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Polycyclic aromatic hydrocarbons in water and bottom sediments of a shallow, lowland dammed reservoir (on the example of the reservoir Blachownia, South Poland)

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Abstract: The content of polycyclic aromatic hydrocarbons (PAHs) in water and sediments of the Blachownia reservoir (South Poland) was investigated. Spatial variability of PAH concentrations in the longitudinal profile of the tank was determined. PAHs in samples were determined by gas chromatography coupled with mass spectrometric detection (GC-MS QP-2010 Plus Shimadzu) using an internal standard. Concentrations ranged from 0.103 μg/L to 2.667 μg/L (Σ16 PAHs) in water samples and from 2.329 mg/kg d.w. to 9.078 mg/kg d.w. (Σ16 PAHs) in sediment samples. A pollution balance was calculated and it was estimated that the inflow load was 17.70 kg PAHs during the year and the outflow load was 9.30 kg PAHs per year. Accumulation of about 50% of the annual PAH loads (8.90 kg) is a threat to the ecological condition of the ecosystem. It was calculated that the PAH loads in bottom sediment were about 80 kg, which limits their economic use. Improvement of the ecological status of this type of reservoir can be achieved by removing the sediment. Analysis of the diagnostic ratios obtained for selected PAHs showed that the potential sources of PAH emissions in small agricultural – forest catchments can be combustion of a coal, wood, plant material (low emission, forest fires, burning grass, etc.). Transportation is also significant.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds that consist of fused aromatic rings and do not contain heteroatoms or carry substituents. Differences in the configuration of rings may lead to differences in physical and chemical properties. The individual PAHs differ in boiling point, water solubility, or susceptibility to sorption (Tobiszewski and Namieśnik 2012). Different is also the interaction of PAHs with plant and animal organisms (Kalinowski and Załęska-Radziwiłł 2009, Załęska-Radziwiłł et al. 2008). They are dangerous to the environment and humans. Some of them have been identified as carcinogenic, mutagenic or teratogenic (Rogula-Kozłowska et al. 2012, Włodarczyk-Makuła 2011, Włodarczyk-Makuła 2012). Of more than 100 compounds in this group, in practice, the list of sixteen compounds is used: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluorantene, benzo(k)fluorantene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene (EPA 1984).

In waters, they originate from wastewaters from certain industries (coke-making industry, iron smelting industry, wood industry), municipal sewage, and diffuse pollution associated with transport and low-emission (Bathi et al. 2008, Khalili et al.1995, Kostecki and Czaplicka 2001, Pistelok and Jureczko 2014, Rogula-Kozłowska et al. 2012, Stein et al. 2006). These compounds can also be of natural origin--volcanic eruptions and fires (Załęska-Radziwiłł et. al. 2008). In the air hydrocarbons with fewer (2 and 3) rings are present partially in the gas phase, partially in the form adsorbed on the surface of dust, and the higher, mainly as adsorbed on the surface of particulate matter. These pollutants can enter surface waters along with melting and rainy waters, and can be an important source of these compounds (Kubiak 2013, Sapota 2002, Wolska 2002).

In the aquatic environment, PAHs are mainly suspended, which is due to their low water solubility. These compounds are subject to sorption on the particulate suspensions. After falling to the bottom, they accumulate in bottom sediments, where they can affect aquatic organisms, accumulate in them and become a sensitive indicator of anthropopression (Duodu et al. 2017, Feng et al. 2016). In suitable environmental conditions some of PAHs contained in bottom sediments may undergo desorption and become a secondary water contamination. PAHs can also pose a threat to adjacent ecosystems, for example getting through the floods, into the floodplain land. The analysis of bottom sediments provides a wide range of information on sources of water pollution in river catchments supplying them and determining the way of their management in the environment or utilization (Kostecki 2003, Kostecki and Czaplicka 2001).

Determining the relationship between selected PAHs can be used to define the origin of the pollutant. Table 1 shows PAH diagnostic ratios with their typically reported values for particular processes.

The aim of the study was to obtain knowledge about the role of lowland dam reservoir as the reactor in which the quality of water and bottom sediments is formed. The novelty scientific studies were to attempt to determine the relationship between the morphometry of the reservoir and PAHs concentration in sediments. In determining the spatial variability of concentrations in the longitudinal profile of the reservoir, its depth diversity was taken into account.

The aim of the study was to demonstrate the specificity of the self-cleaning processes taking place in the lowland reservoirs. Using the balance method, the ecosystem's ability to accumulate organic pollutants was determined.

Research Methodology

The object of studies

The reservoir in Blachownia is an example of a typical lowland, dammed reservoir formed by damming the Stradomka river. Such reservoirs are important elements in local water management. By small differences in the level of damming they maintain the correct level of groundwater, thus reducing the effects of drought and floods during the spring and summer. They are valuable ecosystems enhancing biodiversity of flora and fauna. Additionally, they are a recreation area for local communities.

The reservoir has an area of 47 hectares, and a capacity of about 500 000 m^3. Its maximum depth in the area of the dam is about 2.0 m, and the average depth is about 1.0 m. The reservoir is fed by surface watercourses the Stradomka and the Trzepizurka. The total catchment area of the reservoir is equal to 113.33 km^2, including the Stradomka catchment – 67.89 km^2, and the Trzepizurka catchment – 22.11 km^2 (Siwiński 2015). Population density in the municipalities bordering the reservoir fluctuates between 80–113 people/km^2. The land use in the area is dominated by woodland (47.2–62.0%) and agricultural lands (25.0–43.9%), while urbanized areas account for only 8.9–13.0% (CSO 2015). Before the analyzed reservoir, wastewater from mechanical-biological wastewater treatment plant (WWTP), from the village Herby, serving approximately 4,300 residents, and the capacity in 1100 m^3/d, is fed to the Stradomka river. In addition, part of the village located in the catchment of the reservoir does not have a sewage system. Municipal wastewater management relies mainly on retention of sewage in cesspools, and its transport to the wastewater treatment plant (KZGW 2012).

Sampling sites

Water samples were collected at four points, five times from May to September in 2013, at monthly intervals: W1 – the Stradomka river inlet stream, W2 – the Trzepizurka river inlet (the Aleksandrowski stream) to the reservoir, W3 – the reservoir, the place at the „lido", W4 – the reservoir, outlet from the reservoir.

