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PCBs AND HEAVY METALS IN WATER AND BOTTOM SEDIMENTS OF THE KOZŁOWA GÓRA DAM RESERVOIR

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Abstract: The aim of the presented research was to analyse the pollution of the Kozłowa Góra Dam Reservoir with PCBs (28, 52, 101, 118, 138, 153, 180) and heavy metals (Zn, Cu, Ni, Cd, Pb, Cr). The investigated water and bottom sediments were sampled from two sampling points in November, 2009. The sampling points were located in the southern part of the Kozłowa Góra Dam Reservoir. The samples of bottom sediments were taken from the surface layer of 5 cm thickness. The extraction of PCBs from the bottom sediments was performed according to the EPA 3550B standard. For the sequential extraction analysis of metals from the sampled bottom sediments, the method suggested by Tessier was applied. Based on the obtained results the water and bottom sediments from the Kozłowa Góra Dam Reservoir were polluted with polychlorinated biphenyls. The highest concentration of the investigated PCB congeners in bottom sediments was determined in the sampling point No. 1 (2.78 μg/kg d.m.), whereas in the sampling point No. 2 this level was over 20-fold lower which might result from the inflow of these compounds with the waters of the Brynica river. In both sampling points the investigated bottom sediments were predominated by higher chlorinated PCBs with comparable contents of 86% and 85%, respectively. The level of pollution in the investigated bottom sediments (calculated per dry matter) with polychlorinated biphenyls did not exceed the level of TEL (< 0.02 mg/kg). The PEL value (3.5 mg/kg) was exceeded in the case of cadmium in the bottom sediment from the sampling point No. 2 and also lead (91 mg/kg) from both sampling points. The first two fractions with the mobile forms of metals are the most sensitive fractions to any changes of the environmental conditions in the benthic zone. In those fractions significant contents of lead, cadmium, nickel and zinc were observed.

INTRODUCTION

At present, the pollution of bottom sediments is one of major environmental problems due to the potential harmful effect of pollutants on living organisms and also on human health. When introduced to surface water most toxic organic compounds with low solubility and of poor biodegrability are transported in water and as a result they end up in bottom sediments [3]. Therefore, the increased concentrations of trace elements (i.e. Hg, Zn, Pb, Cd, Cu, As) and POPs (i.e. pesticides, polycyclic aromatic hydrocarbons, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, polychlorinated biphenyls) in bottom sediments of rivers and water reservoirs are observed [3, 28]. Particularly high concentrations of harmful compounds are observed near the points of anthropogenic sources of contamination, i.e. places where wastewater from urban and agricultural areas is discharged. Bottom sediments are not only considered the main 'repository' of persistent and toxic contaminants, which are introduced to the environment, but they are also an integral part of water environment and life environment for many water organisms [3].

In order to determine bioavailability of heavy metals and their potential risk to living organisms the speciation analysis is currently applied instead of the analysis of the total metal concentration. The speciation analysis allows for quantitative determination of particular chemical forms typical for metals bound in bottom sediments [15, 25]. Metals bound in bottom sediments via physical adsorption and chemisorptions, e.g. due to changes in salinity (i.e. ion exchangeable form) can be easily released from sediments to water. Also metals bound to carbonates can be released when significant acidification of environment occurs. The performed speciation analyses of heavy metals in various bottom sediments confirmed that the fraction of carbonates plays a significant role in binding cadmium [16, 31, 32], lead [16, 18] and copper [20]. The release of metals that were bound during co-precipitation with hydrated iron and manganese oxides is more difficult. Also, metals that are bound to organic matter can be released to open water as a result of decomposition of organic matter. Only metals present in the soluble fraction in concentrated mineral acids can be considered to be immobilized.

PCBs can be also introduced into surface water and bottom sediments with the residues of paints used for painting boats and ships and as a result of surface water run-off from polluted areas and discharge of industrial and municipal wastewater. Wastewater treatment allows only for removal of PCBs adsorbed on solid particles suspended in water, whereas the soluble fraction is not removed and is transferred to water environment. PCBs present in surface waters are easily adsorbed in suspensions and bottom sediments or they are transported by river. Some PCB congeners out of 209 show high bioaccumulation, toxicity, potential carcinogenesis and high persistence in the environment [8].

PCBs might occur in tissues of aquatic organisms (e.g. fish) in concentrations that are even thousand times higher than in water. Due to accumulation in food chain, these compounds can get into the human body, and thus pose a serious threat to human health [10, 30, 35].

