomass and the subsequent sedimentation and penetration of PAHs from the upper water layer to the bottom layers and finally bottom sediments.

The highest fluctuations in the sum of the 16 determined PAHs occurred in the water samples collected from the bottom layer of the reservoirs. The values were as follows: 0.142 µg/L for Dzierżno Duże, 0.666 µg/L for Dzierżno Małe and 1.29 µg/L for Pławniowice. In Dzierżno Duże the contents of three PAHs were observed in the hypolimnion (bottom layer of a lake): ACY (0.0400 µg/L), ACE (0.0330 µg/L) and PHE (0.0660 µg/L). In Dzierżno Małe, the highest percentage was determined for PAHs with higher molecular weight (five-ring PAHs – 55.6 %; six-ring PAHs – 27.5 %). In the Pławniowice hypolimnion the five-ring PAHs dominated (66.1%). The concentration of BaP (one of the most toxic aromatic hydrocarbons) (Duodu et al. 2017) was 0.255 µg/L.

Higher concentrations of PAHs with higher molecular weight in the bottom water layers point to the important role played by the sedimentation process in the transport of PAHs into deeper water layers and bottom sediments. It may be assumed that the higher concentrations observed in the bottom water layers result from the mentioned sedimentation of suspensions that contain PAHs adsorbed on their surface (Tobiszewski and Namieśnik 2012, Duodu et al. 2017). In suitable environmental conditions some of PAHs contained in bottom sediments may undergo desorption and be present in the bottom layer of water (Pohl et al. 2018). Additionally, in the bottom layer the environmental conditions are usually different than in the surface water layer. The temperature is lower and oxygen depletion or anaerobic conditions are observed which affects the biodegradation or biotransformation of PAHs to less complex metabolites (Lawal 2017).

The Regulation of the Minister of Maritime Economy and Inland Navigation of 11 October 2019 in force in Poland defines environmental quality standards for priority substances which should not be exceeded due to the protection of human health and the environment (Table 3).

The cited regulation provides guidelines for the concentration of naphthalene, anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene at the level of annual average environmental quality standards (AA-EQS) and maximum allowable concentration environmental quality standards (MAC-EQS). In the case of Dzierżno Duże, the MAC-EQS was exceeded at the inflow for BghiP. In the case of Dzierżno Małe, BbF and BkF concentrations exceeded both AA-EQS and MAC-EQS at all measuring points. In the surface water samples the MAC-EQS value for BghiP was also exceeded. In turn, in Pławniowice, BbF and BkF concentrations exceeded the AA-EQS and MAC-EQS guidelines at the inflow and in the surface layer. Similarly, in the case of BghiP the concentration value exceeded MAC-EQS. The classification of water quality on the basis of the cited regulation shows that exceedances occur mainly at the inflow and in the bottom water zone. This shows how much influence on the quality of water in the reservoir has the quality of the supplied water and how big is the role of PAH sorption in suspension and sedimentation of these pollutants into the deeper layers of water where they can then be adsorbed on bottom sediment.

One of the most toxic aromatic hydrocarbons is benzo(a)piren. According to the regulation, the occurrence of BaP in the aquatic environment can be considered as an indicator of the occurrence of other PAHs, therefore for the purposes of comparisons with environmental quality standards for aquatic flora or fauna or the corresponding AA-EQS in water it is enough to monitor hydrocarbon. BaP concentration exceeded AA-EQS in Dzierżno Małe (bottom layer of water). In the case of Pławniowice, the exceedance of AA-EQS at the inflow and the exceedance of AA-EQS and MAC-EQS in the bottom layer of water were noted. The concentrations at this level may have negative effects on the environment and humans and measures should be taken to reduce the concentration of this compound in the analyzed aquatic environments.

PAHs in the sediments

Table 4 presents concentrations of the determined PAHs in the bottom sediments of the three studied reservoirs in the Hydrotechnical System of the Kłodnica River

