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CONCENTRATION OF SELECTED PRIORITY SUBSTANCES IN KLODNICA RIVER CATCHMENT

ZAWARTOŚĆ WYBRANYCH SUBSTANCJI PRIORYTETOWYCH W ZLEWNI RZEKI KŁODNICY

Abstract: The paper presents results of research on concentrations of selected priority substances in the Klodnica River catchment. Two metals were selected: cadmium and mercury, as well as six polycyclic aromatic hydrocarbons (PAHs): anthracene, benzo[a]pyrene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene. Mercury was determined with the method of cold vapor atomic absorption spectrometry (CV AAS) using RA-915$^+$ analyzer with RP-91 attachment produced by Lumex. Cadmium was determined with the method of direct electrothermal atomic absorption (ET ASS) using AAnalyst 600 appliance produced by Perkin Elmer. PAHs were analyzed with high-performance liquid chromatography method with fluorescence detection (HPLC-FLD) using liquid chromatograph HP 1050 produced by Hewlett Packard. The research was carried out in 2008 in four measurement campaigns, once every quarter. In all campaigns 28 measurement points, located in the Klodnica River catchment, were examined. The obtained results were compared with permissible concentration values for priority substances in surface waters included in the proposal of the UE concerning Environmental Quality Standards, and with requirements determined by the Polish legislation as limit values of water quality indicators.

Keywords: priority substances, river catchment, screening study

Upper Silesia is the biggest industrial district in Poland. In this area there are 21 mines, which belong to “Katowicki Holding Weglowy” and “Kompania Weglowa”. There are also many coal mines which do not function nowadays but which in the past contributed to degradation of natural environment of the Upper Silesia Industrial Region (GOP). In the vicinity of energy sources many other branches of industry also appeared, eg metallurgical industry, power industry, engineering industry and chemical industry. The Klodnica River is the longest river flowing through the region of GOP. It is one of

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the right-bank tributaries of the Odra River. It is over 75 km long, 40 km of which are within GOP. The spring of the Klodnica River is situated in the southern part of Katowice, in Murckowski Forests. The river flows through the biggest cities of the Upper Silesia, such as: Katowice, Ruda Slaska, Mikolow, Zabrze, Bytom, Gliwice and ends its course in Kedzierzyn-Kozle flowing into the Odra River [1]. The most important tributaries of the Klodnica River are: Bielszowicki Brook, Czarniawka Brook, Bytomka Brook, Drama Brook, Toszecki Brook (right-bank), and Jamna Brook and Gieraltowicki Brook (left-bank). In the course of the river three big dam reservoirs are located: Dzierzno Duze Lake on the Klodnica River, Dzierzno Male Lake on the Drama River and reservoir Plawniowice on the Toszecki Brook. The biggest pollution discharge is drained to the Klodnica River in its main course, where the river and its tributaries flow through densely populated and industrially most active areas of the Upper Silesia. The main sources of pollution of the Klodnica River are: precipitation sewage and thawing sewage flowing down from industrial and post-industrial areas, sewage flowing into the river from the areas where industrial and municipal landfills are located, discharge of mine water containing a lot of salt and untreated household sewage from cities and communes where there are no sewage treatment plants, or where sewage cannot be treated properly with the currently applied technology. In the catchment of the Klodnica River there are 23 sewage treatment plants, 11 of which function, 2 are to be modernized and three are planned to be built in the future [2]. As far as the efficiency is concerned these plants can be divided into small and big. Small sewage treatment plants are located mainly on the tributaries of the Klodnica River, and these are sewage treatment plants of the efficiency of several thousand m^3/day. Middle and big sewage treatment plants are located on the Klodnica River and their efficiency is several dozen m^3/day. Most of them are mechanical-biological sewage treatment plants.

Polish and European regulations regarding priority substances

According to regulations of the Water Framework Directive (WFD) established by the European Parliament and the Council of Europe on 23 October 2000, Poland, as a Member State, has to undertake actions that will guarantee protection of inland surface waters, passing waters, coastal waters and groundwaters. One of the main principles of the WFD is to achieve good chemical status of waters, that is assessed by taking into consideration the presence of substances that are proved to have or are highly probable to have a harmful influence on ecosystems and water organisms as well as on human health (the so called “priority substances”). The main act regulating protection of waters in Poland is the act of 21 April 2001, Environmental Protection Act, with its further amendments and executive regulations [3, 4]. A full list of priority substances can be found in Annex X of the WFD [5] and in the Regulation of the Minister of the Environment dated 10 November 2005 on register of priority substances in the field of water policy (DzU 05.233.1987) [6, 7]. The Regulation of the Minister of the Environment on ways of classifying the state of uniform parts of surface waters, that came into force in 2008, defines limit values of water status indicators [8]. Using these indicators it is possible to unequivocally interpret results of the carried out research. Implementation of the principles of the WFD means that good chemical status of waters will be achieved by 2015, establishing at the same time the year 2025 as a deadline for elimination of substances recognized as priority hazardous substances from group of priority substances. As a support for implementing the WFD the European Union has started a project "Source Control of Priority Substances in Europe" (SOCOPSE), which was realized under EU FP6 in the period of 2006–2009. Under this project Institute for Ecology of Industrial Areas (IETU), as one of the participants, was obliged to make a case study and prepare reports on effective possibilities for reduction of the emission of mercury, cadmium and polycyclic aromatic hydrocarbons [9].

