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Bartosz NOWAK[1] and Izabela FULARA[2]

CONCENTRATION OF SELECTED PRIORITY SUBSTANCES IN KLODNICA RIVER CATCHMENTS

ZAWARTOŚĆ WYBRANYCH SUBSTANCJI PRIORYTETOWYCH W ZLEWNI RZEKI KLODNICY

Abstract: Results of research on concentration of selected priority substances in Klodnica River catchments were presented. To the research were chosen following priority substances: cadmium, mercury, anthracene, benzo[a]pyrene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[g,h,i]perylene and indeno[1,2,3-c,d]pyrene. Mercury was determed with the method of cold vapour atomic absorption spectrometry (CV AAS) using RA-915$^+$ analyzer with RP-91 attachment produced by Lumex. Cadmium was determed with the method of direct electrothermal atomic absorption (ET AAS) using AAnalyst 600 appliance produced by Perkin Elmer. PAHs were analysed with high-performance liquid chromatography method with fluorescence detection (HPLC-FLD) using liquid chromatograph HP 1050 produced by Hewlett Packard. The results of the research were compared with allowable concentration of priority substances in surface waters included in the proposal of UE concerning Environmental Quality Standards, and with requirements of the Polish legislation as the values determining water state indicators.

Keywords: priority substances, river catchments, screening study

Klodnica is the longest river flowing through the region of the Upper Silesia Industrial District (GOP). It is one of right-bank inflows of Odra river. It is over 75 km long, 40 km of which is situated in GOP. The river-head of Klodnica is situated in the southern part of Katowice, in Murckowski Forests. The river flows through the biggest cities of Upper Silesia, such as: Katowice, Ruda Slaska, Mikolow, Zabrze, Bytom, Gliwice and it ends its course in Kedzierzyn-Kozle flowing into Odra [1]. The most important inflows of Klodnica are right-bank: Bielszowicki Stream, Czarniawka Stream, Bytomka Stream, Drama Stream, Toszecki Stream and left-bank: Jamna Stream, Gieraltowicki Stream. In the course of the river three big barrage reservoirs are located: large Dzierzno Lake on Klodnica River, small Dzierzno Lake on Drama Stream and reservoir Plawniowice on Toszecki Stream. The biggest pollution discharges are drained to Klodnica in its main course, where the river and its inflows flow through densely populated and most industrialized avtive areas of Upper Silesia.

The main sources of pollution of Klodnica River are sewage discharge and that sewage flowing down from industrial and post-industrial areas, sewage flowing into river from the areas, where industrial landfills and dumping-grounds are located, discharges of mine waters that contain a lot of salt and sewages from region of cities and communies where there are no sewage treatment plant, or where sewage can not be refined in a sufficient way with the use of applied technology [2].

[1] Department of Environmental Protection, Division of Groundwater and Soil, Institute for Ecology of Industrial Areas, ul. Kossutha 6, 40-844 Katowice, tel. 32 254 60 31 wew. 299, fax 32 254 17 17, email: nowak@ietu.katowice.pl
[2] Central Laboratory, Institute for Ecology of Industrial Areas, ul. Kossutha 6, 40-844 Katowice, tel. 32 254 60 31 wew. 146, fax 32 254 17 17, email: i.fulara@ietu.katowice.pl

Polish and European regulations in aspect of priority substances

One of main principles of The Water Framework Directive (WFD) is to achieve good chemical condition of waters, that is assessed by taking into consideration presence of substance that are proved to have or are highly probable to have a harmful influence on ecosystems and water organisms as well as on people's health (so called priority substances). A full list of priority substances can be found in annex X WFD [3]. A regulation by Minister of Environment on ways of classifying condition of uniform parts of surface waters, that came into force in 2008, contains limit values of markers of condition of waters [4]. Thanks to those markers it is possible to unequivocally interpret results of undertaken research. Through realisation of principles of WFD it is assumed that good chemical condition of waters will be achieved till 2015, establishing at the same time year 2025 as a deadline for elimination of substances recognised as priority dangerous substances from group of priority substances.

This paper presents results of screening research on content of chosen priority substances in catchment of Klodnica River. Two heavy metals: mercury and cadmium were chosen for research as well as compounds of group of polycyclic aromatic hydrocarbons: anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i] perylene, indeno[1,2,3-c,d]pyrene. Received contents of mercury, cadmium and above-mentioned PAHs in surface waters were compared with regulations of EU - Environmental Quality Standards (EQS) [5], and with regulations of Polish legislation [4]. Acceptable contents of mercury, cadmium and PAHs according to EQS and according to Polish legislation were presented in Table 1.