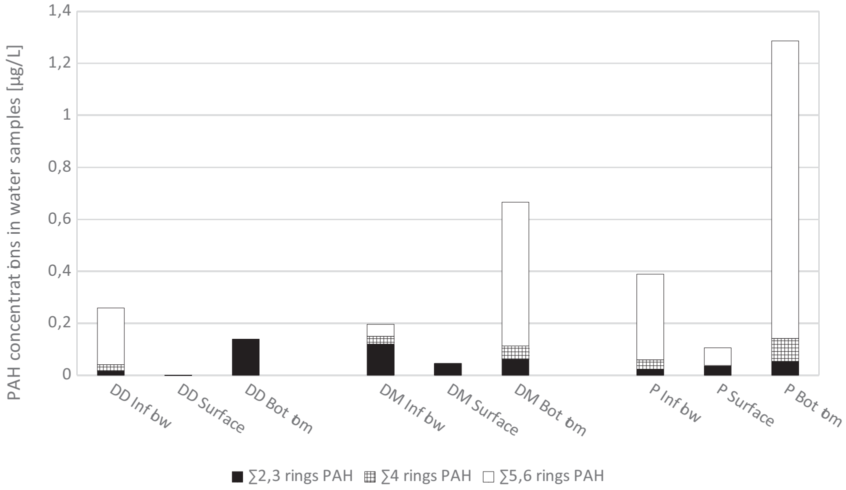

Fig. 3. PAH concentrations in water samples including the number of rings

The pollution of upper layer of bottom sediment with PAHs in Dzierżno Małe and Pławniowice was similar. The sum of the determined hydrocarbons was 6.95 µg/g for Dzierżno Małe and 7.48 µg/g for Pławniowice. The highest PAH concentrations were 0.955 µg/g (BghiP) in Dzierżno Małe and 1.11 µg/g (FLA) in Pławniowice. The percentage of PAHs with a given number of rings in the bottom sediments was also similar (Figure 4). The hydrocarbons with higher molecular weight (i.e. four-, five- and six-ring PAHs) dominated. In the case of PAHs concentration in the bottom layer of sediment the sum was respectively 5.91 µg/g for Dzierżno Małe and 3.14 µg/g for Pławniowice. For Pławniowice the concentration was two times smaller than for upper layer for this reservoir. Whereas the distribution of PAH homologs due to the number of rings was comparable to the upper layer of Pławniowice sediments and the upper and bottom layers of sediments from Dzierżno Małe.

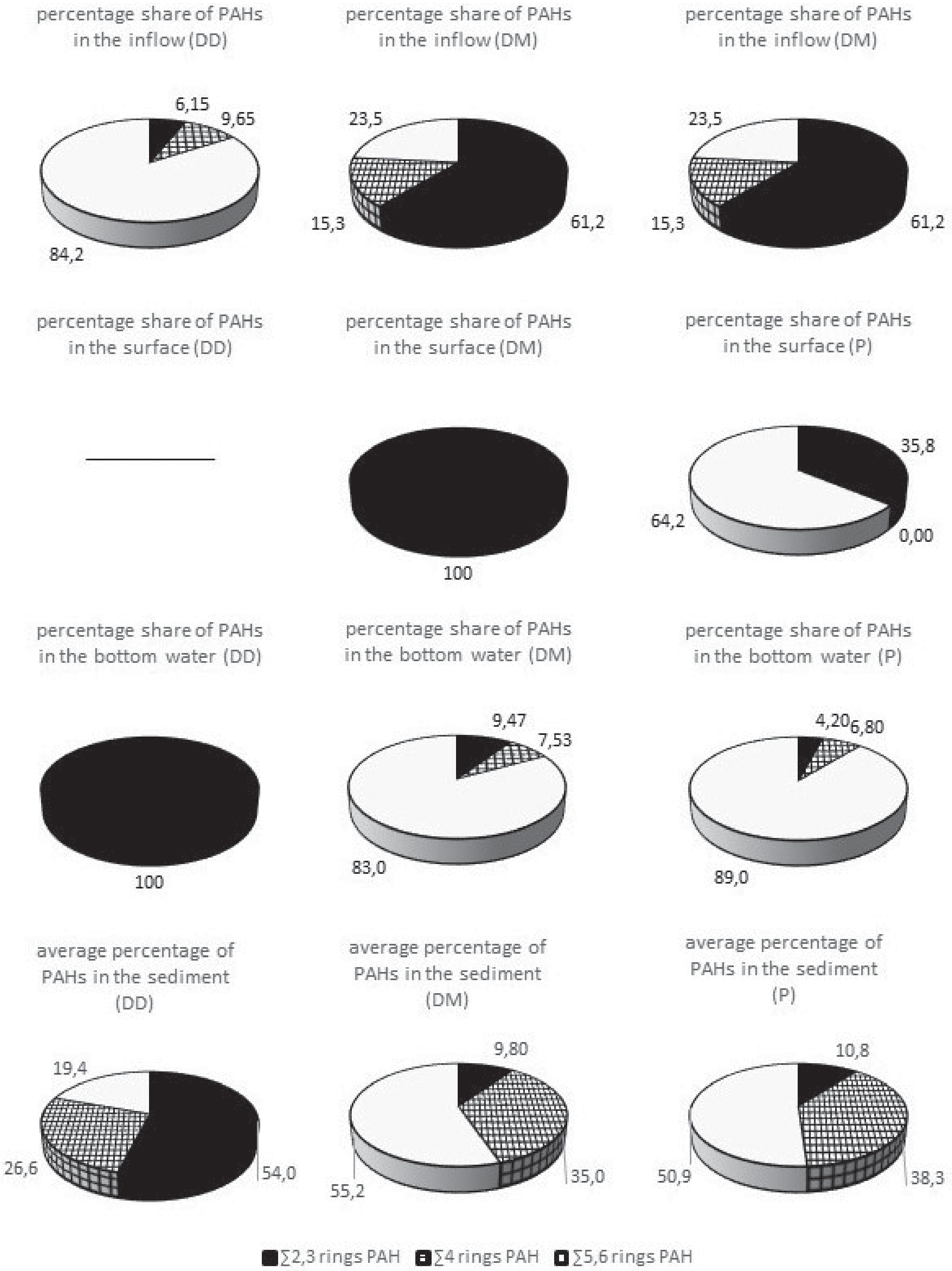

Fig. 4. Percentage of PAHs at the subsequent measurement points at the reservoirs in the Hydrotechnical System of Kłodnica River

