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HEAVY METALS IN BOTTOM DEPOSITS OF "KORYTOW" RESERVOIR

METALE CIĘŻKIE W OSADACH DENNYCH ZBIORNIKA KORYTÓW

Abstract: The aim of this study was to determine and to evaluate heavy metals (Cd, Cu, Pb, Zn) concentrations in sediments of "Korytow" reservoir, located on Pisia-Gagolina river. In analyzed sediments concentrations of heavy metals was diversified due to their natural concentrations. Concentrations of Zn, Cu, Cd in upper layers were lower than concentrations in lower layers which means, that mean concentration of this metals in sediments is reducing. Concentration of Pb was balanced (117.1 mg/kg) in each sample core. Mean Pb concentration is much higher than natural geochemical background. Results of this work shows that concentration of toxic metals (Cd and Pb) in sediments was high. It confirms that water environment is polluted by heavy metals.

Keywords: heavy metals, bottom sediments, surface waters reservoirs

Development of civilisation has led to introducing heavy metals into the natural environment in amounts remarkably excessing the natural load. Bottom sediments accumulate many elements, some of which are heavy metals, hazardous for natural environment, as well as animals and people [1]. Their amount might be several orders of *eg* 15 magnitude higher than in the water phase [2–5]. The examining of metals in lake sediment has been used for long years in observing the environmental effects [6–8]. Human activities (such as industrial wastes, settlement wastes etc.) as well as geological structure constitute the main source of metals in aquatic ecosystems [9–12]. Metals cannot be biologically degraded like organic contaminants and thus they accumulate especially in the sediment by being absorbed in complex structures. Metals which accumulate in the sediment may turn into factors threatening the ecosystem

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well-being and may constitute a danger and risk factor for the environment [13–14]. Heavy metals in surface waters does not stay in water phase for a long time [14–15]. As a result of various environmental processes heavy metals are removed from waters into sediments. In polluted deposits, concentrations of past and present widely industrial--used heavy metals are usually magnified [16–18]. Sediments with high concentration of toxic and harmful components are also potential source of pollution. Heavy metals are not permanently fixed on sediments and can be released back to the water, as a result of chemical and biochemical processes which takes place in deposits, as a result of changes in environmental conditions [19]. Heavy metals accumulated in sediments in changeable conditions can migrate to water phase [16, 18] or be absorbed by plants [20]. It is very important to obtain reliable information about the toxicity of the lake's sediments. Different bioavailability of forms in which pollutants exists in the environment results in their different biological activities [21, 22].

The aim of this study was to determine and to evaluate heavy metals (Cd, Cu, Pb, Zn) concentrations in sediments of "Korytow" reservoir, collected from 3 sample points located on Pisia-Gagolina river in Zyrardów district.

Study area

The "Korytow" reservoir is located in the village of Korytow, 3.5 km far from the centre of Zyrardow (Fig. 1). Its front barrage, with the other at the top, is situated on the

Fig. 1. The "Korytow" reservoir

38th km of the course of the Pisia-Gagolina river, and it closes the catchment area covering 73.0 square km. The body was created in 1910 by pile-up of waters of the river, by a front earth dam with a weir having abutments made of bricks. It is located in a natural valley, without side dams. The water body is not eguipped with any other devices to let flood water in, the whole flow goes through the main section of the weir [19, 23, 24]. Due to significant surface (3.4 ha) and natural shape of the shoreline as well as little depth in the area, the body is a natural refuge for animals and plays a role of bird sanctuary [19, 23].

Methods

Sediments were sampled from 3 sample points from “Korytow” reservoir by scooping up sediment with a plastic spade. Sample points are shown in Fig. 2.

Fig. 2. Location of sampling sites in the Korytow reservoir (source: © użytkownicy OpenStreetMap http://www.openstreetmap.org/, CC BY-SA, http://creativecommons.org/licenses/by-sa/2.0/.)

