IOŚ-PIB
Environmental Protection and Natural Resources
Ochrona Środowiska i Zasobów Naturalnych
sciendo
Vol. 29 No 4(78): 10-15
DOI 10.2478/oszn-2018-0016

Katarzyna Maj-Zajezierska*, Piotr Koszelnik*

Contamination of bottom sediments by lead, zinc and cadmium in Rzeszow reservoir

* Department of Environmental Engineering and Chemistry, Rzeszow University of Technology; e-mail: kmaj@stud.prz.edu.pl

Keywords:
Bottom sediment, heavy metal, lead, zinc, cadmium, Rzeszow reservoir

Abstract
The aim of the present study was to determine the level of contamination of the bottom sediments in the Rzeszow reservoir by the selected heavy metals Pb, Cd and Zn, and to identify the potential environmental risks of heavy metals content basing on available assessments and classification of bottom sediments. The Rzeszow reservoir is situated on the Wisłok River in the Podkarpackie Voivodeship, southeaster Poland, was constructed on 1974. Nowadays, as a result of silting, the reservoir reduced its surface and depth, which does not have a positive effect on the assumed functions it is to perform. The study was conducted in 2016. The samples of sediment were collected in five locations. Samples were taken twice: in June and in October. The following concentrations have been determined: cadmium - 0.01 ÷ 0.92 mg•kg–1, zinc - 54.39 ÷ 128 mg•kg–1, lead - 2.98 ÷ 25.42 mg•kg–1. The decline trend in the sediment is following: Zn > Pb > Cd. For the assessment of sediment contamination, following methods: aquatic sediment quality classification used by the Polish Geological Institute - I class, Regulation of the Minister of Environment of April 16 2002 on the types and concentrations of substances contaminating the excavated material – unpolluted and LAW sediment classification – Pb - I/I-II, Cd - I/I-II/II and Zn - I/I-II. The obtained results were compared with the results obtained by the other authors in earlier years, which led to the estimated changes in the concentration of the tested metals.

1. INTRODUCTION

Heavy metal pollution in bottom sediments can be a serious threat to ecosystem and human health. The sediments are the source of contamination, which comes from industry and agriculture. Contamination in the sedimentation process falls to the bottom and is deposited in the bottom sediments. For this reason, they constitute a source of information on the changes in pollution over time. The top surface (0–5 cm) of bottom sediment gives information about the sedimentation processes and the remobilization processes, which can be observed in recent times. The sediments absorb persistent and toxic chemicals; for this reason, their contamination are many times higher than water [Szarek-Gwiazda 2013, Tarnawski, Baran 2018].
The heavy metals in sediments are derived from natural inputs and anthropogenic emissions. Consequently, sediment-associated contaminations can influence the concentrations of trace metals in both water and biota. The major problems with the trace metals are with respect to their effects on aquatic organisms due to the long biological half-life. Therefore, the monitoring of micropollutants in sediment is important and plays an important role in the assessment of quality of the surface water [Baran *et al.* 2011, Szarek-Gwiazda 2013, www.mapgeochem.pgi.gov.pl].
The significance of trace metals for each water reservoir depends individually on the properties of each element. Zinc is used for coating steel sheets and cast iron in order to protect against corrosion (e.g., in cars, in construction). The dispersion of zinc in the metallic form is small, while its compounds are easier to migrate, which are used for the production of rubber, plant protection preparations, fertilizers, pharmaceuticals and cosmetics [Kabata-Pendias, Mukherjee 2007]. Zinc contents in Poland's sediments do not exceed 100 mg·kg^{-1} on average, while there are significant regional differences [www.mapgeochem.pgi.gov.pl]. The geochemical background of cadmium in Polish sediments is in the range of < 0.5–2.6 mg·kg^{-1}. values are found in the areas of mining, processing and metallurgy [www.mapgeochem.pgi.gov.pl]. Cadmium is found in waters usually with zinc but in much smaller quantities. The water reservoirs in cities are exposed to lead emitted

