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RENATA GRUCA-ROKOSZ*, LILIANNA BARTOSZEK*, JANUSZ A. TOMASZEK*

HEAVY METALS IN THE BOTTOM SEDIMENTS OF THE SOLINA RESERVOIR

The concentrations of heavy metals in the bottom sediments of the Solina reservoir were assessed. Total concentrations of copper, nickel, lead and zinc (except one station) correspond to the level of their natural concentrations in non-polluted reservoirs. The concentration of cadmium exceeds slightly a geochemical background value at three measurement points.

1. INTRODUCTION

Economic and communicational activities have been intensified which increases considerably contamination of aquatic ecosystems. The assessment of the contamination level is extremely important, especially in terms of heavy metal pollution.

Surface waters are continually polluted with heavy metals found in industrial wastes, municipal sewage, run-offs, precipitations, etc. These pollutants are accumulated in bottom sediments. Because the metals are not biodegradable, they have an adverse effect on plants and animals [1]. Heavy metals accumulated in sediments may be secondarily released into the water due to a stronger water turbulence, the appearance of the agents that react with heavy metals to form compounds that are insoluble in water and a decrease in pH of bottom layers caused by a natural degradation of organic compounds present in bottom sediments [1], [2].

The concentrations of heavy metals in bottom sediments depend heavily on the quality and quantity of the contaminants discharged and on chemical composition of water [3]–[5].

Generally, the sediments properties reflect successfully long-term changes in contamination of aquatic ecosystems. They are considered frequently to be much more

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^{*} Rzeszów University of Technology, Department of Environmental and Chemistry Engineering, 2 Wincentego Pola Street, 35-959 Rzeszów. Tel: +48 17 8651361, E-mail: renatagr@prz.rzeszow.pl.

useful indicators of aquatic ecosystem contamination than unstable properties of chemical composition of water [6].

The paper deals with the contamination of bottom sediments of the Solina reservoir by heavy metals. The character of our investigation was preliminary and we attempted to assess very roughly the contamination of the reservoir deposits. Only a total amount of heavy metals in the sediments was determined.

2. THE AREA OF STUDY

The Solina reservoir is situated in the San River in the Bieszczady Mountains. It is the biggest man-made lake in Poland. This reservoir and the Myczkowce reservoir in the same river accumulate 18% of retention waters in Poland.

The drainage basin of the reservoir is of a highland nature. It is dominated by forests, meadows and pastures. The share of arable land does not exceed a few per cent of the area. Buildings are mainly found in valleys near the river and stream estuaries. There are no industrial plants. The agricultural utilization of the area is poor, few small towns earn their living mainly from tourism [7].

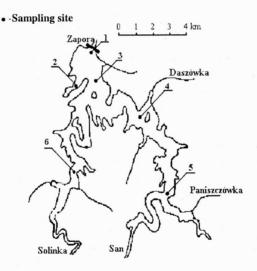


Fig. 1. The Solina reservoir - sampling sites

Six sites for sample collecting were chosen in such a way as to take into account the character of the reservoir (figure 1). The sites are as follows:

- 200 metres from the dam, site 1,
- in the Nelson Bay, site 2,
- in a central part of the reservoir, site 3,

• near the place where the Daszówka River flows into the Solina reservoir, site 4,

• below the place where the San River and the Czarny Stream flow into the Solina reservoir, site 5,

• near the place where the Wołkowyjka River and the Solinka River flow into the Solina reservoir, site 6.

Samples of bottom sediments were collected four times, in August and October 2000, and in July and October 2001. The concentrations of copper, lead, zinc, nickel and cadmium were measured in the surface layer of sediments only, because we assumed that potential pollutants in deeper layers could hardly pass from bottom sediment to water [8].