Table 1. Diagnostic ratios used with their typically reported values for particular processes

PAH ratio	Value range	Source	Reference
∑LMW/∑HMW	< 1	Pyrogenic	Zhang et al. 2008
	> 1	Petrogenic	
∑COMB/∑PAHs	~ 1	Combustion	Ravindra et al. 2008a
FL/(FL + PYR)	< 0.5	Petrol emissions	Ravindra et al. 2008b
	> 0.5	Diesel emissions	
ANT/(ANT + PHE)	< 0.1	Petrogenic	Pies et al. 2008
	> 0.1	Pyrogenic	
FLA/(FLA + PYR)	< 0.4	Petrogenic	De La Torre-Roche et al. 2009
	0.4–0.5	Fossil fuel combustion	
	> 0.5	Grass, wood, coal combustion	
BaA/(BaA + CHR)	0.2–0.35	Coal combustion	Akyüz and Çabuk 2010
	> 0.35	Vehicular emissions	
	< 0.2	Petrogenic	Yunker et al. 2002
	> 0.35	Combustion	
IcdP/(IcdP + BghiP)	< 0.2	Petrogenic	Yunker et al. 2002
	0.2–0.5	Petroleum combustion	
	> 0.5	Grass, wood and coal combustion	
BbF/BkF	2.5–2.9	Aluminium smelter emissions	
BaP/BghiP	< 0.6	Non-traffic emissions	Katsoyiannis et al. 2007
	> 0.6	Traffic emissions	

ΣLMW – sum of two and three-ring PAHs; ΣHMW – sum of four and five ring PAHs; ΣCOMB – sum of FLA, PYR, BaA, CHR, BkF, BbF, BaP, IcdP and BghiP; ΣPAHs – sum of total 16 investigated PAHs; FL – Fluoren; PYR – Pyrene; ANT – Anthracene; PHE – Phenanthrene; FLA – Fluoranthene; BaA – Benzo(a)anthracene; CHR – Chrysene; IcdP – Indeno(1,2,3-cd)pyrene; BghiP – Benzo(g,h,i)perylene; BbF – Benzo(b)fluoranthene; BkF – Benzo(k)fluoranthene, BaP – Benzo(a)pyrene.

Samples of bottom sediments (points S1–S5) were collected once with a Birge-Ekman bottom sampler at five points along the central axis of the reservoir: S1 – the Stradomka river inlet zone, S2 – the reservoir island, S3 – the reservoir middle, S4 – the reservoir jetty, S5 – the reservoir dam, outlet from the reservoir (Fig. 1).

Polycyclic aromatic hydrocarbons were measured in water and bottom sediment samples. Thickness of sediment layer, sediment humidity and organic matter were determined. In addition, water flow rates were measured (inflow and outflow from the tank), which were the basis for calculating the pollution balance.

Analytical Methods

Sample preparation

Samples of water and bottom sediments were stored in sealed vessels without light at temperatures between 0°C and 4°C. Samples were prepared according to a diagram of procedure of PAHs determination (Fig. 2). For each matrix, analytical recovery was determined according to the methodology presented in Kubica K. et al. (1998).

Determination of PAHs

In the test samples 16 compounds belonging to PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a) anthracene, chrysene, benzo(b)fluorantene, benzo(k)fluorantene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-cd) pyrene, and benzo(g,h,i)perylene) were determined. Prepared samples were analyzed for PAHs content by gas chromatography coupled with mass detector GC-MS (GC-MS QP-2010 Plus Shimadzu) using an internal standard. The sample was injected at 1 µl per column type ZB-5MS (30 m × 0.25 mm × 0.25 µm). The information on metrological characteristics of the analytical procedure is shown in the table (Table 2).

In all collected samples of bottom sediments (points S1–S5), analyzed concentrations of 16 PAHs were higher than the limit of quantification.

Quality assurance and quality control system (QA/QC)

Based on the information contained in the work of Konieczka and Namieśnik (Konieczka and Namieśnik 2010) the quality assurance and quality control system was developed. Solutions of the analytes were prepared in dichloromethane, stored at 4°C and brought to room temperature before use. The stock standard solution was obtained by tenfold dilution the certified PAHs standard (2000 µg/ml concentration) in dichloromethane. The stock deuterated standard solution was received 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 5 concentration levels. The range of PAH concentrations in working solutions was 0.006–0.400 µg/ml, while the concentration of the internal standard was 0.088 µg/ml (calibration for water sample). The calibration curve for bottom sediment samples ranged from 0.030 µg/ml to 3.000 µg/ml, with an internal standard concentration of 0.300 µg/ml.