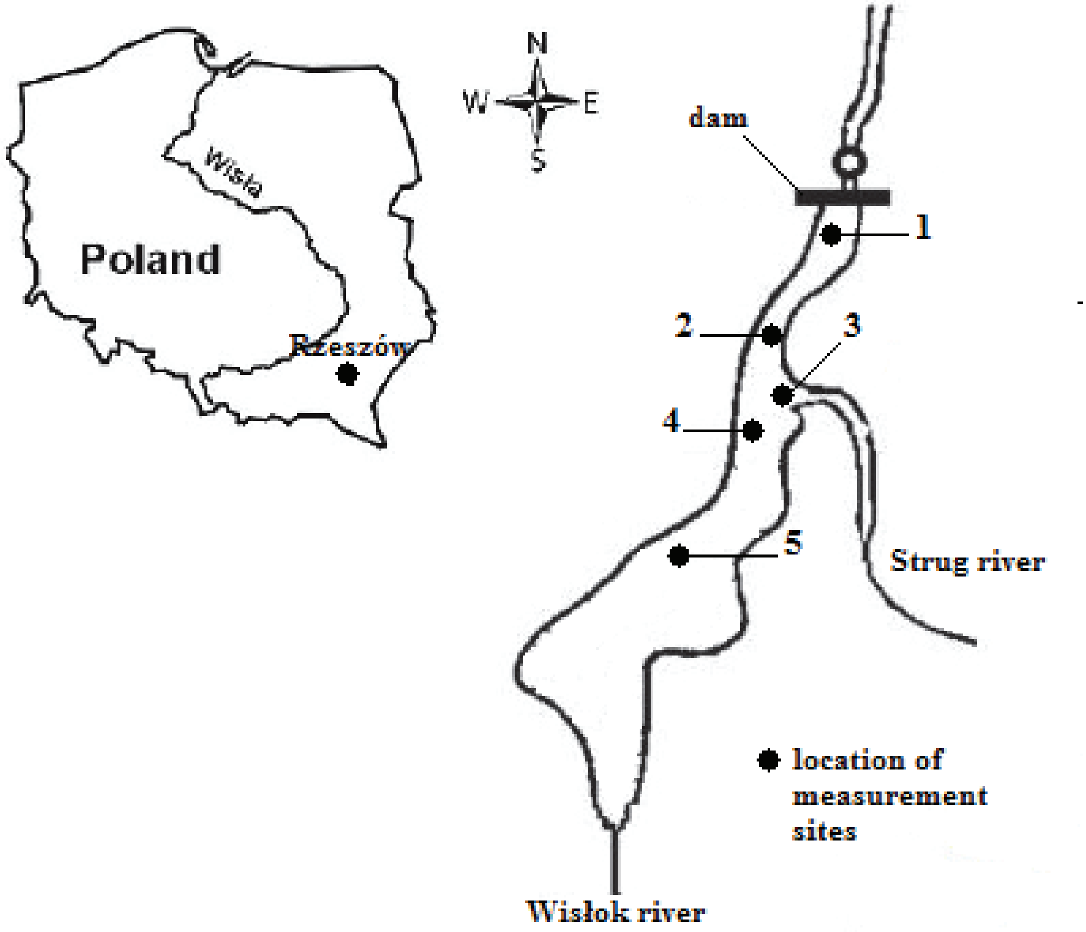

Figure 1. Location of the bottom sediment measurement sites

by industry and communication. The main sources of lead contamination are from paints, from car exhaust emissions and from industry. Lead is toxic to plants and animals. In Poland, the background contents in bottom sediments change from 30 to 45 mg·kg^{-1} [Kabata-Pendias, Mukherjee 2007].

The study is aimed at the determination of the level of lead, zinc and cadmium accumulated in the bottom sediments in Rzeszów reservoir and the assessment of sediment contamination by these metals.

2. MATERIAL AND METHODS OF STUDY

2.1. Study area

The object of investigations was the water reservoir in Rzeszów, placed in the grounds of Rzeszow city, in the south of the centre, on the Wisłok River. The water reservoir was constructed in 1974 as the water intake for Rzeszów city water supply system, reservoir flood control and the for recreation purpose. Currently, the surface area is 0.68 km^2 and the mean depth is ca. 2 m [Koniarz *et al.* 2015, Koszelnik *et al.*2004, Tarnawski, Baran 2018].