Table 4. PAHs concentration in the sediment bottom samples of the studied reservoirs (unit: [µg/g])

Compound	Bottom layer of sediment			Upper layer of sediment		
	Range	Mean	SD	Range	Mean	SD
DZIERŻNO DUŻE						
NP	4.86–8.88	6.87	2.01	5.34–9.76	7.55	2.21
ACY	0.477–0.883	0.68	0.203	0.442–0.818	0.63	0.188
ACE	2.26–4.20	3.23	0.966	2.49–4.61	3.55	1.06
FL	2.50–4.62	3.56	1.06	2.83–5.25	4.04	1.21
PHE	5.76–10.7	8.22	2.46	6.86–12.7	9.78	2.92
ANT	1.65–3.07	2.36	0.706	2.19–4.05	3.12	0.933
FLA	3.57–6.61	5.09	1.52	4.12–7.64	5.88	1.76
PYR	2.38–4.20	3.29	0.908	2.74–4.82	3.78	1.04
BaA	1.36–2.40	1.88	0.519	1.67–2.94	2.3	0.635
CHR	1.33–2.46	1.89	0.565	1.61–2.98	2.29	0.685
BbF	1.99–3.17	2.58	0.593	2.45–3.91	3.18	0.731
BkF	0.831–1.43	1.13	0.299	1.07–1.85	1.46	0.387
BaP	1.36–2.20	1.78	0.418	1.70–2.74	2.22	0.522
IcdP	0.759–1.32	1.04	0.281	1.04–1.82	1.43	0.386
DahA	0.485–0.800	0.64	0.155	0.540–0.880	0.71	0.172
BghiP	1.12–1.90	1.51	0.391	1.22–2.07	1.64	0.425
∑PAHs	32.7–58.8	45.8	10.7	38.3–68.8	53.6	12.5
∑2.3 rings PAH	17.5–32.3	24.9	6.05	20.1–37.2	28.7	6.96
∑4 rings PAH	8.64–15.7	12.2	2.87	10.1–18.4	14.3	3.36
∑5.6 rings PAH	6.54–10.8	8.68	1.74	8.02–13.3	10.6	2.14
DZIERŻNO MAŁE						
NP	0.0720–0.132	0.102	0.024	0.0880–0.160	0.124	0.0294
ACY	–	< MQL	–	–	< MQL	–
ACE	0.0300–0.400	0.034	0.004	0.0270–0.0510	0.039	0.00980
FL	0.0440–0.820	0.063	0.016	0.0550–0.103	0.079	0.0196
PHE	0.205–0.379	0.292	0.071	0.253–0.469	0.361	0.0882
ANT	0.0480–0.0880	0.068	0.016	0.0610–0.113	0.087	0.0212
FLA	0.470–0.872	0.671	0.164	0.562–1.04	0.802	0.196
PYR	0.366–0.644	0.505	0.113	0.439–0.775	0.607	0.137

BaA	0.269–0.475	0.372	0.084	0.311–0.549	0.430	0.097
CHR	0.354–0.656	0.505	0.123	0.427–0.791	0.609	0.149
BbF	0.541–0.865	0.703	0.132	0.657–1.05	0.853	0.160
BkF	0.212–0.366	0.289	0.063	0.243–0.417	0.330	0.0710
BaP	0.406–0.656	0.531	0.102	0.484–0.782	0.633	0.122
IcdP	0.434–0.756	0.595	0.131	0.514–0.894	0.704	0.155
DahA	0.243–0.397	0.320	0.063	0.253–0.415	0.334	0.0661
BghiP	0.631–1.07	0.852	0.180	0.708–1.20	0.955	0.202
∑PAHs	4.33–7.48	5.90	1.29	5.08–8.81	6.95	1.52
∑2.3 rings PAH	0.399–0.721	0.559	0.131	0.484–0.896	0.690	0.168
∑4 rings PAH	1.46–2.65	2.053	0.485	1.74–3.16	2.45	0.579
∑5.6 rings PAH	2.47–4.11	3.290	0.672	2.86–4.76	3.81	0.776
PŁAWNIOWICE						
NP	0.0490–0.0910	0.070	0.0171	0.0740–0.136	0.105	0.0253
ACY	–	< MQL	–	–	< MQL	–
ACE	–	< MQL	–	0.0330–0.0610	0.0470	0.0114
FL	0.0270–0.0490	0.0380	0.0090	0.0400–0.0740	0.0570	0.0139
PHE	0.136–0.252	0.194	0.0474	0.334–0.618	0.476	0.116
ANT	0.0260–0.0480	0.0370	0.0090	0.0660–0.122	0.0940	0.0229
FLA	0.311–0.577	0.444	0.109	0.778–1.44	1.11	0.271
PYR	0.217–0.383	0.300	0.0678	0.568–1.00	0.784	0.176
BaA	0.109–0.191	0.150	0.0335	0.304–0.536	0.420	0.0947
CHR	0.189–0.349	0.269	0.0653	0.433–0.801	0.617	0.150
BbF	0.268–0.428	0.348	0.0653	0.693–1.12	0.900	0.169
BkF	0.135–0.233	0.184	0.0400	0.295–0.509	0.402	0.0874
BaP	0.204–0.330	0.267	0.0514	0.530–0.856	0.693	0.133
IcdP	0.207–0.359	0.283	0.0621	0.485–0.843	0.664	0.146
DahA	0.149–0.245	0.197	0.0392	0.228–0.374	0.301	0.060
BghiP	0.247–0.421	0.334	0.0710	0.602–1.02	0.813	0.172
∑PAHs	2.27–3.96	3.12	0.687	5.46–9.50	7.48	1.65
∑2.3 rings PAH	0.238–0.440	0.339	0.0825	0.547–1.01	0.779	0.189
∑4 rings PAH	0.826–1.50	1.16	0.275	2.08–3.78	2.93	0.692
∑5.6 rings PAH	1.21–2.02	1.61	0.329	2.83–4.71	3.77	0.768

