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Examination of Trace Amounts of Some Heavy Metals in Bottom Sediments of Selected Lakes of South-Eastern Poland

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Abstract

Concentrations of heavy metals in bottom sediments of three selected reservoirs from South-Eastern Poland are presented. Masluchowskie and Piaseczno lakes are located at the Pojezierze Łęczyńsko-Włodawskie region and the artificial reservoir Zalew Zemborzycki is located at the Lublin town border. The metal concentrations were measured by XRF method.

Keywords: Heavy metals, bottom sediments, concentration, lakes

Introduction

Pollution of the environment is reflected by levels of contamination of rivers, lakes and other reservoirs. There are sites of accumulation of impurities coming from human activity, due to dissolution, precipitation and adsorption. Contaminating elements and compounds are transported by water and gather in bottom and alluvial sediments. Recently, the problem of some heavy metal concentrations in bottom sediments was widely examined [1-6, 12-17].

In this paper the concentrations of heavy metals in bottom sediments of some lakes of South-Eastern Poland were examined. Lakes are located at 51°15' - 51"45'N, 22°50' - 23°20'E, at the agriculture region of the Wyżyna Lubelska. Artificial lake Zalew Zemborzycki is 40 km from both lakes and is situated at the border of Lublin town (population 400,000, heavy industry).

Experimental

Bottom sediments from deep points were taken with a special sampler (Fig. 1), and from shallow sites (up to 4 m) with a tube sampler [6]. The mean depth of the profile was 15 cm. In every point the depth of the lake was measured and 5 portions of the sediment were collected and treated as one sample. A distribution of collection points for the examined lakes is presented in Figure 1. They were selected allowing for bathymetric maps of the lakes, their depth and profile of the bottom. These maps enable us to collect samples from the same depth and consider sediment transportation, caused by thermic movement of water and gravimetric sedimentation.

Examined lakes are karst origin and were formed 10-12 thousands years ago, at the end of Baltic Glaciation Era [4, 5]. The maximum depth is 38 m for Piaseczno and 8 m for Maśluchowskie lake. Zalew Zemborzycki was formed as an artificial lake in 1974, in the valley of the Bystrzyca river. Its greatest depth is 3 m.

All collected samples were carefully dried at 50°C, then at 80°C. Dry samples were grounded in a porcelain mortar and sieved through a nylon sieve (1 mm). From the 50 g portion 2 g was pressed with KBr to form pellets for heavy metal analysis. The fluorescence spectrometer XRF (ED-XRF) was applied with semiconductor detector by Canberra, (USA). The fluorescent spectra were analyzed with the AXIL ver. 3.2 computer program by Canberra (^{55}Fe, ^{109}Cd, and ^{241}Am isotopes were applied as a source of radiation). For the calculation of the examined metal concentration K_a and L_a lines were considered. The limit of detection ranged 2-10 ppm, depending on the matrix, as the detection level increases with atomic number. The measurement error ranged from 3 to *9%* of the measured