2.2. Sample collection and analysis

The samples were collected from five set locations twice: on June and on October 2016. Two samples were taken from each site. The sediments were collected from the 10 cm layer. The samples were dried, grinded and passed through a sieve. The prepared samples were mineralized with HNO_3 in a microwave digestion process (MARS 6, CEM). The values of heavy metals (Pb, Cd, Zn) were determined by the atomic emission spectrometer with inductively coupled plasma (ICP-OES, GBC Quantima E 1330). The concentration of heavy metals were expressed as mg·kg^{-1} of sediment dry matter.

Table 1. Contents of heavy metals in samples of bottom sediments presented as mg·kg^{-1}d.m

x	Pb		Cd		Zn	
Location	**VI 2016**	**X 2016**	**VI 2016**	**X 2016**	**VI 2016**	**X 2016**
1	22.35	13.52	0.86	0.76	110.55	79.82
2	25.42	21.38	0.03	0.02	74.32	54.39
3	23.81	23.69	0.01	0.01	75.55	72.64
4	13.54	8.72	0.59	0.75	55.21	104.30
5	13.22	2.98	0.80	0.92	80.15	128.00
M	19.66	14.06	0.46	0.49	79.15	87.83
SD	5.84	8.63	0.41	0.44	19.98	28.72
Gb	15		0.5		73	

M: mean SD: Standard deviation Gb: Geochemical background

3. RESULTS AND DISCUSSION

The results of the analysis of sediment samples are presented in Table 1. The decline trend in the sediment is following: Zn > Pb > Cd. The results indicate that the studied sediments differently accumulated the heavy metals depend on the location of sampling points. The relationship between the concentration of metals in the sediments and the series of sampling was not observed.

The amount of zinc in the sediments was various, contains in the range from 54.39 mg·kg^{-1} to 128 mg·kg^{-1}. Similar results have been presented in the studies by Tarnawski and Baran [2018] and Bartoszek et al. [2015]. Koszelnik et al. [2004] presented that the mean concentration of Zinc has been varied over the years: in 1995, it was 144 mg·kg^{-1}, but in 2003, it reduced to -92 mg·kg^{-1}. Content of lead oscillates in the range 2.98–25.42 mg·kg^{-1}.

The lower concentration of lead was observed in sites 4 and 5, in locations remote from the dam. The levels of Pb in sediments were close to the results received by Tarnawski and Baran [2018]. In the past, the concentration of lead in the sediments in Rzeszow reservoir was higher; in years 2009–2013 the mean was 53.5 mg·kg^{-1} [Bartoszek *et al.* 2015]. Spatial distribution of lead in the bottom sediments of Rzeszów reservoir performed by Koniarz et al. [2015] showed the concentration in the range 7–15.85 mg·kg^{-1}. Lead concentrations for the Carpathian reservoirs: Dobczycki, Czorsztyński and Rożnowski were presented by Szarek Gwizda [2013] at a similar level.

Cadmium is present in the range of 0.01–0.92 mg·kg^{-1}. The lower concentration of Cd in the sediment was in the position 2 and 3 than in other. The higher concentration was received by Tarnawski and Baran [2018] and Bartoszek et al. (2015). Szarek-Gwiazda [2013] received the higher concentration for Dobczycki, Czorsztyński and Rożnowski reservoirs.

By comparison, the results received for the Besko reservoir, located on Wislok river, for Cadmium and Zinc were comparable (average Cd: 0,80 mg·kg^{-1} and Zn: 116,20 mg·kg^{-1}). On the Besko reservoir, lead obtained the highest mean concentration – 41,65 mg·kg^{-1} [Baran *et al.* 2011].