This paper presents results of screening research of the content of selected priority substances in the catchment of the Klodnica River. Two heavy metals: mercury and cadmium were selected for research as well as compounds from the group of polycyclic aromatic hydrocarbons: anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene. The obtained contents of mercury, cadmium and PAHs in surface waters were compared with regulations of the EU Environmental Quality Standards (EQS) [6], and with regulations of the Polish legislation [8]. Acceptable contents of mercury, cadmium and PAHs according to EQS and according to the Polish legislation are presented in Table 1.

Table 1

Allowable concentrations of mercury, cadmium and selected PAH by EQS [6], and by Polish legislation [8]

Priority substances	EQS		DzU 2008, no. 162, issue 1008	
	Annual average concentration [μg/dm^3]	Maximum allowable concentration [μg/dm^3]	Annual average concentration [μg/dm^3]	Maximum value of concentration [μg/dm^3]
Mercury and its compounds	0.05	0.07	—[3]	0.07
Cadmium and its compounds	0.08–0.25[1]	0.45–1.5[1]	—[3]	0.45–1.50[2]
Anthracene	0.10	0.40	—[3]	0.40
Benzo[a]pyrene	0.05	0.10	—[3]	0.10
Σ Benzo[b]fluoranthene + Benzo[k]fluoranthene	0.030	not applicable	0.030	—
Σ Benzo[g,h,i]perylene + Indeno[1,2,3-cd]pyrene	0.002	not applicable	0.002	—

[1] Depending on water hardness classes [6]; [2] Depending on water hardness classes [8]; [3] No available data.

Properties of selected priority substances

Mercury

Elemental mercury, its inorganic salts and organic compounds belong to the group of metals responsible for trace but dangerous pollution of the environment. The toxicity of these compounds has been known for many years. Mercury can accumulate in various parts of living organisms and cause enzymatic disturbances and mutagenic lesions in DNA, which may result in many medical complications and diseases [10]. Mercury shows high chemical and biological activity, variability of phase states (liquid, gaseous and solid). Mercury compounds of different physico-chemical properties occur in different natural cycles, the most important of them being atmospheric and hydro-biological cycles. Mercury is introduced to the environment from many anthropogenic and natural sources. The natural sources of mercury emission to the environment are volcanic eruptions, reemission from soil and rock surface and natural processes of biomass combustion. The anthropogenic sources of mercury are combustion of coal, waste combustion, cement production, chlor-alkali manufacturing industry and non--ferrous metal production. Mercury infiltrates into water as a result of atmospheric precipitation deposition as well as surface and groundwater run-off. Its chemical form depends mainly on oxidation-reduction conditions. In water, where oxidation conditions are prevailing, the most popular mercury compounds are $HgCl_4^{2-}$ and $HgOH^+$. However, in places where reduction conditions are dominant the most popular are CH_3HgS^- and HgS^{2-} [11]. In water where redox conditions change, mercury can be observed mainly in the form of CH_3HgCl and CH_3Hg^{2+}. Mercury compounds have the ability to accumulate in bottom sediments, therefore the increase of their concentrations is a good indicator of pollutant inflow to water ecosystem. The content of this metal in water is scattered and may vary depending on the type of water and its origin [12–18]. It was assumed that the average content of Hg in the sea and ocean water was at the level of 0.005 μg/dm^3, and in the river water – at the level of 0.01 μg/dm^3 [11].

Cadmium

Cadmium is an element which might pose a serious threat to health as it can be easily absorbed by living organisms. This element when absorbed by organisms can create complexes with proteins, which may result in its accumulation in liver and kidneys. Cadmium strongly interacts with iron, zinc, copper and selenium. Increased concentration of these elements decreases toxic activity of cadmium. The toxicity of cadmium consists in disorders of reproductive functions, abnormal functioning of liver and kidneys and may cause hypertension and cancer [10, 11]. Cadmium is present in high dispersion in rocks. The natural source of cadmium emission to the environment is reemission from soil and rock surface. The main anthropogenic source of cadmium is production of non-ferrous metals and phosphorus fertilizers. The natural concentration of cadmium in waters is estimated at 0.1 ppb level. It is mainly shaped by anthropogenic factors. Generally, this element does not remain long in solution, because it is quickly precipitated in form of carbonates or absorbed by loams, hydroxides and metal oxides. In rivers the cadmium concentration is relatively low, it reaches the level of 10–500 ng/dm^3, whereas in the sea and ocean waters it is even lower (0.5 to 10 ng/dm^3) [19, 20].