Sediments were sampled in autumn 2006 and in winter 2007. Sediment cores from each sample point were partitioned into 5 cm lengths. The collected sediment samples were packed into polyethylene bottles and transferred to the laboratory, where they were dried at room temperature. In dry sediments grain size fractions and heavy metals were analyzed. For determining the relationship between grain size and metal contents, the sediment samples were fractionated into six grain sizes by an controlled sieve shaker.

From samples collected in autumn 2006 < 250 μm grain size of bed sediments has been used. It was caused by a fact that those grain size fraction is dominant part of bottom sediment and does not have accidental pollutions [13]. From samples collected in winter 2007 < 63 μm and 100–250 μm grain size of bed sediments has been used. It was caused by influence of grain size on result of analysis.

From dried and sieved samples, 1 g of sediments was weighed out to mineralization with mixture of $HNO_3 + HClO_4$ (4 : 1) acids in a Teflon bomb. In obtained solutions the total concentration of Zn, Cu, Pb and Cd was determined using *flame atomic absorption spectrometer* (FAAS) of Philips company, England. The same procedure without samples was used as a control. Three measurements were conducted for each sample. Quality assurance and quality control (QA/QC) for metals in sediment samples were estimated by determining metal concentrations in the Merck Standard solutions (Merck, Darmstadt, Germany). The detection limit was calculated based on the estimated instrumental detection limit assuming that 1 g of a sample is digested or diluted to 100 cm^3. Detection limits (mg/kg of dry matter) for Cu, Pb, Cd and Zn were: 0.01; 0.03, 0.002 and 0.01, respectively.

Results and discussion

In samples from autumn 2006 the dominant was grain size fractions 250–500 μm and 100–250 μm. Amount of grain size fraction < 63 μm was low. The distributions of grain size fractions within different depths, was similar. The lowest amount of grain size fraction < 63 μm was in sample point next to the dam (S) and on the right side of reservoir (P) in top layer of sediments. Low concentration of smallest parts (< 63 μm) may be caused by high flow in this part of reservoir or lack of costal vegetation. In deeper layer of sediments percentage amount of fraction < 63 μm was higher, and its percentage part was close to concentration in sample point L (on the left side of reservoir). Sample point L was close to coast of reservoir, next costal vegetation what caused higher accumulation of < 63 μm parts. In samples from winter 2007 the distributions of grain size fractions was similar. The dominant was grain size fractions 250–500 μm and 500–1000 μm. Amount of grain size fraction < 63 μm was higher than in autumn 2006, and similar in each sample point. This is probably caused by low winter flow.

Comparing grain size < 63 μm and 100–250 μm it is important to know, that proportion between all four heavy metals (zinc, copper, lead, cadmium) are the same for those fractions. What is more in grain size fraction < 63 μm there is much more heavy metals that 100–250 μm fraction. The highest differences was observed for Pb. Analysis shows that dominant metals in sediments were Pb and Zn. The highest concentration of Pb was 117.1 mg/kg, and Zn was 103.3 mg/kg. The highest concentration, over natural geochemical, was observed for Cd. Its highest concentration was 21.8 mg/kg, which shows high anthropogenic pollution [20, 21]. Concentrations of Zn, Pb, Cu was similar to natural geochemical concentrations, or a little higher.

Mean concentration of zinc in analyzed sediments was 52 mg/kg. The highest concentration from all results was 103.3 mg/kg. The highest concentration in upper layer of bottom sediments was 84 mg/kg. Because of outreaching of natural, geochemical concentration of zinc, 100 mg/kg [21, 22], was only in deeper layers of sediments (5–15 cm), it is possible to say, that in upper layer of sediments concentration of zinc was close to natural. Horizontal distribution of zinc was almost the same in each sample point, but a little higher concentrations was observed in sample point on the right side of reservoir (P). The lowest concentrations was observed in sample point on the left side of reservoir (L). Concentration of Zn in upper layer of bottom sediments was higher in autumn than in winter (25 % difference). Analysis of vertical distribution shows that zinc pollution is decreasing for about 10 %.