For the purpose of monitoring the assessment of the quality of bottom sediments in respect to contamination with hazardous organic compound and trace elements is conducted based on geochemical criteria. Depending on the composition bottom sediments are classified according to the level of geochemical background into slightly polluted sediments, moderately polluted sediments and polluted sediments. The criteria for determination of lower limits (i.e. Treshhold Effects Levels – TEL) and upper limits (i.e. Probable Effects Levels – PEL) for pollutants detected in bottom sediments have been also developed [2]. The TEL corresponds to the concentration of chemical components below which the toxic effect is hardly observed. In the case of concentration higher than PEL the harmful effect of pollutants is observed.

In view of the fact that the dam reservoir in Kozłowa Góra is the only fresh water reservoir for the Water Treatment Plant in Kozłowa Góra it is of great importance to determine the degree to which the reservoir is polluted with polychlorinated biphenyls. The obtained results will allow for the assessment whether water and bottom sediments could pose threat to human and animal health.

In this study the distribution of particular heavy metals between chemical fractions of the investigated bottom sediments from the Kozłowa Góra Dam Reservoir was analyzed. The mobility of metals and the possibility of secondary contamination were also estimated.

MATERIALS AND METHODS

Sampling

The Kozłowa Góra Dam Reserovir is located on the south-east outskirts of Świerklaniec commune. This reservoir was formed due to the raised water level of the Brynica River. It covers approx. 5.5 km^2 of the area and its volume is approx. 13 mln m^3. It is relatively shallow with the average depth of 4.5 m. At present, the Kozłowa Góra Dam Reservoir is a water source for the Water Treatment Plant in Wymysłów which belongs to the Upper Silesia Water Supply Company. It also functions as flood control and it may be used for touristic-recreational activities.

The sediments were sampled from two sampling spots in November, 2009. The sampling spots were located in the southern part of the Kozłowa Góra Dam Reservoir, at the outflow (at the dam). The localization of the sampling spots is shown in Figure 1. The samples were taken from the surface layer with the thickness of 5 cm. The tubular Ruttner sampler was used for taking samples of bottom sediments. 3 samples of bottom sediments and 3 dm^3 of water were taken from each sampling spot. The water samples were taken at the depth of approx 0.5 m from the water surface.

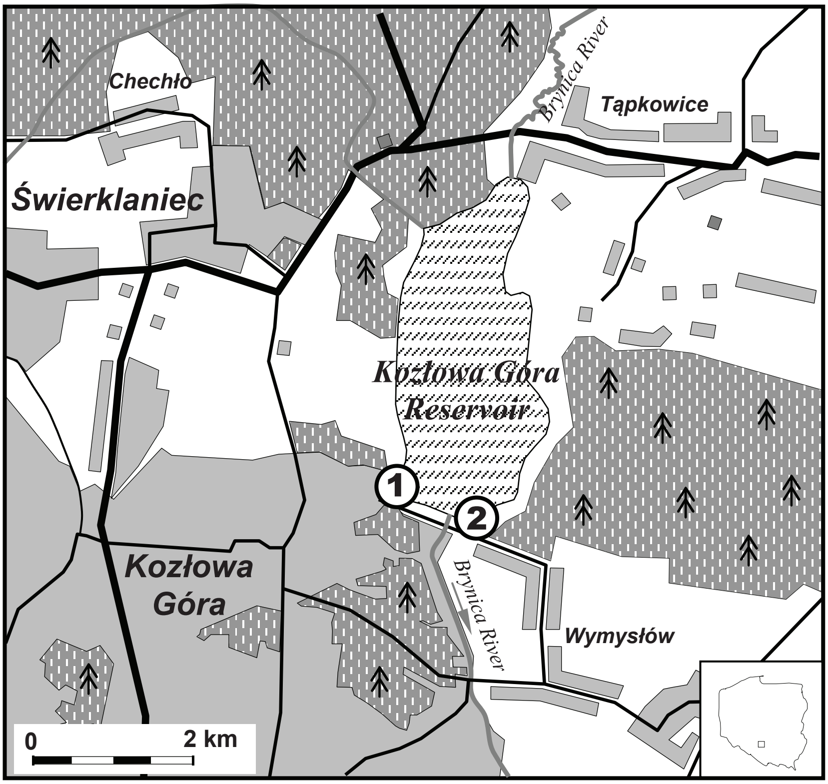


Fig. 1. Location of the Kozłowa Góra Dam Reservoir with the sampling points (**1**) and (**2**)

Analysis of PCBs

The extraction of PCBs from the bottom sediments was performed according to the EPA 3550B standard [7]. The bottom sediment was sampled and dried until it reached the air-dry state and then sieved through the sieve. Next, the sediment was mixed with anhydrous Na_2SO_4 and the hexane-acetone mixture (1:1, v/v) was added. After that the prepared sediment was exposed to pulse sonication in three replications The solution above the sediment was decanted each time and new doses of the hexane: acetone mixture were added to the sediment. The obtained extracts were mixed and evaporated in nitrogen stream. Powdered copper was added to the extract in order to remove sulphur. The extract was shaken for 6 hours. To remove polar compounds the extract was also passed through columns filled with Florosil.