PAHs

Polycyclic Aromatic Hydrocarbons (PAHs) constitute a large group of compounds which contain a few aromatic circles in a particle. Physico-chemical properties of individual aromatic hydrocarbons are different and depend mainly on their molecular masses. Some of PAHs have toxic, cancerogenic and mutagenic properties. Among them the most severe ones are those of compounds which contain in their structure a circle system of benzo[a]anthracene eg: benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene and others. Anthropogenic emission of PAHs is stronger than the emission from natural sources. The anthropogenic sources of PAHs are: combustion of coal and fuels as well as heavy industry based on processing of coal and petroleum [21, 22]. Most of PAHs because of their nonpolarity and high molecular masses are badly soluble in water. Therefore, in water environment PAHs do not undergo hydrolysis but gradually degrade. PAHs combine with colloids and suspensions, and during their sedimentation go into sediments, which explains low concentration of PAHs in water column in comparison with their concentration in sediments. PAHs are introduced to water environment mainly through industrial discharge, surface flows and failures during transportation of liquid fuels. Another important source is deposition of dust coming from burning of the fossil fuels and biomass.

Study of area

Research on the content of priority substances (mercury, cadmium and PAHs) in the catchment of the Klodnica River were conducted in four measurement campaigns in 2008, with sampling frequency once a quarter. The first campaign was made on the 24th of January 2008, the second on the 9th of April 2008, the third between 11th and 12th of September 2008 and the fourth one on the 11th of December 2008. Eight measurement points were examined in four campaigns. The points were situated from the spring of the Klodnica River in Brynow (district of Katowice), through inlets of sewage and run-offs of sewage treated in sewage treatment plants placed in the course of the river next to the mouth of the most important tributaries, right up to the inlet of the Klodnica River to the dam reservoir – Dzierzno Duze and the inlet of the river to the Odra River in Kedzierzyn-Kozle. The register of measurement points of all four campaigns is presented in Fig. 1 and Table 2.

Methods and sample preparation

To determine mercury concentration in waters of the Klodnica River and its tributaries a multifunctional analyzer of mercury RA-915^{+} has been used. Its work is based on Zeeman atomic absorption spectroscopy with the use of modulation with high polarization of light (ZAAS-HFM), together with RP-91 attachment. The attachment is used to determine the concentration of mercury in liquid samples using the technique of "cold vapor", which is produced as a result of reduction of Hg(II) to atomic form.