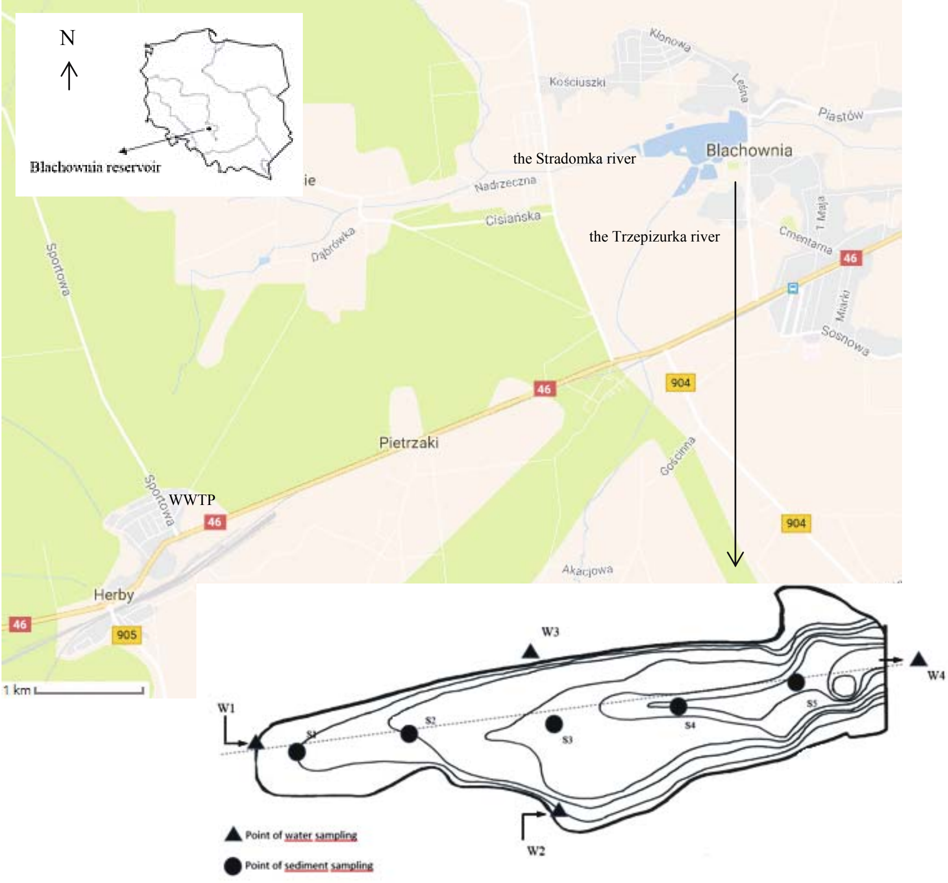

Fig. 1. Blachownia dam reservoir – the distribution of the sampling points

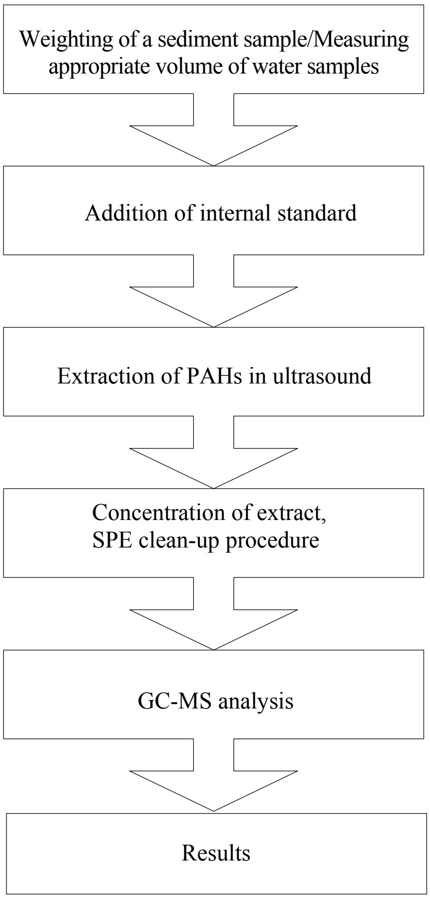

Fig. 2. A diagram of the procedure of PAHs determination in water and sediment samples by GC-MS method

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	0.002 µg/l for benzo(a)piren	0.006 µg/l for benzo(a)piren	0.008 µg/l for benzo(a)piren	90–115	15	up to 20.0	0–20
	0.003 µg/l for others PAHs	0.008 µg/l for others PAHs	0.010 µg/l for others PAHs				
Bottom sediments	7 µg/kg for each PAHs	21 µg/kg for each PAHs	30 µg/kg for each PAHs	70–115	15	up to 30.0	0–25

A standard solution derived from another series than calibration standard was used to check the calibration. For this purpose, the stock standard solution was prepared by diluting in dichloromethane to gave a concentration of 0.016 µg/ml (curve for liquid matrix) or 0.089 µg/ml (curve for constant matrix). The internal quality control of research is also based on the analysis of blind samples and recovery with the working standard, parallel to each measurement series. 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 LOD and LOQ were established using standard solutions at five concentration levels from 0.006–0.400 µg/ml.

Study results

Water characteristics

Tables 3 and 4 summarizes the range of variables for the 16 selected PAHs in water samples. In the case where the results were below the limit of quantification (LOQ) the "Medium-bound" method was used. According to it, where the amounts of physico-chemical or chemical measured in a given sample are below the limit of quantification, the measurement results shall be set to half of the value of the limit of quantification concerned for the calculation of mean values (Commission Directive 2009/90/EC of 31 July 2009).

PAHs content in the water feeding the Blachownia reservoir, showed significant variation depending on the sampling period.

Table 3. Concentrations of polycyclic aromatic hydrocarbons in water samples – samples collected from rivers feeding the reservoir [μg/L]

Hydrocarbon	The Stradomka (W1)					The Trzepizurka (W2)				
	May 2014	June 2014	July 2014	August 2014	September 2014	May 2014	June 2014	July 2014	August 2014	September 2014
Naphthalene	0.013 ± 0.003	0.012 ± 0.002	0.291 ± 0.058	0.021 ± 0.004	0.152 ± 0.030	<0.010	<0.010	0.040 ± 0.008	<0.010	0.863 ± 0.173
Acenaphthylene	<0.010	0.011 ± 0.002	0.011 ± 0.002	<0.010	<0.010	<0.010	0.011 ± 0.002	<0.010	<0.010	<0.010
Acenaphthen	<0.010	<0.010	0.062 ± 0.012	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.066 ± 0.013
Fluorene	<0.010	<0.010	0.073 ± 0.015	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.043 ± 0.009
Phenanthrene	<0.010	0.050 ± 0.010	0.851 ± 0.170	0.046 ± 0.009	0.280 ± 0.056	<0.010	0.100 ± 0.020	<0.010	<0.010	1.382 ± 0.276
Anthracene	<0.010	<0.010	0.220 ± 0.044	<0.010	0.015 ± 0.003	<0.010	<0.010	<0.010	<0.010	<0.010
Fluoranthene	0.019 ± 0.004	0.012 ± 0.002	0.199 ± 0.040	0.017 ± 0.003	0.032 ± 0.006	<0.010	0.056 ± 0.011	<0.010	<0.010	0.115 ± 0.173
Pyrene	0.088 ± 0.018	<0.010	0.112 ± 0.022	<0.010	0.094 ± 0.019	<0.010	0.257 ± 0.051	0.023 ± 0.005	<0.010	0.091 ± 0.018
Chrysene	<0.010	<0.010	0.203 ± 0.041	<0.010	<0.010	<0.010	0.018 ± 0.004	<0.010	<0.010	0.011 ± 0.002
Benzo(a)anthracene	<0.010	<0.010	0.014 ± 0.003	<0.010	<0.010	0.015 ± 0.003	0.114 ± 0.023	<0.010	<0.010	0.033 ± 0.007
Benzo(b)fluoranthene	<0.010	<0.010	0.020 ± 0.004	<0.010	<0.010	<0.010	0.036 ± 0.007	<0.010	<0.010	0.029 ± 0.005
Benzo(k)fluoranthene	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.013 ± 0.002	<0.010	<0.010	0.036 ± 0.006
Benzo(a)pyrene	0.009 ± 0.002	<0.008	<0.008	<0.008	<0.008	0.010 ± 0.002	0.028 ± 0.005	<0.008	<0.008	<0.008
Dibenzo(a,h)anthracene	<0.010	<0.010	0.059 ± 0.012	0.019 ± 0.004	0.020 ± 0.004	<0.010	0.058 ± 0.012	<0.010	<0.010	<0.010
Indeno(1,2,3-cd)pyrene	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	no data	<0.010	<0.010	<0.010
Benzo(g,h,i)perylene	<0.010	0.031 ± 0.006	0.019 ± 0.003	<0.010	0.028 ± 0.005	<0.010	0.130 ± 0.024	<0.010	<0.010	<0.010
The sum of PAHs	0.129	0.116	2.134	0.103	0.621	0.025	0.821	0.063	–	2.669