To determine PCBs in the sampled water the solid phase extraction (SPE) was applied [17]. 1 dm^3 of sampled water was passed through the Bakerbound columns with the Octadecyl C_{18} filling. The Bakerbond columns were initially preconditioned with 2 x 6 cm^3 aliquots of n-hexane and 1 x 6 cm^3 aliquot of distilled water. Then, 1 dm^3 of the investigated water was passed through the columns to prevent them from drying out. Afterward the columns were rinsed with 6 cm^3 of distilled water and air-dried. Next, 1.5 cm^3 of n-hexane was used to wet the stationary phase. After 5 min. the extract was slowly aspirated into the test tube. The elution step was repeated with a fresh aliquot of n-hexane. The extract was subsequently concentrated to a volume of 0.1 cm^3.

The extract was condensed in vacuum and then subject to qualitative and quantitative analysis by gas chromatography (CGC). The separation was done on a DB-5 column (30 m x 32 mm x 1 μm). The quadrupole mass spectrometer MS 800 working in a selective mode of ion monitoring was used for detection [13]. The analysis was conducted according to programmed temperature values: 40°C – 40°C/min, 120°C – 5°C/min, 280°C – 15 min. The carrier gas flow was set at 70 kPa. The quantification of PCBs was obtained through the single ion monitoring (SIM) m/z. For each PCB three representative ions were selected.

The determination of PCBs was performed for each sample and each four injections of the obtained extract. In order to check the procedure for determination of PCBs in bottom sediment, the recovery values were also determined. The samples of bottom sediment were enriched with Ehrenstorfer's PCB MIX3 at the concentration of 10 ng/μl.

Then, the determination of biphenyls was carried out using the abovementioned procedure. The obtained recovery rates ranged from 65 to 91% and were within the typical ranges provided in literature references [35].

Analysis of heavy metals

The samples of bottom sediments were first dried in the laboratory in air-dry conditions, and then in a dryer at 105^0C for 24 h. Three different samples of the same bottom sediments were prepared for the analyses. A mixture of concentrated acids HNO_3 and HCl (1:3, v/v, aqua regia) was used for the extraction of metals (i.e. Zn, Cu, Ni, Cd, Pb, Cr) from the bottom sediment samples. The determination of heavy metals was conducted with the use of atomic absorption spectrometry (spectrometer novAA 400, Analytik Jena). In view of the studies performed by Dąbrowska [6] no significant influence of the particle size of bottom sediments on the occurrence of the chemical forms of heavy metal was observed, therefore the metal speciation was performed for the particle size smaller than 0.25 mm. In order to monitor water sediments in Poland, the concentration of heavy metals is determined in the fraction of particle size < 0.2 mm [1]. For the sequential extraction analysis of metals from the sampled bottom sediments, the method suggested by Tessier was applied (Table 1) [21, 26]. The overall concentration of metals in the sediments determined after mineralization with the use of aqua regia was compared with the sum of metal concentrations in the extracted fractions.

Table 1. Scheme of analytic procedures in sequential extraction

Fraction	Sequential extraction procedure per 1g of dry sediment	Forms of metals
I	8 cm^3 1 M $MgCl_2$, pH=7, temp. 22^{0}C, shaking 1 h	Exchangeable
II	8 cm^3 1 M CH_3COONa, acidet CH_3COOH, pH=5, temp. 22^{0}C, shaking 5 h	Bounded with carbonates
III	20 cm^3 0.04 M NH_2OHHCl in 25% (v/v) CH_3COOH, temp. 96^{0}C, shaking 6 h	Bounded with Fe and Mn oxides
IV	3 cm^3 0.02 M HNO_3 i 5 cm^3 30% H_2O_2, pH=2, temp. 85^{0}C, shaking 2 h, 5 cm^3 30% H_2O_2, temp. 85^{0}C, shaking 3 h 5 cm^3 3.2 M CH_3COONH_4 in 20% (v/v) HNO_3, temp. 22^{0}C, shaking 0.5 h	Bounded with organic matter – sulfides
V	2 cm^3 65% HNO_3 + 6 cm^3 36% HCl, temp. 100^{0}C, 2 h	Residue

The concentrations of heavy metals in water samples (acidified to pH = 2 with 65% HNO_3) were determined by atomic absorption spectrometry [9]. Other parameters including pH, colour, turbidity (turbidimeter TN-100, Eutech Instruments) and total organic carbon content (carbon analyzer TOC multi N-C, Analytik Jena) were also determined.