3. THE METHOD OF ANALYSIS

The samples of bottom sediments were collected by means of a probe of our own design [9]. Surface layers of three bottom sediments collected at the same place were averaged, dried to a constant weight and homogenized. Each sample (about 2.5 g) was mineralised in the mixture of HCl and HNO₃, and then analysed for heavy metals by means of AAS method using atomic absorption spectrometry (Perkin Elmer AAnalyst 300).

4. THE DISCUSSION OF RESULTS

The contents of heavy metals are given in table 1.

Table 1

	Cu			Pb			Ni			Zn			Cd		
	mg kg ⁻¹ of d.w.		mg kg ⁻¹ of d.w.		mg kg ⁻¹ of d.w.			mg kg ⁻¹ of d.w.			mg kg ⁻¹ of d.w.				
	max	min	mean	max	min	mean	max	min	mean	max	min	mean	max	min	mean
1	36.31	28.28	32.76	31.22	13.13	22.38	51.41	24.84	40.28	124.16	104.78	113.48	0.67	0.59	0.64
2	34.38	21.69	30.19	20.05	17.95	18.97	32.30	7.16	17.24	194.56	134.91	154.4	1.04	0.31	0.57
3	37.57	28.22	33.37	27.13	10.73	20.18	51.20	9.78	31.54	147.8	90.62	124.84	0.35	0.12	0.24
4	32.87	26.57	28.63	19.51	11.94	15.42	33.35	21.27	27.50	125.28	106.79	114.37	0.58	0.13	0.28
5	32.19	27.89	30.26	31.83	13.84	19.40	52.99	26.35	37.33	137.68	113.20	122.96	0.68	0.45	0.54
6	32.43	29.72	31.24	33.71	16.10	21.92	41.67	25.11	33.16	136.71	107.76	120.06	0.56	0.21	0.31

Minimum, maximum and mean concentrations of heavy metals at six points of the reservoir

For lack of standards set for admissible concentration of heavy metals in bottom sediments, the assessment of sediment contamination was carried out based on geochemical classification (table 2) proposed by MÜLLER [10].

Table 2

The purity class	The bottom	Cu	Pb	Ni	Zn	Cd	Igeo	
according to I_{geo}	sediment quality	mg kg ⁻¹ of d.w.						
0	non-contaminated	<67.5	<30	<102	<142.5	<0.45	<0	
1	slightly contaminated	135	60	204	285	0.9	1	
2	moderately contaminated	270	120	408	570	1.8	2	
3	moderately – heavily contaminated	540	240	816	1140	3.6	3	
4	heavily contaminated	1080	480	1632	2280	7.2	4	
5	heavily – extremely heavily contaminated	2160	960	3264	4560	14.4	5	
6	extremely heavily contaminated	>2160	>960	>3264	>4560	>14.4	>5	
The geochemical background		45	20	68	95	0.3		

The classification of bottom sediments contamined by heavy metals according to the geochemical index I_{geo}

For each average concentration of the metal determined a respective geoaccumulation index was calculated. Such indices allow classification of bottom sediments according to their contamination by particular metals (table 3). A geochemical background (i.e., the concentrations of metals occurring in muddy sediments according to TUREKIN and WEDEPHOL [10]) was used in calculations as a reference value.

Geoaccumulation indices were calculated as follows:

$$I_{\rm geo} = \log_2 C_n / 1.5 \ B_n \, ,$$

where:

 C_n – metal concentration,

 B_n – the value of geochemical background of a chemical element in muddy sediment.