Table 4. Concentrations of polycyclic aromatic hydrocarbons in water samples – samples collected from the reservoir [µg/L]

Hydrocarbon	Lido reservoir (W3)					Reservoir – outlet (W4)				
	May 2014	June 2014	July 2014	August 2014	September 2014	May 2014	June 2014	July 2014	August 2014	September 2014
Naphthalene	<0.010	<0.010	0.544 ± 0.109	0.114 ± 0.023	0.105 ± 0.021	0.046 ± 0.009	<0.010	0.075 ± 0.015	0.037 ± 0.007	0.213 ± 0.043
Acenaphthylene	<0.010	0.014 ± 0.003	<0.010	<0.010	<0.010	<0.010	0.012 ± 0.002	<0.010	<0.010	<0.010
Acenaphthen	<0.010	<0.010	0.012 ± 0.002	0.031 ± 0.006	<0.010	<0.010	0.014 ± 0.003	<0.010	<0.010	<0.010
Fluorene	<0.010	<0.010	<0.010	0.027 ± 0.005	<0.010	<0.010	0.016 ± 0.003	0.012 ± 0.002	<0.010	<0.010
Phenanthrene	0.401 ± 0.080	0.088 ± 0.018	0.085 ± 0.017	1.274 ± 0.255	0.041 ± 0.008	0.028 ± 0.006	0.260 ± 0.052	<0.010	0.235 ± 0.047	0.158 ± 0.032
Anthracene	0.430 ± 0.086	<0.010	<0.010	0.016 ± 0.003	0.018 ± 0.004	<0.010	<0.010	<0.010	<0.010	<0.010
Fluoranthene	0.332 ± 0.066	0.032 ± 0.006	<0.010	0.069 ± 0.014	0.024 ± 0.005	0.031 ± 0.006	0.027 ± 0.005	0.024 ± 0.005	0.018 ± 0.004	0.036 ± 0.007
Pyrene	0.732 ± 0.146	0.047 ± 0.009	<0.010	0.034 ± 0.007	0.063 ± 0.013	0.020 ± 0.004	0.025 ± 0.005	0.018 ± 0.004	<0.010	0.070 ± 0.014
Chrysene	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Benzo(a)anthracene	0.030 ± 0.006	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Benzo(b)fluoranthene	0.049 ± 0.009	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.023 ± 0.004	<0.010	0.011 ± 0.002
Benzo(k)fluoranthene	<0.010	<0.010	<0.010	0.014 ± 0.002	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Benzo(a)pyrene	0.014 ± 0.003	<0.008	<0.008	<0.008	0.015 ± 0.003	0.013 ± 0.002	<0.008	<0.008	<0.008	0.014 ± 0.003
Dibenzo(a,h)anthracene	<0.010	<0.010	0.055 ± 0.011	<0.010	0.021 ± 0.004	<0.010	<0.010	0.059 ± 0.012	<0.010	0.022 ± 0.004
Indeno(1,2,3-cd)pyrene	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Benzo(g,h,i)perylene	0.017 ± 0.003	0.036 ± 0.007	<0.010	<0.010	0.025 ± 0.005	0.013 ± 0.002	<0.010	<0.010	<0.010	0.026 ± 0.005
The sum of PAHs	2.005	0.217	0.696	1.579	0.312	0.151	0.354	0.211	0.290	0.550

In the Stradomka river (W1) the sum of the PAHs ranged from 0.103 to 2.134 μg/L. The maximum value occurred in the first decade of July 2014. This month, the highest concentrations of PAHs tested (especially naphthalene, phenanthrene, anthracene, fluoranthene, pyrene, and chrysene) were observed. The dominant pollution in the Stradomka river inlet stream was phenanthrene, the highest concentration was 0.851 μg/L (VII 2014) and 0.280 μg/L (IX 2014). Benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene was not detected in any of the samples.

In the Trzepizurka river (point W2) the PAHs fluctuation was higher compared to the values found in the Stradomka river. In August 2014, there was no presence of test compounds at the inlet to the reservoir. In September, the sum of the PAHs was 2.669 μg/L, and the dominant compound (similar to the Stradomka river) was phenanthrene, with the highest concentration of 1.382 μg/L (IX 2014). A high concentration compared with other compounds, was also observed for naphthalene 0.863 μg/L (IX 2014).

Varied values of PAHs concentrations in water were found at a point located in the reservoir (W3). The total of 16 PAHs at the place at the, "lido" (W3) ranged from 0.217 to 2.005 μg/L. The highest concentrations of PAHs were observed in May 2014, respectively, phenanthrene – 0.401 μg/L, anthracene – 0.430 μg/L, fluoranthene – 0.332 μg/L, pyrene – 0.732 μg/L. The highest share in the total of 16 PAHs, had two and three ring hydrocarbons (70–80%). The concentration of phenanthrene in August 2014 was 1.274 μg/L, and this compound was dominant at the place at the, "lido". At W3, the naphthalene concentration of 0.544 μg/L was found in June.

The lowest sum of PAHs was in the outlet from the reservoir (W4): 0.151–0.550 μg/L, based on the values in other water sampling points. Naphthalene and phenanthrene were dominant. None of the samples contained anthracene, chrysene, benzo(a)anthracene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene.