RESULTS AND DISCUSSION

Characteristics of the investigated water

The concentrations of PCBs determined in the investigated water are presented in Table 2.

With reference to the obtained results, the water sampled from the Kozłowa Góra Dam Reservoir was polluted with polychlorinated biphenyls. However, no heptachlorobiphenyl (PCB 180) was determined in the investigated samples.

Table 2. Concentration of PCBs in the water

Sampling points	PCBs, ng/dm^3						
	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB153	PCB 180
1	1.1±0.2	2.0±0.4	0.7±0.1	1.1±0.2	1.2±0.3	1.2±0.3	nd[1]
2	1.9±0.4	1.3±0.4	2.4±0.5	0.3±0.1	0.4±0.1	1.9±0.5	nd[1]

[1] nd – not detected

In water taken from the sampling point No. 1 six congeners of PCBs were detected. The total concentration was equal to 7.3 ng/dm^3. The highest concentration was determined for tetrachlorobiphenyl i.e. PCB 52 (2.0 ng/dm^3), whereas the lowest concentration was determined for pentachlorobiphenyl PCB 101 (0.7 ng/dm^3). The ratio of lower (LCB) and higher chlorinated biphenyls (HCB) was 39% and 61%, respectively.

In the sampling point No. 2 six congeners of PCBs were found, similarly to the sampling point No. 1. The highest concentration was observed for the congener of PCB 101 (2.4 ng/dm^3), which belongs to the group of pentachlorobiphenyls, whereas the lowest value was determined for PCB 118 (0.3 ng/dm^3) – a representative of the same group. The total concentration of congeners detected in this point was comparable to the water sampled from the sampling point No. 1 and amounted to 8.1 ng/dm^3. The fate of PCBs in surface water is strongly affected by sorption and desorption. The dynamics of sorption in water significantly influences the distribution of PCBs between liquid phase and sediment, sedimentation of PCBs, remobilization from the sediment and potential evaporation, and also introduction to the food chain. The concentration of particular PCB congeners in aquatic organisms depends on bioavailability, which is correlated with the n-octanol/water partition coefficient (K_{ow}) [8, 12, 36]. The analyzed HCB show higher values of K_{ow} (6.4–8.27) and stronger ability to bind to suspension or bottom sediments, which results in decreasing their bioavailability to living organisms. PCBs and toxic coplanar biphenyls present in bottom sediments can pose a significant threat to living organisms due to the fact that they can be accumulated in fatty tissue. As lyophilic compounds they can easily penetrate through cell membranes of living organisms and are immediately included in trophic circulation, which poses threat also to human health [8]. In water sampled from both sampling points the following polychlorinated biphenyls predominated: PCB 52 (sampling point No. 1) and PCB 28 (sampling point No. 2). The partition coefficient K_{ow} ranged from 5.8 to 6.1. These higher chlorinated biphenyls are bioavailable and can pose a significant threat to aquatic organisms [10]. The total concentration of 6 congeners in the investigated water was low (i.e. 7.3–8.2 ng/dm^3) in comparison to the results obtained by Kalajzic *et al.* [14]. These researchers proved that the concentration of PCBs in water sampled from the artificial reservoir (which was the source for drinking water for the population of Calgari city, Saridina, (IT) was considerably higher with the average value of 0.84 mg/dm^3. In water sampled from Lake Michigan the concentration of PCBs was lower (0.34– 1.74 ng/dm^3) [11], and in water sampled from Lake Ontario it was 0.31–42.75 ng/dm^3 [19].

The concentrations of heavy metals and values of selected water quality parameters for the water sampled from the Kozłowa Góra Dam Reservoir are listed in Table 3.

The water had slightly alkaline pH (7.7– 7.9) and color index was at the level of 25– 30 mgPt/dm^3. Turbidity and the total organic carbon content were 5.9 NTU and 17.8 mgC/dm^3, respectively. However, at the sampling point No. 1 and at the sampling point No. 2 they were 7.2 NTU and 19.8 mgC/dm^3, respectively. The concentrations of heavy metals in the investigated water was low. The concentrations of zinc, copper, nickel, cadmium, lead and chromium were following: 0.017–0.011; 0.012–0.014; 0.017–0.014; < 0.01; 0.01–0.016; < 0.01 mg/dm^3.