Table 1

Mean concentrations of Zn, Cu, Pb, Cd in sediments of "Korytow" reservoir

Concentration [mg/kg d.m.]		Zn	Cu	Pb	Cd
Total		52.6	27.8	67.9	2.9
Autumn		59.1	21.9	79.4	2.1
Winter	Mean	49.4	30.8	62.1	3.4
	< 63 μm	54.3	33.9	68.1	4.3
	100–250 μm	44.3	28.5	56.4	2.4

Mean concentration of cadmium in analyzed sediments was 2.9 mg/kg. The highest concentration from all results was 2.73 mg/kg. The highest concentration in upper layer of bottom sediments was 2.17 mg/kg. In both cases it is strong anthropogenic pollution [18]. Horizontal distribution of cadmium was almost the same in each sample point, but a little higher concentrations was observed in sample point next to the dam (S), were lower flows causes sedimentation of suspensions. Concentration of cadmium in upper layer of bottom sediments was higher in winter than in autumn (10 % difference). Analysis of vertical distribution shows that cadmium pollution is decreasing for about 10 %, but historical and present cadmium pollution was and still is very high.

Mean concentration of copper in analyzed sediments was 27.85 mg/kg. The highest concentration from all results was 63.61 mg/kg. The highest concentration in upper layer of bottom sediments was 49.92 mg/kg. In both cases it concentration is higher then natural [19]. Horizontal distribution of copper was almost the same in each sample point. It is similar to Zn and cadmium distribution. Differences of concentrations between three points are low, but the highest concentrations was observed in sample point next to the dam (S). The lowest concentrations was observed in sample point on the left side of reservoir (L). Concentration of Cu in upper layer of bottom sediments was higher in winter than in autumn (30 % difference). Analysis of vertical distribution shows that copper pollution is decreasing for about 25–80 %. That shows that historical concentration was much higher than present and pollution is decreasing.

Mean concentration of lead in analyzed sediments was 68 mg/kg. The highest concentration from all results was 117.1 mg/kg. Concentration of lead is higher then natural [19]. Horizontal distribution of lead was almost the same in each sample point. It is similar to Zn, Cd and Cu distribution in sediments of "Korytow" reservoir. The highest concentrations was observed in sample on the right side of reservoir (P). Concentration of lead in upper layer of bottom sediments was higher in autumn than in winter (20 % difference). Analysis of vertical distribution shows that lead concentrations, excluding sample point P, are almost the same for all depths, which means that historical and present concentrations of this metal are still the same.

Difference of metals contents in the sediment "Korytow" reservoir resulted mainly from the character of the surrounding catchment. Lead and cadmium in sediment of river Pisia-Gagolina and "Korytow" reservoir are characterized by high and different levels to geochemical background, which is determined by geochemical structure of that area as well as its management status. It seems that sediments from those flows are not genetically closely associated with the material of direct catchment of studied rivers.

In Poland there are not legally biding regulations referring to bottom sediments classification, which would comply with commonly used categorization of polluting elements. The first Polish geochemical classification of riverbed sediments and lake bed sediments was made by Polish Geological Institute and is used in State Environmental Monitoring. Sediments were divided into 3 classes according to their metal content, based on geochemical criteria [25].

Table 2

Classification of water sediments based on geochemical criteria [25]

Mark	Description	Unit	Cd	Cu	Pb	Zn
Geochemical background	—	mg/kg	< 0.5	6	10	48
Class I	slightly polluted sediments	mg/kg	< 1	< 20	< 50	< 200
Class II	moderately polluted sediments	mg/kg	< 5	< 100	< 200	< 1000
Class III	polluted sediments	mg/kg	< 20	< 200	< 500	< 2000

Conclusions

1. The dominant grain size fraction in sediments was 250–500 μm and 100–250 μm. The distributions of grain size fractions within different depths, was similar.