Table 1

Allowable concentrations of mercury, cadmium and selected PAHs by EQS [5], and by Polish legislation [4]

Priority substances	EQS		(DzU 2008 Nr 162, poz. 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	-	0.07
Cadmium and its compounds	0.08÷0.25[1]	0.45÷1.5[1]	-	0.45÷1.50[2]
Anthracene	0.10	0.40	-	0.40
Benzo[a]pyrene	0.05	0.10	-	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-c,d]pyrene	0.002	not applicable	0.002	-

[1] Depending on water hardness classes [5]
[2] Depending on water hardness classes [4]
- No available data

Study of area

Researches on content of priority substances (mercury, cadmium and PAHs) in catchment of Klodnica River were conducted in four measurement sessions in 2008, with sampling frequency once a quarter. First session was conducted on 24th January 2008, second on 9th April 2008, third between 11th and 12th September 2008 and the fourth one on

11th December 2008. Eight measurement points were examined in the four sessions. The points were situated from the spring of Klodnica River in Brynow district of Katowice, through inlets of sewage and run-offs of sewage from sewage treatment plants placed in the course of the river next to mouth of most important inflows, right up to inlet of Klodnica River to barrage reservoir "Dzierzno Duze" and the inlet of the river to Odra River in Kedzierzyn-Kozle.

Methods of analysis

To determine concentration of mercury in waters of Klodnica River and its inflows a multifunctional analyser of mercury RA-915+ has been used. Its work is based on Zeeman atomic absorption spectroscopy with use of modulation with high polarisation of light, together with RP-91 attachment. The attachment is used to determine concentration of mercury in liquid samples with use of technique of "cold vapour". Limit of detection of the used method is 0,002 μg/dm^3. Cadmium in the waters was determined with technique of Electrothermal Atomic Absorption Spectrometry (ET AAS), with use of spectrometer AAnalyst 600 produced by Perkin Elmer. Limit of detection of the used method is 0.2 μg/dm^3. In order to determine concentration of PAHs the samples of water were extracted with SPE technique with use of octadecyl-(C_{18}) phase. Extracts were analysed with technique of high performance liquid chromatography with fluorescence detection (HPLC-FLD) with use of liquid chromatograph HP 1050 produced by Hewlett Packard. Limit of detection of used method is different depending on determined compound and is, as follows: anthracene 0.009 μg/dm^3, benzo[a]pyrene 0.003 μg/dm^3, sum (benzo[b]fluoranthene and benzo[k]fluoranthene) 0.004 μg/dm^3, sum (benzo[g,h,i]perylene and indeno[1,2,3-c,d]pyrene) 0.003 μg/dm^3.

Results

Concentrations of mercury, cadmium and concentration of chosen PAHs for Klodnica River and its inflows that were obtained in four measurement sessions are shown in Tables 2 and 3.

Table 2

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

Number of sampling point	Hg [μg/dm^3]				Cd [μg/dm^3]			
	Sesion I	Sesion II	Sesion III	Sesion IV	Sesion I	Sesion II	Sesion III	Sesion IV
„K1"	-	0.086	0.100	-	-	1.010	0.200	-
„D1"	-	0.016	-	-	-	<DL	-	-
„D2"	-	0.010	-	-	-	0.370	-	-
„D3"	-	0.048	-	-	-	0.220	-	-
„K4"	-	0.266	0.707	-	-	0.650	<DL	-
„K5"	0.137	0.182	0.458	0.108	<DL	0.500	0.380	0.510
„D4"	-	-	0.070	-	-	-	<DL	-
„K8"	-	0.236	-	-	-	0.330	-	-
„D5"	-	0.146	0.893	-	-	0.460	0.340	-
„D6"	-	-	0.069	-	-	-	<DL	-
„K9"	-	0.339	-	-	-	0.220	-	-

„D7”	0.163	0.190	0.084	0.083	<DL	<DL	0.220	<DL
„D8”	--	0.129	-	-	-	<DL	-	-
„D9”	-	0.189	0.296	-	-	0.650	0.300	-
„D10”	-	0.402	0.244	-	-	0.690	<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	0,600	0.590	<DL	<DL
„K14”	-	0.475	0.088	-	-	0.530	<DL	-
„K15”	-	0.179	-	-	-	<DL	-	-