Table 3. Concentration of heavy metals in water and values of chosen water quality parameters

Sampling points	pH -	Turbidity NTU	Colour mgPt/dm^3	TOC mgC/dm^3	Heavy metals, mg/dm^3					
					Zn	Cu	Ni	Cd	Pb	Cr
1	7.7	5.9	25.0	17.8	0.017	0.012	0.017	<0.01	0.010	<0.01
2	7.9	7.2	30.0	19.8	0.011	0.014	0.014	<0.01	0.016	<0.01

Characteristics of the investigated bottom sediment

Based on the obtained results the investigated bottom sediments from the Kozłowa Góra Dam Reservoir are polluted with polychlorinated biphenyls (Table 4).

In the sampling point No. 1 the presence of 7 studied PCB congeners was observed. However, higher chlorinated PCB with code 180 was not found in the water. The highest concentrations of PCBs in the investigated sediments were observed in the case of HCB (86% of the total PCBs) (PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180), whereas in water this level was over 1.5 fold lower (Fig. 2).The presence of higher chlorinated congeners of PCBs might result from their improved adsorption on sediment particles [8, 34]. According to literature references higher chlorinated congeners show high values of n-octanol/water partition coefficient K_{ow} and n-octanol/carbon K_{oc} partition coefficient, which determines the ratio of the concentration of PCBs adsorbed by organic carbon [mg/g] and the concentration of PCBs in water [mg/cm^3] [12]. Due to these properties PCBs with higher number of chlorine atoms in a molecule are strongly adsorbed by the organic fraction of bottom sediments. The sorption of PCBs is also affected by the value of sediment/water partition coefficient (K_p), which describes the hydrophobic sorption of contaminants. With the increase in the number of chlorine atoms in a molecule of biphenyl the value of sediment/water partition coefficient (K_p) also increases. Lower chlorinated biphenyls are less persistent in bottom sediments than higher chlorinated congeners.

In the sampling point No. 2 only 4 congeners of PCBs with codes 52, 101, 138 and 153 were detected, whereas PCB 28 and PCB 118 were additionally detected in water. The highest concentration was determined for PCB 153 (42 ng/kg d.m.), whereas the lowest was for PCB 52 (18 ng/kg d.m.). Polichlorinated biphenyls show high ability to accumulate in sediments. This ability is stronger with the increase of the number of chlorine atoms in a molecule. However, among PCBs there are some congeners with a smaller number of chlorine atoms, and thus they show lower sorption ability to accumulate on the sediment particles than the congeners with a higher number of chlorine atoms. This phenomenon can be accounted for low concentration of PCB 52 in sediments. Therefore, the lack of PCB 28 and PCB 118 in the sediment and their presence in water may be caused by present contamination of water with PCB 28 and PCB 118. PCB 28 and PCB 118 present in water were not able to undergo sorption on the sediment particles within this time frame.

Table 4. Concentration of PCBs in the bottom sediments

Sampling points	PCBs, ng.kg d.m.						
	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB153	PCB 180
1	156±2.7	239±2.7	295±3.8	412±4.0	494±5.1	583±5.4	603±4.7
2	nd[1]	18±1.2	23±2.6	nd	37±3.1	42±3.2	nd

[1] nd – not detected

The higher total concentration of the analysed congeners of PCBs in bottom sediments was determined in the sampling point No. 1 (2782 ng/kg d.m.), whereas in the sampling point No. 2 this level was over 20 fold lower. This may result from the inflow of these compounds with the waters of the Brynica River, which can indicate the presence of an unidentified source of pollution located somewhere along the river, e.g. breakdown

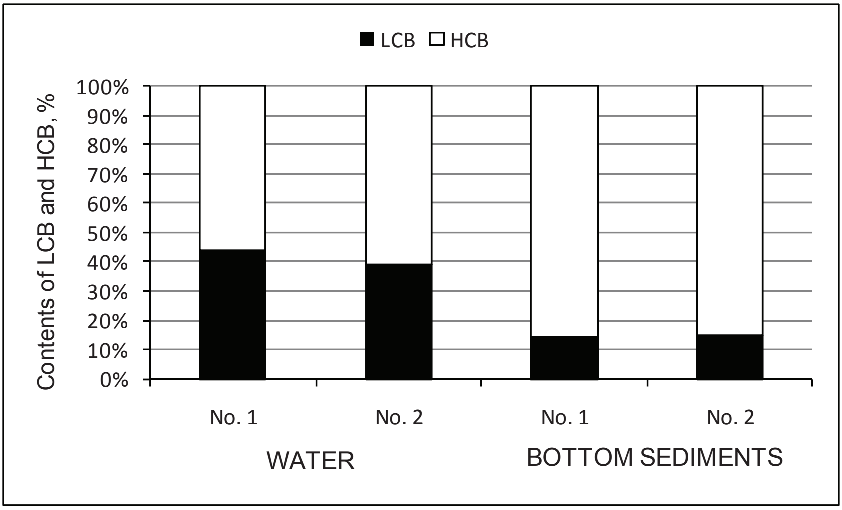


Fig. 2. Percentage contents of lower and higher chlorinated biphenyls in the water and bottom sediments (No. 1 and No. 2 – sampling points)

of one of the several hundreds of transformers in the area of the city or an uncontrolled landfill site.