Table 2. The limit value of trace elements in sediments (presented as mg·kg–1d.m.) [Macdonald et al. 2000, http://ekoinfonet.gios.gov.pl]

Heavy metal	RME	PEL	PEC	LEL	SEL
Pb	200	91	128	31	250
Cd	7.5	3.5	4.98	0.6	10
Zn	1000	315	459	120	820

RME- Regulation of the Minister of the Environment of 16 April 2002

The sediment quality was compared with the criteria established and used by the Chief Inspectorate of Environmental Protection [http://ekoinfonet.gios.gov.pl]. Up to 2012, there was one legal act in Poland regarding the quality of sediments. This was the Regulation of the Minister of the Environment of 16 April 2002 on the types and concentrations of substances that cause the spoil is contaminated [Journal of Laws No. 55, item 498] (RME). Nowadays, from 2013 onwards, the research in the subsidence monitoring of bottom sediments are carried out based only on geochemical and ecotoxicological criteria. By comparison, the obtained concentrations of metals in the sediments of the Rzeszow reservoir with the Regulation of the Minister of the Environment of 16 April 2002 (Table 2), it was found that the sediments were unpolluted. Pb, Cd and Zn are on a lower level than the standards presented by the Polish regulation on the types and concentrations of substances responsible for causing the output to be regarded as polluted [Journal of Laws No. 55, item 498].

An important element of the assessment of concentration of pollutants in bottom sediments is their potential impact

Table 3. Classification of bottom sediments quality, used by Polish Geological Institute [Bojakowska 2001, Bojakowska Sokołowska 1998]

Heavy metal	Geochemical background	I noncontaminated	II moderately contaminated	III highly contaminated	IV very highly contaminated
Pb	15	30	100	200	> 200
Cd	< 0.5	1	3.5	6	> 6
Zn	73	200	500	1000	> 1000

Table 4. Geoaccumulation indexes for metals [Müller 1981]

Index Value	Class	Description of sediment quality
Igeo ≤ 0	0	uncontaminated
0 < Igeo < 1	1	uncontaminated to moderately contaminated
1 < Igeo < 2	2	moderately contaminated
2 < Igeo < 3	3	moderately to strongly contaminated
3 < Igeo < 4	4	strongly contaminated
4 < Igeo < 5	5	strongly to extremely contaminated
5 < Igeo	6	extremely contaminated

Table 5. Permissible concentration of heavy metals in bottom sediments by LAW classification [Länderarbeitsgemeinschaft Wasser 1998]

Element	Pb	Cd	Zn	Sediment quality
I	≤ 25	≤ 0.3	≤ 100	I - Uncontaminated
I-II	≤ 50	≤ 0.6	≤ 200	I-II - Contaminated / Moderately polluted
II	≤ 100	≤ 1.2	≤ 400	II - Moderately polluted
II-III	≤ 200	≤ 2.4	≤ 800	II-III - Moderately polluted / Heavily contaminated
III	≤400	≤ 4.8	≤ 1600	III - Heavily polluted
III-IV	≤ 800	≤ 9.6	≤ 3200	III-IV - Strongly / Very heavily polluted
IV	> 800	> 9.6	> 3200	IV - Very heavily polluted

on the functioning of aquatic ecosystems. In terms of ecotoxicological criteria, the mean levels of elements are lower than the probable effect concentration (PEC) and the probable effect level (PEL) (Table 2) [Macdonald *et al.* 2000]. The contaminated bottom sediments may adversely affect the benthic organisms, hence the threat to benthic organisms was determined by the two toxicity indicators SEL (the severe effect level) and LEL (the lowest effect level) (Table 2). The level of toxicity described by SEL was not exceeded and the values have not exceeded the level of heavy metals at which the leaching of sediments can occur. For LEL, the values were exceeded for zinc and the half of the samples tested for cadmium.

Following the Polish Geological Institute classification presented on Table 3 [Bojakowska 2001, Bojakowska Sokołowska 1998], the tested sediments were classified as Class I. All the concentrations were below the limited value. Other geochemical criterion – the Geoaccumulation Index (Igeo) worked out by Müller (Table 4) – classified the sediments as unpolluted – Class 0 and from unpolluted to moderately polluted – Class I. The threat was calculated according to the Müller formula (1981): I_{geo}=log2Cn/1.5·Bn (Cn – means the content of the element in the sediment, Bn – the value of the geochemical background) [Müller 1981].