< MQL – PAH concentration below the method quantitation limit

The determined PAH concentrations were significantly higher in sediments of Dzierżno Duże compared to the rest of the reservoirs (Figure 5). The sum of the 16 PAHs was 53.6 µg/g in the upper layer and 45.8 µg/g in the bottom layer. In the examined sediment, the following compounds dominated: PHE (9.78 µg/g upper layer, 8.22 µg/g bottom layer), NP (7.55 µg/g upper layer, 6.87 µg/g bottom layer), FLA (5.88 µg/g upper layer, 5.09 µg/g bottom layer) and FL (4.04 µg/g upper layer, 3.56 µg/g bottom layer). The percentage share of PAHs was different than for the other two reservoirs. The highest percentage in the bottom sediment sample was observed for the two and three-ring PAHs (average 54.0%) whereas the lowest one was determined for the PAHs with higher molecular weight (five and six-ring PAHs – average 19.4%) (Figure 4).

The PAH concentrations at Dzierżno Duże inflow point were lower in comparison to the concentrations observed in the watercourses supplying the remaining two reservoirs. However, the total PAH concentration determined for the bottom sediment of Dzierżno Duże was by nearly eight times higher than the values determined for the bottom sediments in the remaining reservoirs. The catchment area size of Dzierżno Duże is 545.01 km^2 while that of Dzierżno Małe is 177.99 km^2 and of Pławniowice is 121.79 km^2. Additionally, spatial development forms in the catchment area are different. Agricultural and forest areas constitute over 90% of the entire area of the Dzierżno Małe and Pławniowice catchments. In the case of Dzierżno Duże these areas constitute 69%, while built-up and transport areas are 24% (130.80 km^2). It shows a significantly affected by spatial development forms in the catchment area on the degree of bottom sediment pollution with PAH compounds. PAHs are introduced into the reservoir not only with the inflow water but also with surface runoff and as deposition from the air.

Comparing the degree of bottom sediment contamination of the Hydrotechnical System of the Kłodnica River reservoirs, the impact of differential anthropopressure on the contamination of bottom sediment by PAHs was demonstrated. In particular, it has been shown that industrialized surfaces have a dominant role in the pollution of bottom sediments of anthropogenic aquatic ecosystems (Figure 6).