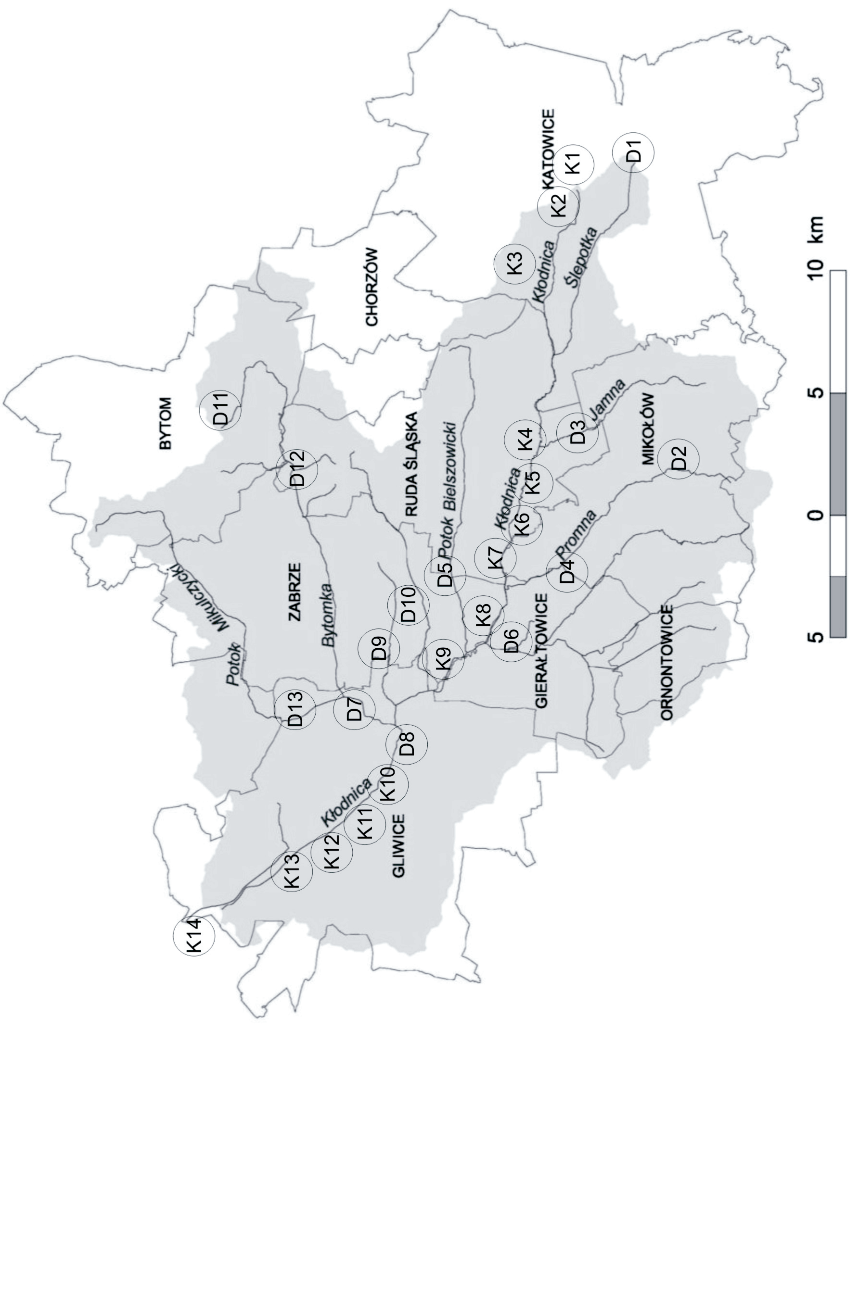

Fig 1. Chart of sampling points in the catchment of Klodnica River [2]

Table 2

List of sampling points in the catchment of Klodnica River

Mark of the sampling points	Entitle of the sampling points	Session I 24.01.2008	Session II 9.04.2008	Session III 11–12.09.2008	Session IV 11.12.2008
"K1"	Inlet of Klodnica River to city of Katowice, 74 km of river	–	+	+	–
"D1"	Slepiotka Stream, left inflows of Klodnica River	–	+	–	–
"K2"	Inlet of sewage to sewage treatment plants – mechanical- -biological type	–	–	+	–
"K3"	Outlet of sewage to sewage treatment plants – mechanical--biological type	–	+	+	–
"D2"	Jamna Stream, left inflows of Klodnica River	–	+	–	–
"D3"	Jamna Stream, left inflows of Klodnica River, before outlet to Klodnica River, 64.5 km of river	–	+	–	–
"K4"	Klodnica River after outlet of discharges waters "Halemba--Wirek" Colliery, 63 km of river	–	+	+	–
"K5"	Klodnica River, Ruda Slaska water-gauge, 63.8 km of river	+	+	+	+
"K6"	Inlet of sewage to sewage treatment plants – mechanical--biological-chemical type	–	–	+	–
"K7"	Outlet of sewage to sewage treatment plants – mechanical--biological-chemical type	–	+	+	–
"D4"	Promna Stream, left inflows of Klodnica River, before outlet to Klodnica River, 58.6 km of river	–	–	+	–
"K8"	Klodnica River after outlet of Promna Stream, 55 km of river	–	+	–	–
"D5"	Bielszowicki Stream, 54.4 km of river	–	+	+	–
"D6"	Outlet Jasienica Stream to Klodnica River, 1.3 km of river	–	–	+	–
"K9"	Klodnica after outlet Bielszowicki Stream, 53.8 km of river	–	+	–	–
"D7"	Bytomka Stream – Gliwice water-gauge, 2.7 km of river	+	+	+	+
"D8"	Bytomka Stream – Gliwice, before outlet to Klodnica River	–	+	–	–
"D9"	Discharges waters of "Sosnica-Makoszowy" Colliery	–	+	+	–

Table 2 contd.