Characteristics of bottom sediments

Table 5 summarizes the content of the polycyclic aromatic hydrocarbons in bottom sediment samples. In this case, the "Medium-bound" method also was used. Sediments in the Stradomka river inlet (point S1) had more than 60 cm in thickness, with 93.1% hydration, and the content of organic substances was approximately 48.5%. In this area of the reservoir, sedimentation of suspensions carried with waters occurs. There was a relatively high PAH content in this reservoir zone (sum of the concentrations of 16 PAHs – 9 062 μg/kg s.m.). Unlike other sediment samples, there was a significant participation of 2-ring hydrocarbons – 1 778 μg/kg d.m. (19.6% of total concentrations of PAHs) and 3-ring – 1 378 μg/kg d.m. (15.2% of the total PAHs concentrations).

Lower sum of the concentrations values of 16 PAHs occurred in the point S2 located in the height of the island. Narrowing a cross-section of the tank and a small depth at this point resulting in an increase in the linear velocity of the water flow, reduces the possibility of sedimentation As a result, their thickness in this area of reservoir was lower, ranged from 20 to 40 cm. Hydration of sediments amounted 79.6%, mineral content increased to 81.9%. At this point the sum of the concentrations of 16 PAHs was 2 329 μg/kg d.m. In relation to point S1, decrease in the share of 2- and 3-ring hydrocarbons (16%) was observed.

In the points located on the reservoir (point S3 and S4), sediments hydration ranged from 87–88.4%, while the content of organic matter in the sediments ranged from 22.6–25.2%. Sediments thickness varied – from 20 cm to over 60 cm. The sum of the concentrations of PAHs was similar (6 318 μg/kg – 6 766 μg/kg d.m.); whereas 4-ring to 6-ring hydrocarbons dominated.

Sediment accumulation occurred in the area of the reservoir dam (S5). Sediment thickness exceeded 60 cm, while the organic matter content was 77.4%. In this area, the highest value of the sum of concentrations of 16 PAHs – 9 078 μg/kg d.m., was observed. PAHs dominated the 4-ring compounds, with a share of more than 45%, and the share of hydrocarbons 5 and 6 was also high.

The balance of polycyclic aromatic hydrocarbons

On the basis of the results obtained an estimated, simple balance of PAHs pollution in the Blachownia reservoir was prepared. The basis of this assessment was adopted, including pollution load entering and exit of the dammed lake.

Calculations take a mean flow rate (Q) obtained as a result of own measurements. The following results were the Stadomka river inlet stream Q = 0,6 m^3/s, the Trzepizurka river inlet stream Q = 0,2 m^3/s, outlet from the reservoir Q = 0,8 m^3/s, respectively.

Taking into account the size of the bottom of the reservoir, mean values of the thickness and hydrations of the sludge layer, it was estimated that the mass of dry sediments was about 12 tons.

In order to calculate the pollutant load (L) in liquid samples, the following formula was used:

$$L\left[\frac{\mu g}{d}\right] = C\left[\frac{\mu g}{L}\right] \cdot 1000 \cdot Q\left[\frac{m^3}{s}\right] \cdot 3600 \cdot 24$$

where: C – concentration of tested PAH [μg/L], Q – mean flow rate [m^3/s]. Data on the inflow to the reservoir was presented as the sum of the pollutant loads obtained for selected PAHs in the two rivers: the Stradomka and the Trzepizurka. Accumulation of PAHs was calculated as the difference in load on the inlet and outlet. In the case of the result below the LOQ, "Medium-bound" method was used, which requires using half of the limit of quantification calculating the contribution of each non-quantified compounds (Commission Directive 2009/90/EC of 31 July 2009, Commission Regulation (EU) No 589/2014 of 2 June 2014). The results are shown in the table (Tab. 6).

Based on the pollutant balance, it was estimated that 17.70 kg of PAHs (a total of 16 selected compounds) flew to the reservoir per year. The dominated pollutant was a phenanthrene – over 6 kg per year. Approximately 20% of the inlet load was naphthalene (3.01 kg/year). Pyrene (1.65 kg/year) and fluoranthene (1.30 kg/year) are also included in the dominant PAHs in waters flowing to a reservoir. Loads of other PAHs do not exceed 1 kg/year, in inlet stream.

Average pollutant load at outflow was 9.30 kg/year. In this case, the dominant hydrocarbons were also phenanthrene (3.48 kg/year) and naphthalene (1.91 kg/year). It has been estimated that the annual accumulation of polycyclic aromatic hydrocarbons in the Blachownia reservoir was 8.40 kg. The most

Table 5. Concentrations of polycyclic aromatic hydrocarbons in bottom sediment samples [µg/kg d.m.]

Hydrocarbon	The Stradomka estuary (S1)	The Blachownia reservoir			
		Island (S2)	Middle (S3)	Jetty (S4)	Dam (S5)
Naphthalene	1 778 ± 521	31 ± 9	141 ± 41	31 ± 9	166 ± 49
Acenaphthylene	37 ± 11	34 ± 10	34 ± 10	34 ± 10	39 ± 12
Acenaphthen	93 ± 28	38 ± 11	55 ± 16	38 ± 11	76 ± 23
Fluorene	132 ± 39	39 ± 12	73 ± 22	39 ± 12	142 ± 42
Phenanthrene	674 ± 202	146 ± 44	567 ± 170	498 ± 149	956 ± 286
Anthracene	442 ± 132	91 ± 27	137 ± 41	695 ± 208	178 ± 53
Fluoranthene	1 029 ± 308	315 ± 94	1 042 ± 312	852 ± 255	1 640 ± 490
Pyrene	844 ± 233	242 ± 67	772 ± 213	611 ± 169	1 241 ± 343
Chrysene	605 ± 181	195 ± 58	534 ± 160	532 ± 159	748 ± 224
Benzo(a)anthracene	429 ± 118	136 ± 38	311 ± 86	410 ± 113	486 ± 134
Benzo(b)fluoranthene	954 ± 219	296 ± 68	922 ± 212	579 ± 133	1 166 ± 268
Benzo(k)fluoranthene	369 ± 98	126 ± 33	342 ± 91	430 ± 114	402 ± 107
Benzo(a)pyrene	482 ± 113	181 ± 43	409 ± 96	370 ± 87	655 ± 154
Dibenzo(a,h)anthracene	155 ± 38	100 ± 24	146 ± 35	360 ± 87	156 ± 38
Indeno(1,2,3-cd)pyrene	522 ± 141	209 ± 56	439 ± 119	901 ± 243	553 ± 149
Benzo(g,h,i)perylene	517 ± 134	151 ± 39	394 ± 102	386 ± 100	474 ± 123
The sum of PAHs	9 062	2 329	6 318	6 766	9 078