2. Grain size fraction < 63μm accumulated much more Zn, Cu, Pb and Cd than other fractions.

3. Total concentrations of analyzed metals were higher than natural geochemical background.

4. Results of this work shows the following order Cd > Pb > Zn > Cu of danger caused by heavy metals.

5. Analysis of vertical distribution shows that Zn and Cd pollution is decreasing for about 10 %, Cu pollution is decreasing for about 25–80 %, Pb concentrations are almost the same for all depths.

6. The biggest danger for water environment is Cd and Pb. Results of this work shows that there is a relationship between concentrations of Zn and Pb and between concentrations of Cu and Cd.

7. Metals collected in sediments of "Korytow" reservoir could be dangerous for local ecosystem.

8. Metals collected in sediments of "Korytow" reservoir have anthropogenic origin.

9. Sediments collected on bottom of the reservoir are covered by a layer of quite clean (unpolluted) sediments, but they may be a source of secondary pollution of water samples from autumn 2006 the dominant was grain size fractions 250–500 μm and

100–250 μm. Amount of grain size fraction < 63 μm was low. The distributions of grain size fractions within different depths, was similar.

References

[1] Slavik R, Julianowa M, Labudikowa M. Screening of the spatial distribution of risk metals In topsoil from an industrial complex. Ecol Chem Eng S. 2012;19(2):259-272. DOI: 10.2478/v10216-011-0020-0.

[2] Skorbiłowicz E, Skorbiłowicz M. Trace elements in a valley of upper river Narew and its selected tributaries, NE Poland. Environ Protect Eng. 2009;35:259-278.

[3] Dermont G, Bergeron M, Mercier G, Richer-Lafl'eche M. Soil washing for metal removal: A review of physical/chemical technologies and field applications. J Hazard Mater. 2008;152:1-31. DOI: 10.1016/j.jhazmat.2007.10.043.

[4] Skorbiłowicz M, Skorbiłowicz E. Content of selected heavy metals in water and riverbed sediments of the Utrata river, Environ Protect Eng. 2009;35:279-292.

[5] Barbusiński K, Nocoń W. Zawartość związków metali ciężkich w osadach dennych Kłodnicy, Ochr Środow. 2011;33:13-17.

[6] ElBilali L, Rasmussen PE, Hall GEM, Fortin D. Role of sediment composition in trace metal distribution in lake sediments. Appl Geochem. 2002;17:1171-1181. PII:S0883-2927(01) 00132-9.

[7] Casas JM, Rosas H, Sole M, Lao C. Heavy metals and metalloids in sediments from the Llobregat basin. Spain Environ Geol. 2003;44:325-332.

[8] Feng B, Yang H. Metal pollution in lake system and its reconstruction by using lake sediments. Bioinformatics and biomedical engineering, 2008 ICBBE The 2nd international conference on 16–18 May. 2008;3689-3692.

[9] Wojtkowska M. Content of selected heavy metals in water and riverbed sediments of the Utrata river, Environ Protect Eng. 2011;3:55-62.

[10] Karadede H, Unlü E. Concentrations of some heavy metals in water, sediment and fish species from the Atatürk Dam Lake, Turkey. Chemosphere. 2000;41:1371-1376. PII: S0045-6535(99)00563-9

[11] Demirak A, Yýlmaz F, Tuna A, Ozdemir N. Heavy metals in water, sediment and tissues of Leuciscus cephalus from a stream in southwestern Turkey. Chemosphere. 2006;63:1451-1458. DOI: 10.1016/j.chemosphere.2005.09.033.

[12] Sekabira K, Oryem Origa H, Basamba A, Mutumba G, Kakudidi E. Assessment of heavy metal pollution in the urban stream sediments and its tributaries. Int J Environ Sci Tech. 2010;7:435-446.

[13] Shrivasta P, Saxena A, Swarup A. Heavy metal pollution in a sewage-fed lake of Bhopal. Lakes Reserv Res Manage. 2003;8:1-4.