Table 3

	Cu		Pb		Ni		Zn		Cd	
Sampling place	mg kg ⁻¹ of d.w.	Igeo								
1	32.76	-1.04	22.38	-0.42	40.28	-1.34	113.48	-0.33	0.64	0.50
2	30.19	-1.16	18.97	-0.66	17.24	-2.56	154.4	0.12	0.57	0.35
3	33.37	-1.02	20.18	-0.57	31.54	-1.69	124.84	-0.19	0.24	-0.93
4	28.63	-1.24	15.42	-0.96	27.50	-1.89	114.37	-0.32	0.28	-0.67
5	30.26	-1.16	19.40	-0.63	37.33	-1.45	122.96	-0.21	0.54	0.26
6	31.24	-1.11	21.92	-0.45	33.16	-1.62	120.06	-0.25	0.31	-0.51

The values of geoaccumulation indices I_{geo} for heavy metals in bottom sediments of the Solina reservoir

The concentrations of copper and nickel at all sampling sites did not exceed the background value over the whole period of investigations. Geoaccumulation indices for these metals reach the values below zero. That is why the bottom sediments are considered to belong to the zero class of purity which means that the sediments are not contaminated by copper and nickel.

Average lead concentrations in the bottom sediments of the Solina reservoir slightly exceed the background values at the sampling sites 1, 3, 5 and 6. However, I_{geo} indices for these values are below zero which means that the sediments are not contaminated by lead.

 I_{geo} calculations for the maximum lead concentration indicated that in three cases only (in July 2001 at the sampling sites 1, 5 and 6) the sediments might be in the first class of purity. This means means that they are slightly contaminated by lead; moreover, the values of I_{geo} slightly exceeded zero and were in the range from 0.057 to 0.17.

Although geochemical background of zinc was exceeded at all sites over the whole investigation period (except site 3, October 2000), the values of geoaccumulation index for average zinc concentrations in the bottom sediments did not exceed zero, with the exception of the site 2 in Nelson Bay, where I_{geo} value reached 0.12. When the highest zinc concentration in sediments is taken into account in the calculations one may conclude that the samples of bottom sediments from station 2 in three cases have been slightly contaminated by zinc (I_{geo} ranging from 0.016 to 0.45). Zero class of purity was exceeded once, at the site 3 (July 2001, I_{geo} reached 0.053).

Cadmium concentration also showed increased values exceeding the background values at the sites 1, 2, 3, and 5 over a whole period of investigation. At the sites 4 and 6 the background value was exceeded once in October 2000. Geoaccumulation index for average cadmium concentration at the sites 1, 2 and 5 ranged from 0 to 1 which allowed us to classify the bottom sediments into the first class of the sediments slightly contaminated. The bottom sediments at the remaining sites were in the zero class of cadmium contamination.

5. CONCLUSIONS

Low concentrations of copper, nickel and lead in the bottom sediments of the Solina reservoir correspond to their concentrations occurring in natural noncontaminated reservoirs. Such concentrations, depending on the place of samples collecting, did not testify to any point source of contamination. Only zinc and cadmium are exceptions to this finding. At site 2 the concentration of zinc in the bottom sediment is the highest. This is probably caused by discharge of sewage from sewage treatment plant in Polańczyk in this place.

Since there are no clear anthropogenic sources which could contaminate bottom sediments by cadmium, one may think that their slight contamination by this metal can be connected with its higher concentration in the soil of the drainage basin of the reservoir. This does not mean however that the area sources and precipitations have no influence on the phenomenon. Comparing our results with the results reported by PASTERNAK in 1972 for the Solina reservoir [11] one may conclude that since that time the concentrations of heavy metals (such as Pb, Cu and Ni) have decreased considerably. On the other hand, nickel concentration is constant. However, Pasternak did not provide any information about cadmium concentration. The above result also confirms the statement that there are no point sources of contamination by heavy metals.

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STĘŻENIE METALI CIĘŻKICH W OSADACH DENNYCH ZBIORNIKA SOLIŃSKIEGO

Oceniono poziom stężenia metali ciężkich w osadach dennych zbiornika solińskiego. Stwierdzono, że ogólna zawartość miedzi, niklu, ołowiu i cynku (poza jednym stanowiskiem) odpowiada poziomom stężeń w naturalnych, niezanieczyszczonych zbiornikach. Stężenie kadmu nieznacznie przekracza wartości tła geochemicznego w trzech punktach pomiarowych.