Table 6. Estimated balance of PAHs in Blachownia reservoir

Hydrocarbon	Estimated balance of PAHs for water samples				Estimated balance of PAHs for sediment samples		
	Average yearly pollutant load [kg/year]		Accumulation [kg]	Participation [%]	Average concentration [g/ton]	Concentration in the entire reservoir [kg/12 ton]	Participation [%]
	Inflow (sum)	Outflow					
Naphthalene	3.01	1.91	1.10	13.01	0.43	5.15	6.40
Acenaphthylene	0.17	0.17	0.00	0.00	0.04	0.43	0.53
Acenaphthen.	0.42	0.17	0.25	2.97	0.06	0.72	0.89
Fluorene	0.45	0.23	0.22	2.62	0.09	1.02	1.27
Phenanthrene	6.60	3.48	3.12	36.97	0.57	6.82	8.47
Anthracene	1.01	0.15	0.86	10.16	0.31	3.70	4.60
Fluoranthene	1.30	0.69	0.62	7.29	0.98	11.71	14.54
Pyrene	1.65	0.70	0.95	11.20	0.74	8.90	11.06
Chrysene	0.92	0.14	0.79	9.31	0.52	6.27	7.79
Benzo(a)anthracene	0.35	0.14	0.21	2.53	0.35	4.25	5.28
Benzo(b)fluoranthene	0.25	0.25	0.00	0.05	0.78	9.40	11.67
Benzo(k)fluoranthene	0.18	0.13	0.05	0.57	0.33	4.01	4.97
Benzo(a)pyrene	0.16	0.20	-0.04	0.00	0.42	5.03	6.25
Dibenzo(a,h)anthracene	0.56	0.55	0.01	0.14	0.18	2.20	2.73
Indeno(1,2,3-cd)pyrene	0.12	0.13	-0.01	0.00	0.52	6.30	7.82
Benzo(g,h,i)perylene	0.54	0.27	0.27	3.16	0.38	4.61	5.73
∑ PAHs	17.70	9.30	8.40	100.00	6.71	80.53	100.00

accumulated was phenanthrene 37% (3.12 kg), next naphthalene 13% (1.10 kg), pyrene 11% (0.95 kg) and anthracene 10% (0.86 kg). Participation of 3 and 4 ring hydrocarbons was high. In two cases (benzo(a)pyrene and indene(1,2,3-cd)pyrene) the value of pollutant balance was negative. However, these values were minor and could be due to measurement errors and the estimated character of the balance.

The graph (Figure 3) shows the correlation between concentration of determined PAHs on the inflow and the participation of PAHs in the total accumulation charge in the reservoir. The higher concentration of compounds on the inflow results, the higher accumulation and concentration in the dammed lake. The correlation coefficient was close to 1 (0.95).

The estimated balance of PAHs showed that the dry weight of sediment per 30 hectare bottom of the reservoir was 12 tons. It was calculated that the average concentration of PAH in the bottom sediment was 6.71 g/ton, which corresponds to more than 80 kg of PAH in the entire dammed lake. The highest participation in the accumulation was noted for fluorantene (14.5%), benzo(b)fluoranthene (12%), pyrene (11%) and phenanthrene (8%).Unlike water samples, the proportion of hydrocarbons with more rings (5 and 6 ring) was higher.

Summary

The water reservoir in Blachownia is a shallow, dammed retention reservoir typical of lowland areas. This type of dammed lake is an important element of flood protection, also can be a source of water supply for industrial plants located around it and meet recreation needs (fishing, water sports) (Siwiński 2015). It is therefore important to ensure adequate water quality in the reservoir.

The type and character of the catchment area suggests that the risk of contamination of the reservoir by PAHs should be relatively small. This hypothesis is not completely confirmed in practice. In most of the analyzed water samples from streams feeding the reservoir, the concentrations of 16 PAHs (EPA list), were low and did not exceed the limit of quantification. Periodically, however, higher values were noted, indicating discharges of wastewater containing PAHs. This is confirmed by the data obtained for water samples of the Stradomka river in July. During this period very high concentrations, particularly, of 3 and 4 ring hydrocarbons were found.

In PAHs transport from the reservoir the solubility of individual compounds (especially 2 and 3 rings) and susceptibility to sorption are favorable (Tobiszewski and Namieśnik 2012). It was found, however, that higher concentration of PAHs in the inflow, results in a higher degree of their accumulation. In sediments in significant concentrations 2 and 3 ring hydrocarbons occurred only in samples collected at the Stradomka estuary, in other sediment samples their share in the sum of PAHs was low.

The Blachownia reservoir is a small depth reservoir with high susceptibility to mixing of water masses by the wind. The amount and organic nature of suspensions present in the water, creates good conditions for PAHs sorption and sedimentation and accumulation of contaminations in sediments. In bottom sediments the content of 4–6 ring hydrocarbons was higher compared to PAHs with fewer rings. According to the literature these compounds are associated with the sludge particles and are not available to living organisms, therefore it is difficult to degrade them. Their mobility is much lower than the dissolved forms. With aging of the sludge their concentration is increased (Duodu et al. 2017, Feng et al. 2016, Kostecki and Czaplicka 2001, Kostecki et al. 2000). This is confirmed by the analysis of the pollution balance in the Blachownia reservoir. In water samples, most were accumulated hydrocarbons of lower molecular weight. In sediment samples, a higher share of 5 and 6 ring hydrocarbons was reported. It is also associated with an exploitation of this reservoir, the last blowdown of which was carried out many years ago.