Mark of the sampling points	Entitle of the sampling points	Session I 24.01.2008	Session II 9.04.2008	Session III 11–12.09.2008	Session IV 11.12.2008
"D10"	Czarniawka Stream after "Makoszowy" Colliery	–	+	+	–
"D11"	Bytomka Stream	–	–	+	–
"D12"	Bytomka Stream – Ruda Slaska	–	–	+	–
"D13"	Mikulczycki Stream outlet to Bytomka Stream, 0.3 km of river	–	+	–	–
"K10"	Klodnica River – Gliwice, 50.5 km of river	–	+	–	–
"K11"	Klodnica River – Gliwice water-gauge, 47.2 km of river	+	+	+	+
"K12"	Inlet of sewage to sewage treatment plants – mechanical-biological-chemical type	–	+	+	–
"K13"	Outlet of sewage to sewage treatment plants – mechanical-biological-chemical type	–	+	+	–
"K14"	Klodnica River outlet to barrage reservoirs Dzierzno Lake, 38.6 km of river	–	+	+	–
"K15"	Klodnica River – Kedzierzyn-Kozle-outlet to Odra River, 0 km of river	–	+	–	–

Samples of water were dripped through membrane filters (cellulose nitrate) with the diameter of 47 mm (diameter of pores 0.45 μm). 1 cm^3 of nitric acid and 1 cm^3 of solution of potassium chromate(VI) were added to the obtained filtrate. Then, the samples were mineralized for 2 hours in water steam-baths in the temperature of 95 ^oC, in oxidizing mixture consisting of $KMnO_4$, HNO_3, H_2SO_4, $K_2S_2O_8$ [23]. Detection limit of the applied method is 0.002 $\mu g/dm^3$. Cadmium in waters was determined using Electrothermal Atomic Absorption Spectrometry (ET-AAS) and AAnalyst 600 spectrometer produced by PerkinElmer. Samples of water were dripped in the same way as samples of mercury. 1 cm^3 of nitric acid was added to the obtained filtrate. Limit of detection of the applied method is 0.2 $\mu g/dm^3$. In order to determine concentrations of PAHs the samples of water were extracted with SPE technique and octadecyl(C_{18}) phase. Extracts were analyzed with the technique of High Performance Liquid Chromatography with Fluorescence Detection (HPLC-FLD), using liquid chromatograph HP 1050 produced by Hewlett Packard. Separation was conducted on Bakerbond PAH 16-Plus column, using gradient elution with mixture methanol and water. Limit of detection of the applied method is different depending on the determined compound and is, as follows: anthracene 0.009 $\mu g/dm^3$, benzo[a]pyrene 0.003 $\mu g/dm^3$, sum (benzo[b]fluoranthene and benzo[k]fluoranthene) 0.004 $\mu g/dm^3$, sum (benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene) 0.003 $\mu g/dm^3$. Laboratory glassware and all other utensils used during the analysis were washed in a laboratory dishwasher (Miele G7883, Ontario). Solutions were prepared with the use of deionized water of high cleanliness Milli-Q (Millipore, Bedford, MA, USA). All reagents used to determine metals had a certified concentration of mercury and cadmium (pro analysis, Merck, Germany). HPLC reagents of cleanliness produced by Baker were used to determine PAHs.

Results and discussion

Concentrations of mercury, cadmium and selected PAHs for the Klodnica River and its tributaries, obtained in four measurement campaigns are shown in Tables 3 and 4.

In most cases the results of particular measurement campaigns for the same measurement points were different. This difference probably results from the fact that weather and water conditions differed during particular measurement campaigns. It may also result from the amount of inflowing pollutants coming from rainwater and household sewage coming to the river from industrial plants and households located in its course. The second measurement campaign was carried out in spring when the river level was high and rainfall in March and at the beginning of April 2008 came to 80 mm. Such a quantity of rainfall could cause that a part of water, and therefore also pollutants, which got into the Klodnica River, came from rainwater flushing. The third measurement campaign was conducted in autumn after heat-wave, when the volume of rainfall from 15th August to 12th September was barely 20.14 mm and as a result the river level was relatively low on its whole length. The remaining two measurement campaigns were conducted in January and December 2008. In both periods the average monthly rainfall was around 40 mm and the river level was medium. The obtained concentrations of mercury for the entire catchment of the Klodnica River in all four measurement campaigns ranged from 0.010 to 0.893 $\mu g/dm^3$, whereas concentrations of cadmium varied from < 0.200 to 1.010 $\mu g/dm^3$. The lowest concentrations were observed in points where the river and its tributaries were not polluted by discharge of water from factories and households. The lowest concentrations of mercury ranging from 0.010 to 0.100 $\mu g/dm^3$ were noticed in left tributaries of the Klodnica River (Slepiotka, Jamna, Promna and Gieraltowicki Brooks) as well as in the Klodnica River itself, near its source. The lowest concentrations of cadmium ranging from < 0.200 to 0.300 $\mu g/dm^3$ were recorded in left tributaries of the Klodnica River (Slepiotka, Jamna, Promna). In the third measurement campaign the concentrations of cadmium in all examined points were not bigger than 0.380 $\mu g/dm^3$, which was probably the result of low river level in this period. The biggest concentration of mercury ranging from 0.296 to 0.893 $\mu g/dm^3$ was obtained for points K4 and D9 located near the outlets of mine water from hard coal mines. High concentrations of mercury were also obtained for measurement points D5 and D10 located on right tributaries of the Klodnica River, such as Czarniawka and Bielszowicki Brook. The highest concentrations of cadmium ranging from 0.650 to 1.010 $\mu g/dm^3$ were obtained for points K4 and D9, as well as for point D10. High concentrations of mercury and cadmium in these points may be caused by the fact that rivers in those regions are supplied mainly with waters coming from rainfall, sanitary sewage and commercial wastes and mine waters from hard coal mines located in this area.