Table 3

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

Number of sampling point	**Anthracene [μg/dm^3]**				**B[a]P[1] [μg/dm^3]**			
	Sesion I	**Sesion II**	**Sesion III**	**Sesion IV**	**Sesion I**	**Sesion II**	**Sesion III**	**Sesion IV**
„K1”	-	<DL	-	-	-	<DL	-	-
„D1”	-	<DL	-	-	-	<DL	-	-
„D2”	-	<DL	-	-	-	<DL	-	-
„D3”	-	<DL	-	-	-	<DL	-	-
„K4”	-	<DL	<DL	-	-	<DL	0.005	-
„K5”	<DL	<DL	<DL	0.011	0.003	<DL	<DL	0.015
„D4”	-	-	<DL	-	-	-	<DL	-
„K8”	-	<DL	-	-	-	<DL	-	-
„D5”	-	<DL	<DL	-	-	0.018	0.018	-
„D6”	-	-	<DL	-	-	-	<DL	-
„K9”	-	<DL	-	-	-	0.004	-	-
„D7”	<DL	<DL	0.012	<DL	0.007	0.006	0.003	0.014
„D8”	-	<DL	-	-	-	0.007	-	-
„D9”	-	<DL	<DL	-	-	<DL	<DL	-
„D10”	-	0.052	0.013	-	-	0.011	0.010	-
„D11”	-	-	<DL	-	-	-	<DL	-
„D12”	-	-	0.010	-	-	-	0.006	-
„D13”	-	<DL	-	-	-	0.003	-	-
„K10”	-	<DL	<DL	-	-	0.006	0.004	-
„K11”	<DL	<DL	0.012	0.031	0.004	<DL	<DL	0.058
„K14”	-	<DL	<DL	-	-	<DL	<DL	-
„K15”	-	<DL	-	-	-	<DL	-	-

Number of sampling point	**Σ B(b)F +B(k)F[2] [μg/dm^3]**				**Σ B(ghi)P +IP[3] [μg/dm^3]**			
	Sesion I	**Sesion II**	**Sesion III**	**Sesion IV**	**Sesion I**	**Sesion II**	**Sesion III**	**Sesion IV**
„K1”	-	<DL	-	-	-	<DL	-	-
„D1”	-	<DL	-	-	-	<DL	-	-
„D2”	-	<DL	-	-	-	<0.004	-	-
„D3”	-	<DL	-	-	-	<DL	-	-
„K4”	-	<DL	<DL	-	-	<DL	0.006	-
„K5”	0.004	<DL	<DL	0.021	0.002	0.004	<DL	0.018
„D4”	-	-	<DL	-	-	-	<DL	-
„K8”	-	<DL	-	-	-	0.004	-	-
„D5”	-	0.014	<DL	-	-	0.028	0.011	-
„D6”	-	-	<DL	-	-	-	<DL	-
„K9”	-	<DL	-	-	-	0.011	-	-
„D7”	0.009	0.011	<DL	0.018	0.010	0.008	0.004	0.022

„D8”	-	0.014	-	-	-	0.012	-	-
„D9”	-	<DL	<DL	-	-	<DL	<DL	-
„D10”	-	0.013	0.006	-	-	0.009	0.006	-
„D11”	-	-	<DL	-	-	-	<DL	-
„D12”	-	-	0.006	-	-	-	0.004	-
„D13”	-	0.007	-	-	-	0.005	-	-
„K10”	-	<DL	<DL	-	-	0.010	0.003	-
„K11”	0.005	<DL	0.006	0.078	0.007	0.004	0.010	0.091
„K14”	-	<DL	<DL	-	-	0.004	<DL	-
„K15”	-	<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-c,d]pyrene

Points located on inlets and outlets of three sewage treatment plants draining treated sewage to Klodnica river were examined during third measurement session. Table 4 presents obtained contents of mercury, cadmium and PAHs on inlets of sewage and outlets of treated sewage from sewage treatment plants. Two of the examined sewage treatment plants were of mechanical-biological-chemical type and one was of mechanical-biological type. In all three cases we can notice a definite improvement of water quality concerning cadmium, mercury and PAHs in points located on outlets of examined sewage treatment plants.