Potential sources of contamination of the Blachownia reservoir should also include transportation (Kalinowski and Załęska-Radziwiłł 2009, Khalili et al. 1995, Sapota 2002), associated with roads in this area (national road no 46, voivodeship roads 904 and 942, dense network of local roads) and pollution from low emission sources (home furnaces). Other ways in which

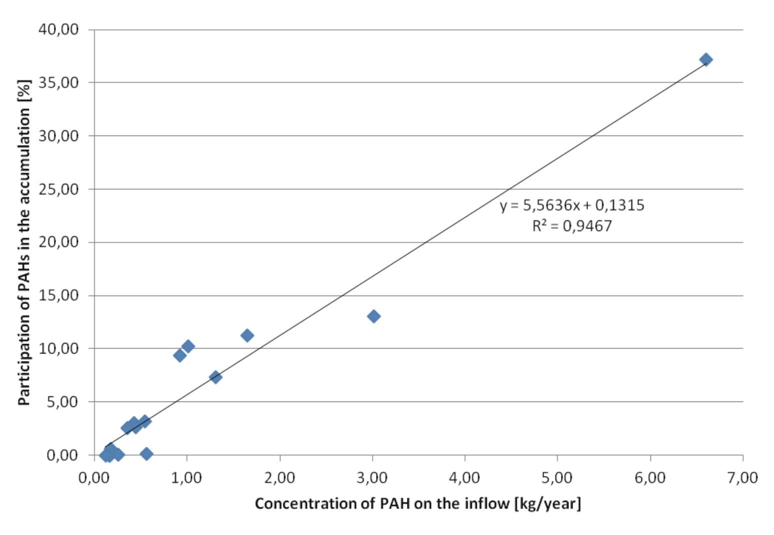

Fig. 3. The correlation between PAH concentration on the inflow and their percentage share in the accumulation

PAHs can enter the surface waters are rain drainage and municipal or industrial wastewater (Khalili et al. 1995, Pistelok and Jureczko 2014, Rogula-Kozłowska et al. 2012).

A much higher percentage of 4, 5 and 6 ring PAHs accumulation, possibly related to transportation suggests paying more attention to minimizing the impact of surface runoff from roads and highways. It is desirable that the rainwater sewages were purified prior to introduction into the reservoir, which will improve the water quality in the ecosystem.

The relationship between selected PAHs may be useful for the identification of pollution emission sources. Table 1 summarizes the characteristic diagnostic ratios with their typically reported values for particular processes used to determine air quality. In turn, Table 7 summarizes the values of characteristic indicators for bottom sediment samples obtained in own research. 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) and transportation. Taking into account the catchment character, it seems that this type of emissions probably may be one of the sources of PAHs in this ecosystem.

The assessment of sediments contamination with PAHs was based on the ecotoxicological criteria: TEC – threshold effect concentration and PEC – probable effect concentration (Macdonald et al. 2000). Values below TEC indicated that the sediments are not polluted, PAH levels between PEC and TEC showed sediments are neither polluted nor non-polluted. In turn, the concentration of PAHs above the PEC values may cause toxic effects and the sediment is classified as polluted (Macdonald et al. 2000, Solberg et al. 2003). Tab. 8 shows the values of TEC and PEC for PAHs and a potential ecological risk of the tested sediments in relation to these indicators.

Most PAH values were between TEC and PEC, few PAH concentrations were lower than the threshold effect concentration. Only at the Stradomka estuary (S1), a concentration of naphthalene was higher than the probable effect concentration. Consequently, the bottom sediments of the Blachownia reservoir can be classified as neither polluted nor non-polluted.

In order to determine the level of contamination of sediments with PAH compounds, a comparison of the results of other researchers was made. Tab. 9 compares the sum of PAHs obtained in bottom sediment samples from point S3 (the middle of Blachownia reservoir) with the data on the other sediment samples collected from lakes or rivers located in different places in the world.

Table 7. Relations between the particular compounds belonging to PAHs in bottom sediments for n = 5

PAH ratio	Average results ± standard deviation
∑LMW /∑HMW	0.310 ± 0.149
∑COMB/∑PAHs	0.710 ± 0.069
FL/(FL + PYR)	0.105 ± 0.030
ANT/(ANT + PHE)	0.343 ± 0.154
FLA/(FLA + PYR)	0.568 ± 0.011
BaA/(BaA + CHR)	0.595 ± 0.023
IcdP/(IcdP + BghiP)	0.326 ± 0.098
BbF/BkF	2.375 ± 0.544
BaP/BghiP	1.102 ± 0.168

Table 8. Sediment quality guidelines for PAHs and potential ecological risk of tested sediments

Hydrocarbon	TEC values according to the literature [µg/kg]	PEC values according to the literature [µg/kg]	Sampling points, category of sediments contamination				
			S1	S2	S3	S4	S5
Anthracene	57.2	845	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC
Fluorene	77.4	536	TEC < PAH < PEC	PAH < TEC	PAH < TEC	PAH < TEC	TEC < PAH < PEC
Naphthalene	176	561	PAH > PEC	PAH < TEC	PAH < TEC	PAH < TEC	PAH < TEC
Phenanthrene	204	1 170	TEC < PAH < PEC	PAH < TEC	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC
Benzo(a) anthracene	108	1 050	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC
Benzo(a) pyrene	150	1 450	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC
Chrysene	166	1 290	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC
Fluoranthene	423	2 230	TEC < PAH < PEC	PAH < TEC	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC
Pyrene	195	1 520	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC	TEC < PAH < PEC
∑ PAHs	1 610	22 800	TEC < PAHs < PEC	TEC < PAHs < PEC	TEC < PAHs < PEC	TEC < PAHs < PEC	TEC < PAHs < PEC