Table 3

Concentrations of mercury and cadmium for Klodnica River and its side streams which were obtained in four measurement sessions [μg/dm^3]

Entitle of sampling point	Hg [μg/dm^3]				Cd [μg/dm^3]			
	Session I	Session II	Session III	Session IV	Session I	Session II	Session III	Session IV
"K1"	—	0.086	0.100	—	—	1.01	0.20	—
"D1"	—	0.016	—	—	—	< DL	—	—
"D2"	—	0.010	—	—	—	0.37	—	—
"D3"	—	0.048	—	—	—	0.22	—	—
"K4"	—	0.266	0.707	—	—	0.65	< DL	—
"K5"	0.137	0.182	0.458	0.108	< DL	0.50	0.38	0.51
"D4"	—	—	0.070	—	—	—	< DL	—
"K8"	—	0.236	—	—	—	0.33	—	—
"D5"	—	0.146	0.893	—	—	0.46	0.34	—
"D6"	—	—	0.069	—	—	—	< DL	—
"K9"	—	0.339	—	—	—	0.22	—	—
"D7"	0.163	0.190	0.084	0.083	< DL	< DL	0.22	< DL
"D8"	—	0.129	—	—	—	< DL	—	—
"D9"	—	0.189	0.296	—	—	0.65	0.30	—
"D10"	—	0.402	0.244	—	—	0.69	< DL	—
"D11"	—	—	0.052	—	—	—	< DL	—
"D12"	—	—	0.053	—	—	—	< DL	—
"D13"	—	0.354	—	—	—	< DL	—	—
"K10"	—	0.142	0.066	—	—	< DL	< DL	—
"K11"	0.131	0.337	0.075	0.369	0.6	0.59	< DL	< DL
"K14"	—	0.475	0.088	—	—	0.53	< DL	—
"K15"	—	0.179	—	—	—	< DL	—	—

Table 4

Concentrations of chosen PAHs for Klodnica River and its side streams witch were obtained in four measurement sessions [μg/dm^3]

Entitle of sampling points	Anthracene [μg/dm^3]				B[a]P^1 [μg/dm^3]				Σ B[b]F +B[k]F^2 [μg/dm^3]				Σ B[g,h,i]P +IP^3 [μg/dm^3]			
	Session I	Session II	Session III	Session IV	Session I	Session II	Session III	Session IV	Session I	Session II	Session III	Session IV	Session I	Session II	Session III	Session IV
"K1"	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—
"D1"	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—
"D2"	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< 0.004	—	—
"D3"	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—
"K4"	—	< DL	< DL	—	—	< DL	0.005	—	—	< DL	< DL	—	—	< DL	0.006	—
"K5"	< DL	< DL	< DL	0.011	0.003	< DL	< DL	0.015	0.004	< DL	< DL	0.021	0.002	0.004	< DL	0.018
"D4"	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—
"K8"	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	0.004	—	—
"D5"	—	< DL	< DL	—	—	0.018	0.018	—	—	0.014	< DL	—	—	0.028	0.011	—
"D6"	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—
"K9"	—	< DL	—	—	—	0.004	—	—	—	< DL	—	—	—	0.011	—	—
"D7"	< DL	< DL	0.012	< DL	0.007	0.006	0.003	0.014	0.009	0.011	< DL	0.018	0.010	0.008	0.004	0.022
"D8"	—	< DL	—	—	—	0.007	—	—	—	0.014	—	—	—	0.012	—	—
"D9"	—	< DL	< DL	—	—	< DL	< DL	—	—	< DL	< DL	—	—	< DL	< DL	—
"D10"	—	0.052	0.013	—	—	0.011	0.010	—	—	0.013	0.006	—	—	0.009	0.006	—
"D11"	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—
"D12"	—	—	0.010	—	—	—	0.006	—	—	—	0.006	—	—	—	0.004	—
"D13"	—	< DL	—	—	—	0.003	—	—	—	0.007	—	—	—	0.005	—	—
"K10"	—	< DL	< DL	—	—	0.006	0.004	—	—	< DL	< DL	—	—	0.010	0.003	—
"K11"	< DL	< DL	0.012	0.031	0.004	< DL	< DL	0.058	0.005	< DL	0.006	0.078	0.007	0.004	0.010	0.091
"K14"	—	< DL	< DL	—	—	< DL	< DL	—	—	< DL	< DL	—	—	0.004	< DL	—
"K15"	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—