The total concentration of PCBs in bottom sediments (120–2782 ng/kg d.m.) was below the data available in the literature. The concentration of PCBs in the bottom sediments from Hartwell Lake (San Francisco, USA) ranged from 19 to 2000 µg/kg [29], whereas the average concentration in the bottom sediments from the Włocławski Reservoir was 28.53 µg/kg [2].

The presence of PCBs in bottom sediments is connected with sedimentation of pollution from wastewater, surface water run off or deposition from the atmosphere. In both sampling points No. 1 and No. 2, the investigated sediments were predominated by HCBs, with comparable ratios of 86% and 85%, respectively (Fig. 2). The increased concentration of higher chlorinated biphenyls may result from their low solubility in water and good adsorption ability on the particles of bottom sediments due to high values of K_{ow}, K_{oc} and K_p partition coefficients K_p [8, 36].

The assessment of the quality of bottom sediments was carried out based on geochemical criteria and types and concentrations of contaminants in various bottom sediments according to the Minister of the Environment's Regulation of 16th April 2002 *on the types and concentrations of the substances which cause that the spoil is polluted* (Dz. U. Nr 55 poz. 498). The threshold level for the concentration of the total of 6 PCB congeners (i.e. 28, 52, 118, 138, 153, 180) present in bottom sediments from dredging of seawater areas, water reservoirs, ponds, natural watercourse, channels and ditches amounts to 0.3 mg/kg. The degree of pollution of the investigated bottom sediments with polychlorinated biphenyls did not exceed this treshold level.

The level of pollution in the investigated bottom sediments (calculated per dry matter) with polychlorinated biphenyls did not exceed the level of TEL (< 0.02 mg/kg) [2]. However, literature data report that the concentration of PCBs in living organisms in water environments is higher than their concentrations in the bottom sediments [30]. This results from the fact that hydrophobic PCBs show tendency towards bioaccumulation in living organisms and towards biomagnification, i.e. increasing its concentration in the food chain [5]. Water and bottom sediments contaminated with polychlorinated biphenyls cause the reduction in population or even the elimination of many species which are important for maintaining the ecological balance in the natural environment (e.g. snails, crabs or fish). Contaminated water and bottom sediments may also be the reason why living organisms develop tolerance towards toxic compounds, which in result may lead to disturbing the natural competitiveness. The composition and concentration of the investigated PCBs in the surface layer of bottom sediments may undergo constant changes caused by decomposition of organic matter present in sediments [12] and exchange of components between water and sediments due to, e.g. sorption-desorption, solution-precipitation [4, 8, 34].

The concentration of the determined chemical forms of heavy metals in the sediment grain fraction with particle size < 0.25 mm is presented in Table 5 and Figure 3.

Table 5. Concentration of chemical forms of heavy metals in the bottom sediments

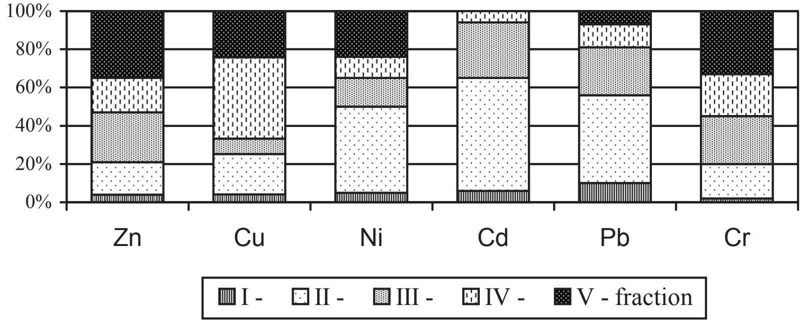
Sampling points	Chemical fraction	Concentration, mg/kg					
		Zn	Cu	Ni	Cd	Pb	Cr
1	I	5±1	0.3±0.1	0.3±0.1	0.1	9±1	0.1
	II	21±1	1.5±0.1	2.5±0.1	1.0±0.1	42±2	0.9±0.1
	III	33±2	0.6±0.1	0.8±0.1	0.5±0.1	23±1	1.2±0.1
	IV	22±1	3.0±0.1	0.6±0.1	0.1	11±1	1.1±0.1
	V	44±3	1.7±0.2	1.3±0.1	<0.1	7±1	1.6±0.2
	Σ	125	7.1	5.5	1.7	92	4.9
2	I	9±1	0.1	0.6±0.1	0.2±<0.1	10±1	0.3±<0.1
	II	40±1	1.1±0.1	2.7±0.1	1.5±0.1	47±2	0.6±0.1
	III	44±2	0.6±0.1	1.2±0.1	2.5±0.1	29±1	1.3±0.1
	IV	30±2	4.2±0.1	0.9±0.1	0.2±<0.1	11±1	1.4±0.1
	V	73±2	2.6±0.1	1.9±0.2	<0.1	12±1	1.9±0.1
	Σ	196	8.6	7.3	4.4	109	5.5
Sediment contaminated	Weakly	200	20	30	1	50	20
	Moderately	500	100	50	5	200	100
PEL		315	197	42	3.5	91	90