Table 9. Comparison of PAH concentrations in bottom sediments around the world

Tested reservoir	∑ 16 PAHs [µg/kg]	Literature
Blachownia reservoir, Silesian Voivodeship, Poland	6 318	This study
Kozłowa Góra reservoir, Silesian Voivodeship, Poland	275	GIOŚ 2017
Drwęckie Lake, Warmia and Mazury, Poland	45 552	GIOŚ 2017
Budziszewskie reservoir, Greater Poland Voivodeship, Poland	1 553	GIOŚ 2017
Reservoirs in the Pomeranian Voivodeship, Poland	7 543–49 908	Bojakowska et al. 2012
Pniewskie Lake, Warmia and Mazury, Poland	10 613	Bojakowska et al. 2012
Surface sediments of the Narew River, north-eastern Poland	21–599	Baran et al. 2002
Łąckie Duże Lake, Masovian district, Poland	24 871	Siebielec et al. 2015
Thane Creek of Mumbai, India	3–320	Basavaiah et al. 2017
Shilianghe Reservoir, eastern China	17– 840	Zhang et al. 2016
Deep Bay, South China	354–128	Qiu et al. 2009
Cienfuegos Bay, Cuba	180–5 500	Tolosa et al. 2009
Thohoyandou, Limpopo Province, South Africa	112– 61 764	Nekhavhambe et al. 2014
Vossoroca reservoir, Parana, Brazil	16–1 646	Sánez et al. 2013
River-reservoir systems in Democratic Republic of Congo	64	Mwanamoki et al. 2014
The Guba Pechenga, Barents Sea, Russia.	1 481	Savinov et al. 2003
Feitsui Reservoir, Taiwan	400	Fan et al. 2010
Mountain lakes, across Tibetan Plateau	98–594	Yang et al. 2016

The sum of 16 analyzed PAHs, in most cases, is higher than PAHs concentration reported in sediments collected from other countries. Compared to sediment samples from Polish lakes and rivers, the Blachownia reservoir is moderately polluted by PAHs.

Note, however, PAHs accumulation in Blachownia was about 50% of pollutant load entering from a water supply and the introduction of PAHs into the reservoir has a continuous character which can lead to degradation of this ecosystem. To improve the ecological condition reclamation works consisting in the removal of sediments outside the reservoir should be carried out and some steps to reduce the contamination of water feeding the reservoir ought to be taken.

Conclusions

The obtained results may provide the basis for administrative decisions and technical measures to improve the ecological status of shallow lowland reservoirs. The most important conclusions are summarized below:

1. Data about the water feeding the Blachownia reservoir (the Stradomka river and the Trzepizurka river) exhibit periodically elevated PAH concentrations. Incidental variability in PAH concentrations indicate discharges of industrial wastewater.
2. Local environmental conditions including catchments of agricultural and forestry character can be a source of PAHs released into surface water.
3. The intensity of water exchange in the reservoir (a retention time) is one of the factors determining the degree of pollutants accumulation. The hydrocarbons of lower molecular weight, 2- and 3-ring, accumulate in the bottom sediments of the reservoir at about 20%. The share of 4-, 5- and 6-ring PAHs in sediments was about 80%. This indicates a role of traffic and low emission in contaminating the reservoir.
4. Demonstration of two groups of PAHs – 2, 3-ring and 4-, 5-, 6-ring PAHs – which differ in degree of accumulation in sediments can be a basis for the protective measures. More attention should be paid to minimizing the surface water contact with surface runoff from roads and highways.
5. Research on the Blachownia reservoir has shown that small, shallow, lowland reservoirs require thoughtful protective measures, in particular limiting the introduction of PAHs into these ecosystems. The obtained results suggest that the use of technical solutions in the form of rainwater sewage treatment or pretreatment equipment, will significantly improve the water quality and the overall ecological status of the dam reservoir.
6. Most of PAH values were between TEC and PEC or below TEC values, therefore the possibility of toxic effects on zoobenthos and plankton organisms are insignificant and the bottom sediments of the Blachownia reservoir can be classified as neither polluted nor non-polluted by PAHs. However, this does not exclude the possibility of toxic effects on organisms, especially in the context of incidental waste discharges.
7. Small depth of the reservoir and therefore great susceptibility to mixing water masses under the influence of wind, amount and organic nature of suspensions present in the water, creates good conditions for sorption, and leads to sedimentation and accumulation of PAHs in sediments. Thus, in this type of limnical ecosystem, suspension of an organic nature is a very important element of PAHs transport from water to bottom sediments.

8. Analysis of the PAH ratios in the bottom sediments showed that probably one of the sources of PAHs in the Blachownia reservoir, are processes associated with burning of coal, wood, plant material (low emission, forest fires, burning grass, etc.); the impact of transportation and water – sewage management is also likely.
9. Accumulation of about 50% pollutant load (analyzed PAHs) constitutes a threat to the ecological condition of the ecosystem. The possibility of draining the reservoir and then removing the contaminated sediments is the way to radically improve the ecological status of shallow, lowland reservoirs. It should also be considered to reduce the contamination of water feeding the reservoir.

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Wielopierścieniowe węglowodory aromatyczne w wodzie i osadach dennych płytkiego, nizinnego zbiornika zaporowego (na przykładzie zbiornika Blachownia, południowa Polska)

Streszczenie: Zbadano zawartość wielopierścieniowych węglowodorów aromatycznych (WWA) w wodzie i osadach dennych zbiornika Blachownia (południowa Polska). Określono przestrzenną zmienność stężeń WWA w profilu podłużnym zbiornika. WWA w próbkach oznaczano metodą chromatografii gazowej sprzężonej z detektorem mas (GC-MS QP-2010 Plus Shimadzu) z użyciem wzorca wewnętrznego. Stężenia wahały się od 0.103 µg/L do 2.667 µg/L (∑16 WWA), w próbkach wody oraz od 2.329 mg/kg s.m. do 9.078 mg/kg s.m. (∑16 WWA), w próbkach osadów dennych. Sporządzono bilans zanieczyszczeń i na tej podstawie oszacowano, że ładunek WWA wprowadzany do zbiornika w ciągu roku wynosi 17.70 kg WWA, a ładunek odpływający – 9.30 kg/rok WWA. Kumulacja około 50% rocznego ładunku WWA (8.90 kg) stanowi zagrożenie dla stanu ekologicznego tego ekosystemu. Obliczono, że ładunek WWA w osadzie dennym badanego zbiornika wynosi około 80 kg, co ogranicza jego gospodarcze wykorzystanie. Poprawę stanu ekologicznego tego rodzaju zbiornika można osiągnąć poprzez usunięcie osadów. Analiza uzyskanych wartości wskaźników diagnostycznych dla określonych WWA wykazała, że potencjalnymi źródłami emisji WWA w niewielkich zlewniach o charakterze rolniczo-leśnym mogą być procesy związane ze spalaniem węgla, drewna, materiału roślinnego (niska emisja, pożary lasów, palenie trawy itp.). Znaczący wpływ wywiera również komunikacja.