Table 5

Concentrations of mercury, cadmium and concentrations of chosen PAHs, which were obtained on inlets and outlets of three sewage treatment plants draining treated sewage to Klodnica River [μg/dm^3]

Priority substances		Sewage treatment plants mechanical-biological type	Sewage treatment plants mechanical--biological-chemical type	Sewage treatment plants mechanical--biological-chemical type
Hg	Inlet of sewage [μg/dm^3]	0.458	0.476	0.283
	Outlet of circumcised sewage [μg/dm^3]	0.257	0.123	0.093
Cd	Inlet of sewage [μg/dm^3]	0.33	< DL	< DL
	Outlet of circumcised sewage [μg/dm^3]	< DL	< DL	< DL
Anthracene	Inlet of sewage [μg/dm^3]	< DL	0.010	0.066
	Outlet of circumcised sewage [μg/dm^3]	< DL	< DL	< DL
B[a]P	Inlet of sewage [μg/dm^3]	0.004	< DL	0.023
	Outlet of circumcised sewage [μg/dm^3]	< DL	< DL	< DL
Σ B[b]F + + B[k]F	Inlet of sewage [μg/dm^3]	0.056	< DL	0.032
	Outlet of circumcised sewage [μg/dm^3]	< DL	< DL	< DL
Σ B[g,h,i]P + + IP	Inlet of sewage [μg/dm^3]	< DL	< DL	0.023
	Outlet of circumcised sewage [μg/dm^3]	< DL	< DL	< DL

[1] B[a]P – Benzo[a]pyrene; [2] B[b]F + B[k]F - Σ Benzo[b]fluoranthene + Benzo[k]fluoranthene; [3] B[g,h,i]P + IP – Σ Benzo[g,h,i]perylene + Indeno[1,2,3-cd]pyrene.

Concentrations of PAHs in the Klodnica River and its tributaries obtained in four measurement campaigns ranged as follows: anthracene from < 0.009 to 0.066 μg/dm^3, benzo[a]pyrene from < 0.003 to 0.058 μg/dm^3, sum (benzo[b]fluoranthene and benzo[k]fluoranthene) from < 0.004 to 0.056 μg/dm^3, sum (benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene) from < 0.003 to 0.028 μg/dm^3. In most measurement points concentrations of PAHs in the analyzed water samples were below the detection limit of the applied analytical method. Concentrations of PAHs were higher and could be determined only in points K4, D5, D9, D10, located behind the outlets of mine water collectors and on right tributaries of the Klodnica River (Czarniawka and Bielszowicki Brook). Sums of contents of six assayed PAHs in points with the highest concentration of these substances were 0.035 μg/dm^3 for point D10 in the third measurement campaign and 0.086 μg/dm^3 in the second one. The sum of concentrations of six PAHs was 0.144 μg/dm^3 for point K11 in the third measurement campaign. Points located on inlets and outlets of three sewage treatment plants draining treated waste to the Klodnica River were examined during the third measurement campaign. The obtained contents of mercury, cadmium and PAHs on inlets of waste and outlets of treated waste from sewage treatment plants are presented in Table 5. Two of the examined sewage treatment plants were of mechanical-biological-chemical type and one was a mechanical--biological one. In all three cases a definite improvement of water quality concerning cadmium, mercury and PAHs in points located on outlets of the examined sewage treatment plants can be noticed.

Conclusions

1. Concentrations of mercury, which were obtained in the carried out research in all points and four measurement campaigns range from 0.010 to 0.893 μg/dm^3. According to the Environment Quality Standards EQS [6] and the Regulation of the Minister of the Environment on ways of classifying the status of uniform parts of surface waters [8] the maximum permissible content of mercury in surface waters should not exceed 0.07 μg/dm^3. Concentrations of mercury did not exceed the limit values only on left-side tributaries of the Klodnica River in points D1, D2 and D3. Concentrations of mercury near to the maximum permissible value were observed in points D4, D6 and D11. In the rest of the examined points the permissible value was considerably exceeded.

2. Concentrations of cadmium obtained in all examined points and four measurement campaigns range from < 0.200 to 1.010 μg/dm^3. Polish legislation as well as European Environment Quality Standards accept the increased content of cadmium up to 1.5 μg/dm^3 depending on the class of water hardness. In 2007 the Voivodeship Inspectorate for Environmental Protection located fifteen points of operational monitoring [6] on the Klodnica River. On this basis waters of the Klodnica River in nine points were classified as class "V" – water of bad quality, and in six points as class "IV" – water of unsatisfying quality. Assuming that waters of the Klodnica River belong to "IV" class of quality, the concentration of cadmium according to EQS [5] and Polish legislation [4] should not exceed 0.9 μg/dm^3. This condition was not fulfilled only in point K1. Assuming that waters of the Klodnica River belong to "V" class of quality, the

concentration of cadmium according to EQS [5] and Polish legislation [4] should not exceed 1.5 μg/dm^3. This condition was fulfilled in all examined points.