Fraction: I - exchangeable, II - carbonates-bound, III - Fe/Mn oxides-bound,
IV - organic matter/sulfides-bound, V – residual (non-dissolved compounds)

The highest concentration of zinc and chromium was observed in the fraction of hardly soluble compounds. This fraction of the metals is not available for microorganisms because these metals will not be released during predictable period of time. The ratio of zinc and chromium in the sediment in this fraction was 35–36% and 33–35%, respectively. This is in agreement with the studies performed by Yao, who investigated the sediment from Dongting Lake [32]. This fraction also predominated in the sediments from Taihu Lake [33], and the Poraj Reservoir [22]. The substantial role in binding zinc and chromium was also performed by the following fractions: hydrated iron and manganese oxides (23–26%), organic-sulfide (17–25%), and carbonate (11–20%). Copper was mainly present in the organic-sulfide (42–49%) and residual (24–30%) fraction. Also in the sediments analyzed by Yuan *et al.* [33], Tokalioglu *et al.* [27] and Sobczyński *et al.* [24], copper was present in those forms. Cadmium was bound to different fractions depending on the place of sampling. In the case of bottom sediment sampled from the sampling point No. 1, the carbonate fraction (59%) predominated, whereas the hydrated iron and manganese oxides fraction (57%) predominated in the samples from the sampling point No. 2. Lead as well as nickel were mainly bound to carbonates, i.e. 46–43% and 45–37% of the total concentration in the sediments, respectively. Moreover, the substantial amount of lead was bound to iron and manganese oxides (25–27%), and nickel was bound to hardly soluble compounds (24–26%). The carbonate fraction also had a significant share of the total content of nickel and lead in the sediments from the Poraj Reservoir fed by the Warta River [22].

The first two fractions with the mobile forms of metals are the most sensitive fractions to any changes of the environmental conditions in the benthic zone. In those fractions significant contents of lead, cadmium, nickel and zinc were observed.

Point No. 1



Point No. 2

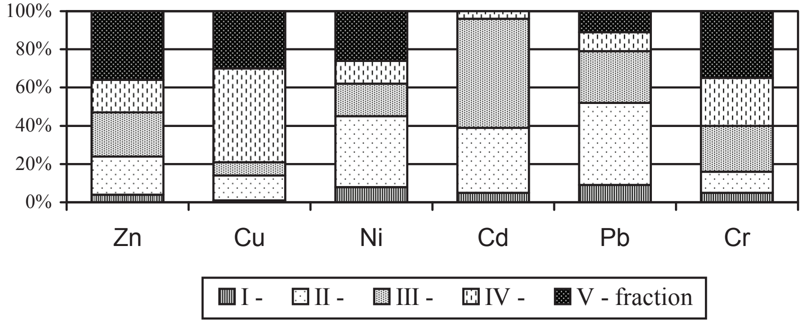


Fig. 3. Percentage of Zn, Cu, Cr, Ni, Cd, Pb, Cr in chemical fractions of sediments (I – exchangeable, II – carbonate, III – Fe and Mn oxides, IV – organic matter/sulfide, V – residual)

The metal total concentration in the grain fraction of the sediment with the particle size < 0.25 mm was analyzed according to the geochemical criteria [1]. It can be stated that the sediment from both sampling points was slightly contaminated with copper and nickel and moderately contaminated with cadmium and lead. In the case of zinc, due to the concentration of the metal, the sediment from the sampling point No. 2 was moderately contaminated and at the point 1 it was weakly contaminated. The PEL value was exceeded in the case of cadmium in the sediment collected at the point 2, and in the case of lead at both sampling points. The level of sediment contamination with metals is significantly lower than in previous years [23]. This implies the improved quality of the sediment.