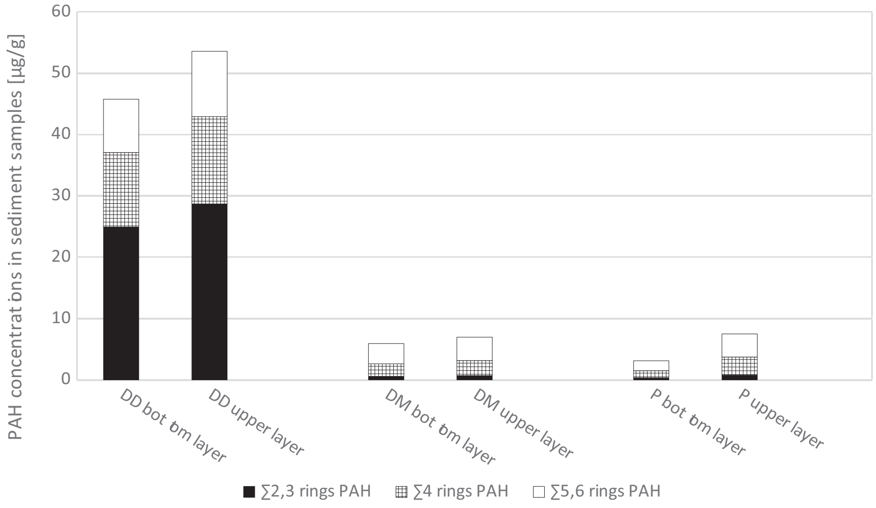

Fig. 5. PAH concentrations in sediment samples including the number of rings

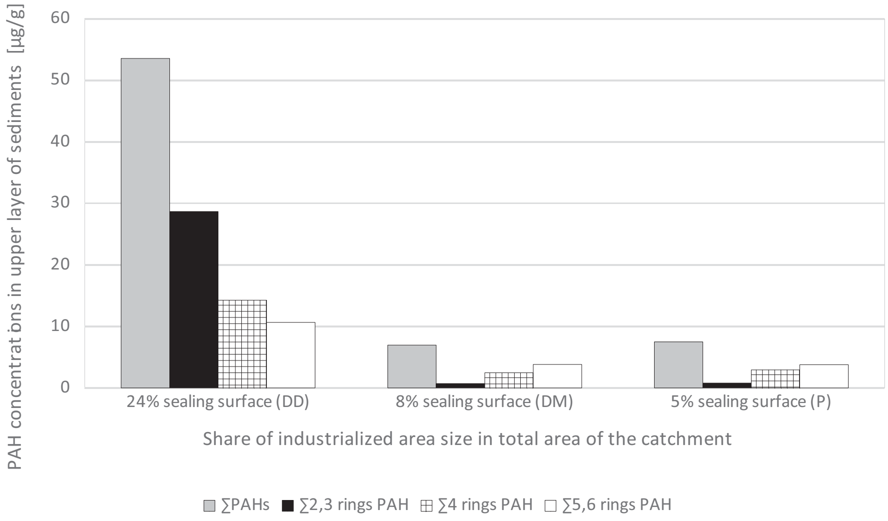

Fig. 6. Correlation between the share of industrialized areas in total area of the catchment and the concentration of PAHs in bottom sediments

The exploitation of mineral deposits, building aggregates or sand is carried out all over the world. Knowledge of the structure and method of managing the drainage basins supplying anthropogenic reservoirs is necessary to develop principles for the protection and exploitation of their water resources.

Ecotoxicological analysis of the tested bottom sediments

The bottom sediment quality assessment is one of the bases for determining the way of their management in the environment or the method of their disposal. Assessment of the quality of bottom sediments of the Hydrotechnical System of the Kłodnica River was carried out on the basis of ecotoxicological criteria: TEC – Threshold Effect Concentration and PEC – Probable Effect Concentration. TEC determines the concentration of the compound below which no toxic effects on organisms are observed (in the table marked as I), while PEC determines the concentration above which toxic effects on organisms are often observed (in the table marked as III). According to He and all (2016), the concentration of PAHs at the levels between the TEC and PEC values will cause sporadic adverse effects (in the table marked as II). Sludge is considered to be toxic to aquatic organisms even when exceeding the PEC threshold content is found for only one chemical compound (Macdonald et al. 2000, Solberg et al. 2003). The tables summarize the classification of bottom sediments for three reservoirs of the Hydrotechnical System of the Kłodnica River (Table 5).

In the case of Dzierżno Duże, the concentrations of selected PAHs in sediments collected from both the upper and bottom layers exceeded the PEC values. This is equivalent to the fact that sediments may cause a toxic effect in this reservoir. In the case of Dzierżno Małe the concentrations of NP (0.102 µg/g) and FL (0.0150 µg/g) in bottom layer and NP (0.124 µg/g) in upper layer were below TEC. The remaining concentrations of selected PAHs in the bottom and the upper layer were between TEC and PEC values. This indicates that sediments of Dzierżno Małe can possibly have sporadic adverse effects. In turn, the sediments collected from Plawniowice were the least contaminated with PAH compounds compared to the other two reservoirs. Below TEC was NP (0.0700 µg/g), FL (0.0380 µg/g), PHE (0.194 µg/g), ANT (0.0370 µg/g) in the bottom layer and NP (0.105 µg/g), FL (0.0570 µg/g) in the upper layer. The remaining detected PAHs were between the TEC and PEC values. On this basis, it can be determined that bottom sediments from Pławniowice can cause possible sporadic adverse effects.

Pollution of the Hydrotechnical System of the Kłodnica River reservoirs against other reservoirs

The pollution of the reservoirs included in the so-called Hydrotechnical System of the Kłodnica River (Dzierżno Duże, Dzierżno Małe, and Pławniowice) in comparison to other reservoirs is presented in Table 6. The average PAH concentration sums obtained for the sampled bottom sediments have been compared with the data on other reservoirs located in different parts of the world.