The LAW (Länder-Arbeitsgemeinschaft Wasser) classification was established in 1997. The LAW classification divides sediments into 7 classes in terms of increasing contamination concentration [Länderarbeitsgemeinschaft Wasser 1998]. The results obtained are classified in class I, I-II and II: Pb - I/I-II, Cd - I/I-II/II, Zn - I/I-II.

In Table 6, the results of comparison of the concentrations of heavy metals in sediments with the used assessments of contamination are presented. The results showed that all the tested sediments are safe for the environment based on indicators RME, PGI, PEL, PEC and SEL. Several results exceeded the value based on the index LEL. The LAW classification and I_{geo} ranked a several samples as moderately contaminated.

4. SUMMARY

1. The average values of the metals tested were in intervals: cadmium - 0.01 ÷ 0.92 mg·kg^{-1}, zinc - 54.39 ÷ 128 mg·kg^{-1}, lead - 2.98 ÷ 25.42 mg·kg^{-1}. The obtained values were comparable to the results obtained by the other authors for the Rzeszów reservoir in previous years. On a similar level, lead concentrations were observed in the bottom sediments for the Carpathian reservoirs: Dobczycki, Czorsztyński and Rożnowski. The average results obtained for lead, zinc and cadmium were lower than the averages presented for the Besko reservoir.

Table 6. Comparison the results with the methods for assessment of sediment contamination

Location and collection date	Element	RME*	PEL/PEC	LEL/SEL	PGI	I_{geo}/class	LAW classification
1 VI 2018	Pb	↓	↓/↓	↓/↓	I	-0.01/0	I
	Cd	↓	↓/↓	↑/↓	I	0.20/I	II
	Zn	↓	↓/↓	↓/↓	I	0.01/I	I-II
2 VI 2018	Pb	↓	↓/↓	↓/↓	I	0.18/I	I-II
	Cd	↓	↓/↓	↓/↓	I	-4.44/0	I
	Zn	↓	↓/↓	↓/↓	I	-0.56/0	I
3 VI 2018	Pb	↓	↓/↓	↓/↓	I	0.08/I	I
	Cd	↓	↓/↓	↓/↓	I	-6.42/0	I
	Zn	↓	↓/↓	↓/↓	I	-0.54/0	I
4 VI 2018	Pb	↓	↓/↓	↓/↓	I	-0.73/0	I
	Cd	↓	↓/↓	↓/↓	I	-0.34/0	I-II
	Zn	↓	↓/↓	↓/↓	I	-0.99/0	I
5 VI 2018	Pb	↓	↓/↓	↓/↓	I	-0.77/0	I
	Cd	↓	↓/↓	↑/↓	I	0.08/I	II
	Zn	↓	↓/↓	↓/↓	I	-0.45/0	I
1 X 2018	Pb	↓	↓/↓	↓/↓	I	-0.73/0	I
	Cd	↓	↓/↓	↑/↓	I	0.01/I	II
	Zn	↓	↓/↓	↓/↓	I	-0.46/0	I
2 X 2018	Pb	↓	↓/↓	↓/↓	I	-0.07/0	I
	Cd	↓	↓/↓	↓/↓	I	-5.00/0	I
	Zn	↓	↓/↓	↓/↓	I	-1.01/0	I
3 X 2018	Pb	↓	↓/↓	↓/↓	I	0.07/I	I
	Cd	↓	↓/↓	↓/↓	I	-6.03/0	I
	Zn	↓	↓/↓	↓/↓	I	-0.59/0	I
4 X 2018	Pb	↓	↓/↓	↓/↓	I	-1.37/0	I
	Cd	↓	↓/↓	↑/↓	I	0.00/I	II
	Zn	↓	↓/↓	↓/↓	I	-0.07/0	I-II
5 X 2018	Pb	↓	↓/↓	↓/↓	I	-2.92/0	I
	Cd	↓	↓/↓	↑/↓	I	0.30/I	II
	Zn	↓	↓/↓	↑/↓	I	0.23/I	I-II

↓- below, ↑- above, 0-II - number of class, RME - Regulation of the Minister of the Environment of 16 April 2002