CONCLUSIONS

The Kozłowa Góra Reservoir is located at the 25 km of Brynica River and constitutes a drinking water source and, therefore, monitoring of micro-contaminants in water is of utmost importance. The micro-contaminants are harmful for human health and also for aquatic organisms living in a reservoir.

Based on the obtained results the water and bottom sediments from the analyzed section of the Kozłowa Góra Dam Reservoir are contaminated with polychlorinated biphenyls. Lower chlorinated biphenyls with code No. 28 and 52 predominated in water sampled from the two sampling points due to the fact that they are highly soluble in water. These compounds pose significant threats to the aquatic environment because of high bioavailablity to aquatic organisms.

The highest total concentration of the analysed congeners of PCBs in the investigated bottom sediment was determined in the sampling point No.1 (2.78 µg/kg d.m.), whereas in the sampling point No. 2 this level was over 20 fold lower, which might result from the inflow of these compounds with the waters of the Brynica river. In the sampling points No. 1 and No. 2, the investigated bottom sediments were predominated by higher chlorinated PCBs, with comparable contents of 86% and 85%, respectively. Increased content of higher chlorinated PCBs might result from their improved adsorption on the sediment particles and poor water solubility. The level of pollution in the investigated bottom sediments (calculated per dry matter) with polychlorinated biphenyls did not exceed the level of TEL (< 0.02 mg/kg).

The PEL value (3.5 mg/kg) was exceeded in the case of cadmium in the sediment from the sampling point No. 2 and also in the case of lead (91 mg/kg) from both sampling points. In unstable environment (e.g. change of pH, oxidation, salinity of water) there is a risk of releasing high quantities of lead, cadmium, zinc and nickel from the bottom sediments of the Kozłowa Góra Dam Reservoir.

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PCB I METALE CIĘŻKIE W WODZIE I OSADACH DENNYCH ZBIORNIKA KOZŁOWA GÓRA

W pracy przedstawiono wyniki badań dotyczące zawartości PCB o kodach 28, 52, 101, 118, 138, 153, 180 oraz metali ciężkich (Zn, Cu, Ni, Cd, Pb, Cr) w wodzie i osadach dennych zbiornika zaporowego w Kozłowej Górze. Próbki pobrano w listopadzie 2009 r. na 2 stanowiskach, które usytuowane były w południowej, wylotowej (przy zaporze) części zbiornika. Osady denne pobrano z wierzchniej warstwy o grubości 5 cm. Ekstrakcję PCB z osadów dennych wykonano zgodnie z normą EPA 3550B, a analizę specjacyjną metali ciężkich wg schematu Tessiera. Otrzymane wyniki badań potwierdzają, że zbiornik Kozłowa Góra w analizowanym fragmencie jest zanieczyszczony polichlorowanymi bifenylami. W wodzie pobranej w punkcie pomiarowym 1 i 2 wykryto 6 kongenerów PCB. Ich sumaryczne stężenie było odpowiednio równe 7.3 ng/dm^3 i 8.1 ng/dm^3. Stężenia badanych metali ciężkich były poniżej 0.2 mg/dm^3. W osadach dennych najwyższe sumaryczne stężenie analizowanych kongenerów PCB oznaczono w 1 punkcie pomiarowym (2782 ng/kg s.m.), natomiast w punkcie pomiarowym 2 było ponad 20-krotnie niższe, co może być skutkiem dopływu tych związków wraz z wodami. Jednak stopień zanieczyszczenia badanych osadów dennych (w przeliczeniu na suchą masę) polichlorowanymi bifenylami nie przekraczał wartości TEL (< 0.02 mg/kg). Ze względu na zawartość miedzi i niklu osady w obu punktach pomiarowych wg kryteriów geochemicznych klasyfikowane były jako słabo zanieczyszczone, natomiast ze względu na zawartość kadmu i ołowiu jako miernie zanieczyszczone. W przypadku cynku, ze względu na stężenie tego metalu, osad w punkcie 2 klasyfikowany był jako miernie zanieczyszczony, w punkcie 1 jako słabo zanieczyszczony. Wartość PEL została przekroczona w przypadku kadmu w osadzie pobranym w punkcie 2, ołowiu w osadach z obu punktów. Na podstawie przeprowadzonej analizy specjacyjnej stwierdzono, że przy niestabilnym środowisku (zmiana pH, natlenienia, zasolenia wody) istnieje możliwość uwalniania się jonów ołowiu, cynku, kadmu i niklu z osadów dennych do toni wodnej zbiornika Kozłowa Góra.