The comparison demonstrates that the bottom sediments of the examined anthropogenic reservoirs are highly polluted with PAHs. The discussed concentrations in the sediments of Dzierżno Małe and Pławniowice are comparable with the results obtained by other researchers. This concentration was 6 950 µg/kg and 7 480 µg/kg in Dzierżno Małe and Pławniowice respectively. Compared to other Polish reservoirs, the average concentrations of PAHs obtained in own research in these reservoirs are comparable or lower. A similar level of average total concentration was obtained in Blachownia reservoir, Poland (6 320 µg/kg), Jasień Pn., Poland (7 540 µg/kg), the Majia River system, China (1 170 µg/kg), Cienfuegos Bay, Cuba (3 960 µg/kg), Thohoyandou, Limpopo Province, South Africa (Nzhelele River 7 040 µg/kg, the Mutale River 5 830 µg/kg, and the Luvuvhu River 5 970 µg/kg). For Dzierżno Duże, the sum of the 16 determined PAHs (53 600 µg/kg) usually was higher than the values presented in the literature.

Yuan et al. (2017) studied the content and sources of PAHs in the Yangzonghai Lake bottom sediments in China. They noted that PAH concentrations significantly changed from the

Table 5. Classification of bottom sediments of the Hydrotechnical System of Kłodnica River based on ecotoxicological criteria

PAH [µg/g]	Literature values*		Sampling points, bottom sediment classification according to ecotoxicological criteria					
	TEC	PEC	DD bottom layer	DD upper layer	DM bottom layer	DM upper layer	P bottom layer	P upper layer
NP	0.176	0.561	III	III	I	I	I	I
FL	0.077	0.536	III	III	I	II	I	I
PHE	0.204	1.170	III	III	II	II	I	II
ANT	0.057	0.845	III	III	II	II	I	II
FLA	0.423	2.230	III	III	II	II	II	II
PYR	0.195	1.520	III	III	II	II	II	II
BaA	0.108	1.050	III	III	II	II	II	II
CHR	0.166	1.290	III	III	II	II	II	II
BaP	0.150	1.450	III	III	II	II	II	II
∑ PAHs	1.610	22.800	III	III	II	II	II	II

* Macdonald et al., 2000, Solberg et al., 2003, I – PAH < TEC (non-contaminated sludge, no toxic effect), II – TEC <PAH <PEC (possible sporadic adverse effects), III – PAH> PEC (contaminated sludge, concentration of the compound that may cause a toxic effect)

bottom to the upper layer of the sediment core. The ∑PAHs concentration ranged from 201 to 1 910 µg/kg. Similarly to own research, Yuan et al. (2017) recorded the difference in PAH concentrations in sediment cores between remote lakes and those closer to developed regions or cities which they attributed to different transportation modes and energy consumption.

A similar correlation was noted by Liu et al. (2012), according to which PAHs concentrations appear to be consistent with the respective regions' degree of industrialization. For the Tuhai-Majia River system, the concentrations of total PAHs ranged from 312 to 3740 µg/kg. Compared with other water systems in the Haihe River basin, these values were considerably higher than the total PAHs concentrations measured in the sediment from the Luan River water system (ranged from 21.0 to 287 µg/kg (Cao et al. 2010)) and lower than those measured in the Haihe River of Tianjin section (ranged from 775 to 255 371 µg/kg (Jiang

Table 6. Comparison of PAH concentrations in the bottom sediments of selected water reservoirs

Examined reservoir	average ∑16 PAHs [µg/kg]	Literature reference
Dzierżno Duże, Poland	53 600*	Present study
Dzierżno Małe, Poland	6 950*	Present study
Pławniowice, Poland	7 480*	Present study
Blachownia, Silesian Voivodeship, Poland	6 320	Pohl et al. 2018
Człuchowskie, Poland	49 900	Bojakowska et al. 2012
Trzesiecko, Poland	22 800	
Krzywa Kuta, Poland	17 900	
Pauzeńskie, Poland	13 900	
Wierzysko, Poland	13 600	
Wegorzno, Poland	11 400	
Dąbrowa Wielka, Poland	11 800	
Tuchomskie, Poland	11 100	
Jasień Pn., Poland	7 540	
Lubiąż, Poland	12 800	
Głebokie, Poland	9 510	
Pniewskie, Poland	10 600	
Thane Creek of Mumbai, India	99.0	Basavaiah et al. 2017
Chitrapuzha River, India	5 050–33 100	Sanil Kumar et al. 2016
Shilianghe Reservoir, Eastern China	213	Zhang et al. 2016
Majia River system, China	1 170	Liu et al. 2012
Tuhai River system, China	589	
Deep Bay, Southern China	354	Qiu et al. 2009
Cienfuegos Bay, Cuba	3 960	Tolosa et al. 2009
Mutshundudi River, Africa	11 700	Nekhavhambe et al. 2014
Nzhelele River, Africa	7 040	
Mutale River, Africa	5 830	
Dzindi River, Africa	2 560	
Luvuvhu River, Africa	5 970	
River-reservoir systems, Democratic Republic of Congo	63.9	Mwanamoki et al. 2014
Feitsui Reservoir, Taiwan	400	Fan et al. 2010
Mountain lakes, across the Tibetan Plateau	176	Yang et al. 2016
Guba Pechenga, Barents Sea, Russia	1 480	Savinov et al. 2003
Danube River, Hungary	8.30–1 200	Nagy et al. 2014
Durance River, France	57–1 530	Kanzari et al. 2015
Ammer River, Germany	112–22 900	Liu et al. 2013
Gulf of Trieste, Italy	214–4 420	Bajt 2014
Porto Atlantic coast, Portugal	**52 000**	**Rocha et al. 2017**