[14] Wildi W, Domink J, Thomas RL, Favarger P, Haller L, Perroud A, Peytremann C. River, reservoir and lake sediment contamination by heavy metals downstream from urban areas of Switzerland. Lakes Reserv Res Manage. 2004;9:75-87.

[15] Wojtkowska M. Obniżenie zawartości metali ciężkich w procesie sedymentacji dla wód Jeziora Zegrzyńskiego w aspekcie jakości wód ujmowanych przez Wodociąg Północny. Chem Inż Ekol. 2000;7;283-292.

[16] Dojlido J, Taboryska B. Zanieczyszczenie metalami ciężkimi osadów dennych w zlewni górnej i środkowej Wisły. Materiały XIII Sympozjum : Proekologiczna gospodarka wodna w zakresie zaopatrzenia w wodę, Polski Komitet Międzynarodowego Stowarzyszenia Jakości Wody, Warszawa; 1994.

[17] Lindström M. Urban land use influences on Trace elements fluxes and surface sediment concentrations of small lakes. Water Air Soil Pollut. 2001;126:363-383.

[18] Parafinuk J, Bojkowska I, Małecka K. Proces samooczyszczania się koryta rzeki Pisi (zachodnie Mazowsze) na podstawie zmian zawartości wybranych metali ciężkich. Przegl Geolog. 2005;53(7):609-614.

[19] Wojtkowska M. Charakterystyka hydrochemiczna górnej zlewni rzeki Pisi-Gągoliny, Infrastruktura I Ekologia Terenów Wiejskich: PAN O/ w Krakowie. 2006;4/3:189-196.

[20] Broma M, Rajfur M, Kłos A, Duczmal K, Wacławek M. Wykorzystanie dżdżownic do oceny zanieczyszczenia gleb metalami ciężkimi, Chem Dydakt Ekol Metrol. 2009;14(1-2):57-64.

[21] Świerk D, Szpakowska B. Occurence of heavy metals in aquatic macrophytes colonising small aquatic ecosystems, Ecol Chem. Eng S. 2011;18(3):369-384.

[22] Franke S, Sagajdakow A, Wolska L, Namieśnik J. Integrated approach – the effective tool for pollution level control of sediments from Lake Turawskie. Ecol Chem Eng S. 2009;16(3):313-321.
[23] Zawadzki K. Ogólna charakterystyka warunków hydrologiczno-meteorologicznych powiatu żyrardowskiego wraz z charakterystyką wybranych potencjalnych źródeł zagrożeń środowiska przyrodniczego. Żyrardów: Operat; 2003.
[24] Zawadzki K. Środowisko fizyczno-geograficzne. Powiat Żyrardów. Żyrardów: Starostwo Powiatowe Żyrardów; 2004. http://bip.powiat-zyrardowski.pl.
[25] Bojakowska I., Sokołowska G.: Geochemiczne klasy czystości osadów wodnych. Przegl Geolog. 1998;46(1):49-54.

METALE CIĘŻKIE W OSADACH DENNYCH ZBIORNIKA KORYTÓW

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Abstrakt: Celem badań było oznaczenie zawartości Zn, Cu, Pb i Cd w osadach dennych zbiornika Korytów, zlokalizowanego na rzece Pisi-Gągolinie. W prowadzonych badaniach obserwowano duże zróżnicowanie stężeń czterech metali w odniesieniu do ich naturalnej zawartości. Stężenia Zn, Cu i Cd w warstwie powierzchniowej osadów były niższe niż w głębszych warstwach, co świadczy o redukcji średniej zawartości metali w osadach. Zawartość ołowiu była wyrównana w głąb osadów (117,1 mg/kg), przekraczając znacznie poziom tła geochemicznego środowiska.. Na podstawie uzyskanych wyników można stwierdzić, że osady charakteryzowały się wysoką zawartością toksycznych metali (Cd i Pb). Potwierdza to znaczne zanieczyszczenie środowiska wodnego metalami

Słowa kluczowe: metale ciężkie, osady denne, zbiorniki wód powierzchniowych