3. Concentrations of PAHs determined for the Klodnica River and its tributaries for both measurement campaigns range as follows: anthracene from < 0.009 to 0.066 μg/dm^3, benzo[a]pyrene from < 0.003 to 0.0180 μg/dm^3, sum (benzo[b]fluoranthene and benzo[k]fluoranthene) from < 0.0045 to 0.032 μg/dm^3, sum (benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene) from < 0.0025 to 0.0275 μg/dm^3. In most of the examined points concentrations of PAHs were on the level unabling their determination with the applied measurement method and comparing these concentrations with values of European Environment Quality Standards EQS [5] or limit values of priority substance concentrations described in the Regulation of the Minister of the Environment [4]. Only few measurement points located near collectors of mine waters from hard coal mines and points located on the inlets of sewage treatment plants operating on the Klodnica River slightly exceeded the permissible concentrations. These are: sum (benzo[b]fluoranthene and benzo[k]fluoranthene) and sum (benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene).

4. The research confirms that there are three "hot points" [2], ie places of considerable exceedence of permissible concentrations of dangerous substances, in the Klodnica River catchment. The first of them is point K4. In this point the concentration of mercury was 0.707 μg/dm^3 in the third measurement campaign and the concentration of cadmium was 0.650 μg/dm^3 in the second measurement campaign. The next "hot point" is point D5, where mercury concentration was 0.893 μg/dm^3 in the third campaign and cadmium concentration was 0.460 μg/dm^3 in the second one. In this point also small excess of PAHs was noticed. The third "hot point" was point D10. The concentration of mercury in this point was 0.402 μg/dm^3 and cadmium concentration was 0.690 μg/dm^3.

5. Points located near inlets of sewage and outlets of treated sewage from three sewage treatment plants operating in the Klodnica River catchment were also examined. In all three cases the comparison of pollutant concentrations on inlets and outlets of sewage, both for mercury, cadmium and PAHs, showed considerable improvement of water quality on outlets of treated sewage.

6. The carried out screening research proved that in waters of serious anthropogenic changes the exceeded permissible concentrations of mercury, cadmium, sum (benzo[b]fluoranthene and benzo[k]fluoranthene) and sum (benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene), defined by the European Environment Quality Standards and Polish legislation may be expected.

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ZAWARTOŚĆ WYBRANYCH SUBSTANCJI PRIORYTETOWYCH W ZLEWNI RZEKI KŁODNICY

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Abstrakt: Przedstawiono wyniki badań zawartości wybranych substancji priorytetowych w zlewni rzeki Kłodnicy. Do badań wybrane zostały dwa metale: kadm i rtęć oraz sześć związków z grupy wielopierścieniowych węglowodorów aromatycznych (WWA): antracen, benzo[a]piren, benzo[b]fluoranten, benzo[k]fluoranten, benzo[g,h,i]perylen, indeno[1,2,3-cd]piren. Rtęć oznaczana była techniką zimnych par absorpcyjnej spektrometrii atomowej (CV AAS) za pomocą analizatora RA-915$^+$ z przystawką RP-91 firmy Lumex, kadm oznaczano metodą absorpcyjnej spektrometrii atomowej z elektrotermiczną atomizacją próbki (ET AAS) za pomocą urządzenia AAnalyst 600 firmy PerkinElmer, WWA analizowano techniką wysokosprawnej chromatografii cieczowej z detekcją fluorescencyjną (HPLC–FLD), przy użyciu chromatografu cieczowego

HP 1050 firmy Hewlett Packard. Badania przeprowadzone zostały w 2008 roku, w czterech sesjach pomiarowych, z częstotliwością raz na kwartał. Łącznie we wszystkich sesjach przebadano dwadzieścia osiem punktów pomiarowych zlokalizowanych w obrębie całej zlewni rzeki Kłodnicy. Otrzymane wyniki badań porównano z dopuszczalnymi stężeniami substancji priorytetowych w wodach powierzchniowych zawartych w propozycji Unii Europejskiej dotyczących standardów jakości środowiska – Environmental Quality Standards (EQS), oraz z wymaganiami określanymi przez polskie prawodawstwo jako wartości graniczne chemicznych wskaźników jakości wód.

Słowa kluczowe: substancje priorytetowe, zlewnia rzeczna, badania screeningowe