2. The concentration of heavy metals analysed in the sediments of the Rzeszów reservoir was higher than the level of the geochemical background. The higher concentrations of Zn and Pb with respect to the background indicate the impact of anthropogenic pollution.
3. The tested samples of sediments did not exceed the value determining contamination of the obtained sediment according to the guidelines of the Regulation of the Minister of Environment of 16 April 2002 on the types and concentrations of substances contaminating the excavated material.
4. According to the classification of PGI, the samples of sediments were classified as unpolluted sediments - class I. The classification was similar, based on the LAW to classes I, I-II and II – from unpolluted to moderately polluted. I_{geo} described the tested sediment also as from unpolluted to moderately polluted.
5. Toxicological assessment for PEC, PEL and SEL indices showed lower concentrations than the limit values. The LED indicator for cadmium and zinc exhibits the possibility of danger to the benthic organisms. In order to check the toxicity of sediments, additional tests should be carried out using indicator organisms, for example, shellfish Heterocypris incongruens, bacteria Vibrio fischeri or plants Sorghum saccharatum, Lepidium sativum, Lepidium sativum.

REFERENCES AND LEGAL ACTS

BARAN, A. TARNAWSKI, M. KACZMARSKI, M., 2011. Assessment of agricultural utilization of bottom sediments from the Besko reservoir. Czasopismo Techniczne. Chemia. V. 108, Nr. 1-Ch, 3-7 [in Polish].

BOJAKOWSKA I.. 2001. Criteria for evaluation of water sediments pollution. Polish Geol Rev 49(3):213–219 [in Polish].

BOJAKOWSKA I., SOKOŁOWSKA G.. 1998. Geochemiczne klasy czystości osadów wodnych. Przegląd Geologiczny. Vol 46. Nr 1., Warszawa, 49–254 [in Polish].

Journal Of Laws Of The Republic Of Poland No. 55 Item 498. 2002. Regulation of the Minister of Environment from April 16th 2002 on the kinds and concentrations of substances which cause that the spoil is polluted, Warsaw

KABATA-PENDIAS A., MUKHERJEE A. 2007. Trace elements from soil to human. Springer Verlag, Berlin–Heidelberg.

KONIARZ T, BARAN A, TARNAWSKI M. 2015. Assessment of the content and spatial distribution of lead in bottom sediment Rzeszów reservoir. Logistyka 4:9195–9205 (in Polish).

KOSZELNIK P., TOMASZEK J.A., SOKÓŁ Z., KRYCZKA R.. 2004. Charakterystyka zbiornika zaporowego w Rzeszowie po trzydziestu latach eksploatacji. V Ogólnopolska Konferencja Naukowo – Techniczna „Ochrona i rekultywacja Jezior", Grudziądz., 2004.

Länderarbeitsgemeinschaft Wasser (LAWA). (1998). Beurteilung der Wasserbeschaffenheit von Fließgewässern in der Bundesrepublik Deutschland – Chemische Gewässergűteklassifikation.

MACDONALD D., INGERSOLL C., BERGER T., 2000. Development and Evaluation of consensus-based Sediment Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Archives of Environmental Contamination and Toxicology, 39: 20–31.

MÜLLER G. 1981. Die Schwermetallbelastung der Sedimente des Neckars und seiner Nebenflüsse. Eine Bestandaufnahme, Chemiker-Zeitung 6: 157–164.

SZAREK-GWIAZDA, E.. 2013. Factors affecting the concentrations of heavy metals in the Raba River and some Carpathian Reservoirs. Kraków: Monografia Studia Naturae 60: IOP PAN (In Polish with English summary).

TARNAWSKI M., BARAN A.. 2018. Use of Chemical Indicators and Bioassays in Bottom Sediment Ecological Risk Assessment. Archives of Environmental Contamination and Toxicology, Volume 74, Issue 3, 395–407.

http://ekoinfonet.gios.gov.pl/osady/mapa/realizacja.html [04.07.18]

http://www.mapgeochem.pgi.gov.pl/poland/index.php?lang=pl [04.07.18]