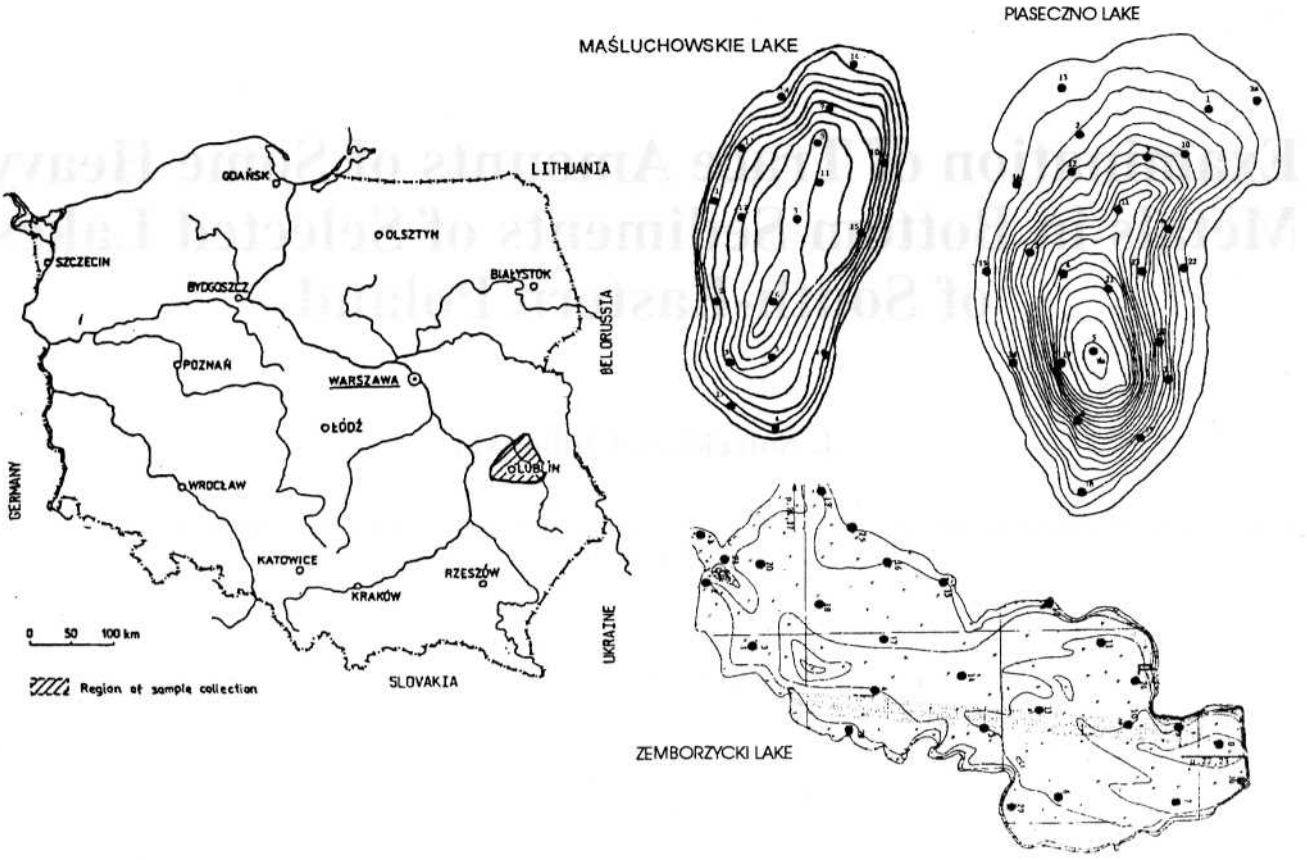

Fig. 1. The map of examined lakes wilh the points of bottom sediment samples.

value. Obtained results allow to analyze concentrations of the following metals: Mn, Fe, Cu, Zn, Sr, Pb, Ba, Cd, and Cr.

In Tables 1-3, the results of measurements of the selected metals in all collected samples are presented with regard to the depth of the reservoir. In no examined sample was the presence of Cd observed. Instead, in three points in Masluchowskie Lake the considerable quantities of Cr ions were detected. The concentration of this element was 160, 171, and 127 ppm, respectively, in points 6, 9 and 11 at depths 7.5, 5.5 and 7.5 m. It should be noted that 7.5 m was the greatest depth for Masluchowskie lake samples. For the comparison, the average concentration of Cr in bottom sediments of the rivers was estimated at 50 ppm.