* average ∑16 PAH concentrations in the upper layer of sediment

et al. 2001)). These results could be attributed to the fact that Tianjin was an old and established industrial city with the largest port in the north of China, while the Luan River largely served a mountainous area where it was primarily utilized for agriculture, which shows how much impact on the concentration of PAHs in sediments has the type of catchment areas management.

Source apportionment

Characteristic ratios can provide information about the anthropogenic sources of PAHs (Liu et al. 2012, Duan et al. 2018). Analysis in this field is necessary to reduce their concentration in the environment in the future. Table 7 summarizes selected diagnostic ratios along with the distribution of possible sources. The analysis of diagnostic ratios shows that their values are similar to the values of indicators determining air quality for low emissions (coal and wood combustion). Taking into account the catchment character, it seems that this type of emissions probably may be one of the sources of PAHs in three examined reservoirs of the Hydrotechnical System of the Kłodnica River.

In the case of the bottom sediments of Dzierżno Duże the PAHs with lower molecular weight, i.e., the pyrogenic origin of PAHs, dominated. The values of the PHE/ANT (3.13), FLA/PYR (1.56), ANT/(ANT+PHE) (0.24), FLA/(FLA + PYR) (0.61), BaA/(BaA+CHR) (0.50) and BaP/BghiP (1.35) ratios are similar to the values of indicators determining air quality for solid fuels combustion (e.g. coal, grass, wood). Taking into account the type of catchment area management (19% of the catchment area is built-up, of which 42% of this area is made by single-family housing and 27% by multi-family housing) this type of PAH source in the reservoir is likely.

For Dzierżno Małe, the diagnostic ratio analysis showed that the pyrogenic processes, rather than the petrogenic ones, seem to be the source of PAHs in its water and bottom sediments. The combustion is indicated as the possible PAH source by the following ratio values: PHE/ANT, FLA/PYR, ANT/(ANT+PHE), FLA/(FLA + PYR), BaA/(BaA+CHR). The BaP/BghiP ratio observed for the bottom sediment samples (0.66) points to the possible participation of traffic (surface runoff from the road) in the reservoir. The population density in the Dzierżno Małe catchment area is less dense than the population density of the Dzierżno Duże catchment area. The single-family housing makes 72% of the buildings. The solid fuel combustion in such buildings may be one of the potential emission sources of PAHs into the environment.

For Pławniowice, similar correlations were observed. The ratios of PHE/ANT, FLA/PYR, ANT/(ANT+PHE), FLA/(FLA + PYR), BaA/(BaA+CHR), IcdP/(IcdP + BghiP) are also similar to the values of indicators determining air quality for solid fuels combustion. In this case, in the catchment area, single-family houses constitute 67% of the urbanized area.

Table 7. Identification of the PAH source based on the diagnostic ratios

	Origin/source	*PHE/ANT*	*FLA/PYR*	*∑LMW/ ∑HMW*	*ANT/(ANT + PHE)*	*FLA/(FLA + PYR)*	*BaA/ (BaA + CHR)*	*IcdP/(IcdP + BghiP)*	*BbF/BkF*	*BaP/BghiP*
Literature data	Petrogenic	> 10[b]	< 1[b]	>1[a]	< 0.1[a. b]	< 0.4[a. b]	< 0.2[a. b]	< 0.2[a. b]	–	–
	Pyrogenic	–	–	<1[a]	> 0.1[a. b]	–	> 0.35[a. b]	–	–	–
	Liquid fuel combustion (e.g. crude oil)	–	–	–	–	0.4–0.5[a. b]	–	0.2–0.5[a.b]	–	–
	Solid fuel combustion (e.g. coal, grass, wood)	< 10[b]	> 1[b]	–	0.24[c]	> 0.5[a. b] 0.53[d] 0.57[c]	0.2–0.35[a.b] 0.46[c] 0.5[d]	0.33[d] > 0.5[a. b] 0.56[c]	–	0.9–6.6[c] > 1.25[d]
	Non-traffic emission	–	–	–	–	–	–	–	–	< 0.6[a]
	Traffic emissions	–	–	–	–	–	–	–	–	> 0.6[a]
	Aluminum smelter emissions	–	–	–	–	–	–	–	2.5– .9[a]	–
Present study	DD bottom sediment*	3.13	1.56	1.31	0.240	0.610	0.500	0.470	2.18	1.35
	DM bottom sediment*	4.15	1.32	0.150	0.190	0.570	0.410	0.420	2.58	0.660
	*P bottom sediment**	*5.06*	*1.42*	*0.150*	*0.160*	*0.590*	*0.410*	*0.450*	*2.24*	*0.850*