Table 4

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 treated sewage [μg/dm^3]	0.257	0.123	0.093
Cd	Inlet of sewage [μg/dm^3]	0.33	<DL	<DL
	Outlet of treated sewage [μg/dm^3]	<DL	<DL	<DL
Anthracene	Inlet of sewage [μg/dm^3]	<DL	0.010	0.066
	Outlet of treated sewage [μg/dm^3]	<DL	<DL	<DL
B[a]P	Inlet of sewage [μg/dm^3]	0.004	<DL	0.023
	Outlet of treated 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 treated 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 treated 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-c,d]pyrene

Conclusion

- ✓ Concentrations of mercury, which were obtained in conducted researches in all point in four measurement sessions range from 0.01 to 0.893 μg/dm^3. According to Environment Quality Standards EQS [6], and under decree by Minister of Environment on ways of classifying condition 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 border markers only on leftside inflows of Klodnica River in points D1, D2 and D3. Concentration of mercury near to maximum permissible value was observed in points D4, D6 and D11. In the rest of examined points content of mercury considerably exceeds the permissible value.
- ✓ Concentrations of cadmium obtained in all examined point in four measurement sessions range from <0.2 to 1.01 μg/dm^3. Polish legislation as well as European Environment Quality standards accept increased content of cadmium up to 1.5 μg/dm^3 depending on class of water hardness. In 2007 Provincial Inspectorate for Environment Protection located fifteen points of operational monitoring [6] on Klodnica River. On this basis waters of Klodnica River in nine points were credited "V" class of quality - waters of bad quality, and in six points Klodnica River was credited "IV" class of quality - water of unsatisfying quality. Providing waters of Klodnica River belong to "IV" class of quality, then 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. Providing waters of Klodnica River belong to "V" class of quality, then 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.
- ✓ Determined concentrations of PAHs in Klodnica River and its inflows for both measurement sessions 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-c,d]pyrene) from <0.0025 to 0.0275 μg/dm^3. In majority of examined points concentration of PAHs was on level enabling its determination with used measurement method and comparing these concentrations with values of European Environment Quality standards EQS [5] as well as to limit values of concentration of priority substances described in decree by Minister of Environment [4]. Only few

measurement points located near collectors of mine waters from hard coal mines and points located on inlets of sewage treatment plants placed on Klodnica River slightly exceed permissible concentration. These are sum (benzo[b]fluoranthene and benzo[k]fluoranthene) and sum (benzo[g,h,i]perylene and indeno[1,2,3-c,d]pyrene).

- ✓ The above research confirmed that there are three "hot points" [2], that is places of considerable excess of permissible concentrations of dangerous substances, in catchment of Klodnica River. First of them is point K4. In this point concentration of mercury was 0.707 μg/dm^3 in III measurement session and concentration of cadmium was 0.65 μg/dm^3 in II measurement session. Next „hot point" is point D5, where concentration of mercury was 0.893 μg/dm^3 in III measurement session and concentration of cadmium was 0.46 μg/dm^3 in II measurement session. In this point also small excess of PAHs were noticed. Third „hot point" is point D10. Concentration of mercury in this point was 0.402 μg/dm^3 and concentration of cadmium was 0.69 μg/dm^3.
- ✓ Examined were also points located near inlets of sewage and outlets of treated sewage from three sewage treatment plants working in catchment of Klodnica River. In all three cases comparing concentrations of pollution on inlets and outlets of sewage, both for mercury and cadmium as well as for PAHs, a considerable improvement of water quality on outlets of treated sewage can be observed.
- ✓ Conducted screening researches have proved, that in waters that are seriously anthropologically changed there may occur a problem of exceeding 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-c,d]pyrene), defined by European markers of environment and Polish legislation.

References

[1] Nocoń W. and Kostecki M.: *Charakterystyka hydrochemiczna Kłodnicy*. Ochr. Środow., 2006, **3**, 39-44.
[2] Website: www.ietu.katowice.pl/Klodnica/index.htm
[3] Website: www.rdw.org.pl
[4] Decree by Minister of Environment, 20 of August 2008, on ways of classifying condition of uniform parts of surface waters. (DzU 2008, Nr 162, poz. 1008).
[5] Directive of The European Parliament and of The Council on environmental quality standards in the field of water policy and amending. Directive 2000/60/EC, Brussels, 17.7.2006, COM(2006) 397, final 2006/0129 (COD).
[6] Glubiak-Witwicka E., Laszczak S., Łatkowska M., Piszczek S., Solich J. i Szumowska A.: Provincial Inspectorate for Environmental Protection in Katowice. Report about environmental condition in 2007 - Surface water.

ZAWARTOŚĆ WYBRANYCH SUBSTANCJI PRIORYTETOWYCH W ZLEWNI RZEKI KŁODNICY

Instytut Ekologii Terenów Uprzemysłowionych

Abstrakt: Przedstawiono wyniki badań zawartości wybranych substancji priorytetowych w zlewni rzeki Kłodnicy. Do badań wybrane zostały następujące substancje priorytetowe: kadm, rtęć, antracen, benzo[a]piren, benzo[b]fluoranten, benzo[k]fluoranten, benzo[g,h,i]perylen, indeno[1,2,3-c,d]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. 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