[a] Tobiszewski and Namieśnik 2012, [b] Duodu et al. 2017, [c] Kong et al. 2010 – coal combustion, [d] Kong et al. 2010 – coal/coke combustion
∑LMW – PAHs with low molecular weight (LMW), such as naphthalene, acenaphthylene, fluorene, phenanthrene or pyrene;
∑HMW – PAHs with high molecular weight (HMW), such as benzo[g,h,i]perylene, indeno[1,2,3-c,d]pyrene or coronene;
* diagnostic ratios calculated for average PAHs in the upper sediment layer

Conclusions

Polycyclic aromatic hydrocarbons were analyzed in three reservoirs located in highly urbanized and industrialized area in Poland. The results show that the management of the catchment area has a significant impact on the degree of contamination of bottom sediments with PAHs. Under the conditions of diversified anthropopressure, neighboring catchment areas may differ significantly in terms of the level of threat they pose to bottom sediments of anthropogenic limnic ecosystems. It has been noted that catchment management, particularly the share of industrialized area size in total area of the catchment, affects the high level of pollution of bottom sediments by PAHs up to the level that may be toxic to plant and animal organisms. The differentiation of bottom sediments into the upper and the lower layers in the sediment core indicated that the higher level of PAH content in the surface layer of sediments (5 cm layer) than in the deeper layers (25 cm layer) may be related to the decomposition of these compounds over a longer period of time. In turn, the analysis of the diagnostic ratios of selected PAHs for bottom sediments showed similarity to the characteristic values for indicators determining the impact of low emissions on air quality. This highlights the role of atmospheric air pollution as a source of PAHs deposition.

Summarizing, the accumulation of difficult to decompose PAHs in bottom sediments is a serious problem for the limousine ecosystem. Improving the quality of flowing water in highly anthropopressive areas does not mean reducing the PAHs content in the bottom sediments of the reservoir. To change this situation requires the use of reclamation methods that take into account the specificities of such pollutants. It should keep in mind that each limousine ecosystem has its own specificity, therefore it is necessary to know the impact of the way its catchment areas is managed indicating possible sources of introducing PAHs into the environment. This is the basis for preventing the pollution of aquatic ecosystems.

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Rozkład przestrzenny, ryzyko ekologiczne i źródła wielopierścieniowych węglowodorów aromatycznych (WWA) w wodzie i osadach dennych antropogenicznych ekosystemów limnicznych w warunkach zróżnicowanej antropopresji

Streszczenie. W badaniach określono stężenia wybranych wielopierścieniowych węglowodorów aromatycznych (WWA) w wodach i osadach dennych zbiorników Hydrowęzła rzeki Kłodnicy oraz określono ich rozkład w zależności od ilości pierścieni, wpływ ekotoksykologiczny na badane ekosystemy wodne oraz możliwe źródła ich pochodzenia. Próbki poddano analizie jakościowej i ilościowej metodą chromatografii gazowej sprzężonej z detektorem masowym GC-MS, wykorzystując kolumnę typu ZB-5MS i jonizację elektronową. Suma 16 WWA w wodzie wahała się w granicach 0.111–0.301 µg/L (średnio 0.200 µg/L) w Dzierżnie Dużym, 0.0410–0.784 µg/L (średnio 0.303 µg/L) w Dzierżnie Małym i 0.0920–1.52 µg/L (średnia 0.596 µg/L) w Pławniowicach. Podczas gdy w osadach wynosiła odpowiednio: 17.3–37.2 µg/g (średnio 26.8 µg/g), 4.33–8.81 µg/g (6.43 µg/g) i 2.27–9.50 µg/g (5.30 µg/g). Stężenie WWA w osadach dennych zbiorników wodnych, których zagospodarowanie przestrzenne zlewni stanowi w ponad 90% grunty rolne i leśne, było do ośmiu razy niższe niż w osadach zbiornika, którego powierzchnia ta wynosi 69%, podczas gdy tereny zabudowane i transportowe 24%. W osadach dennych zbiorników Dzierżno Małe i Pławniowice dominują WWA o 5 i 6 pierścieniach, natomiast w zbiorniku Dzierżno Duże WWA o 2 i 3 pierścieniach. Wyższe stężenia WWA o większej masie cząsteczkowej stwierdzone w przydennych warstwach wody potwierdzają rolę procesu sedymentacji w transporcie tych związków w zbiornikach. Ocena jakości osadów w oparciu o kryteria ekotoksykologiczne wykazała, że WWA mogą powodować toksyczne działanie w Dzierżnie Dużym, natomiast w Dzierżnie Małym i Pławniowicach mogą powodować sporadyczne działania niepożądane. Prawdopodobnym źródłem WWA w zbiornikach jest niska emisja.