In some rivers the mean Cr concentration was as follows: Bug - 13 ppm, Odra - 80 ppm, Warta 70 - ppm, Wisla - 50 ppm [1]. For the more contaminated points the concentration of Cr can be considerably higher. For example, 1200 ppm in Leba and 700 ppm in upper run of Wisla. The concentration of chromium in the bottom sediments of Pojezierze Kaszubskie (NW Poland) ranged from 2 to 45 ppm and its geometrical average was 15 ppm. The calculated geometric mean for 101 lakes of Poland was 9 ppm [4]. The increased concentration of chromium in the bottom sediments of Masluchowskie lake may result from accidental contamination by farm wastes. This lake is located far from industrial centers and has no inflows. For this lake, a correlation observed by Bojakowska et al. [4], concerning the higher concentration of chromium with the concentration of iron and manganese, (see Table 2), can be confirmed.

The results presented in Tables 1-3 show how various may be the concentrations of some metals in the same reservoir.

In Table 1 the selected metal contents in the bottom sediments of horizontal profiles of Piaseczno lake are presented. There were 24 samples of bottom sediments taken along the isotonic lines of the batymetric map (Fig. 1). The Piaseczno lake has no inflow and outflow and its greater depth equals 38 m in the southern part.

The encountered heavy metals are of geochemical origin and they can come from precipitation. Namely aerosols, dusts and superficial waters of surrounding fields and lakes. Generally, the minimal and maximum values of the all examined metal concentrations are close to values obtained for the lakes of the Pojezierze Kaszubskie region [4].

For Piaseczno lake, Kowalik et al. [6] published detailed values of heavy metal contents in water, bottom sediments and biological samples. ASA examinations allow to arrange the decreasing order of the concentrations of the metals: Fe>Zn>Mn>Pb>Cu>Cd>Co for water, bottom sediment and biological samples.

Based on the average arithmetical values of the metal concentrations (established by XRF method from the collected samples) the following order of the metal decreasing concentrations can be presented: Fe>Ba>Mn> >Zn>Sr>Pb>Cu.

Table 1. Piaseczno lake.

No.	Depth [m]	Concentration [ppm]						
		Mn	Fe	Cu	Zn	Sr	Pb	Ba
24	1	129	104	27	9	14	10	107
14	1.3	261	1827	13	97	51	14	62
15	1.3	84	1812	28	29	30	15	167
13	1.5	175	3234	14	98	46	28	153
18	1.5	92	3357	19	52	55	30	264
1	3	157	9954	20	56	68	24	350
22	3	85	2392	18	58	36	26	170
16	4.5	179	3231	17	61	38	27	157
2	5	206	11870	27	43	80	28	392
19	7	114	924	24	15	23	17	134
7	8	178	2013	22	17	37	15	160
12	8	284	6247	28	100	61	54	211
8	8.5	106	6219	35	46	51	20	160
10	9.5	313	8108	31	144	68	82	263
20	14	105	4579	12	74	61	54	238
9	14.5	252	7382	45	106	68	58	183
3	16	191	5795	17	137	51	28	169
23	16	172	2896	23	42	36	30	160
6	18	131	5566	30	89	67	50	207
11	22	238	9250	36	146	75	98	250
4	28	138	7129	30	128	65	88	279
21	32	194	8427	26	133	71	104	294
17	33	289	10600	21	166	70	121	303
5	38	311	11120	24	169	68	126	316
Median		**176.5**	**5681**	**24.0**	**81.5**	**58.0**	**29.0**	**209.0**
Arithmetic mean		**183.8**	**5396**	**24.5**	**85.2**	**53.1**	**48.8**	**212.1**
Stand. deviation		**72.9**	**3464**	**7.9**	**49.2**	**17.8**	**36.0**	**80.0**
Geometric mean		**168.6**	**4066**	**23.2**	**66.3**	**50.0**	**36.6**	**202.4**
Minimum		**84**	**104**	**12**	**9**	**14**	**10**	**62**
Maximum		**313**	**11870**	**45**	**169**	**80**	**126**	**392**

Beside the place occupied by zinc and mangane, the average concentrations of the examined metals from the bottom sediments of this lake also differ from those of Kowalik's paper [6]. The mean concentration of zinc in sediments examined in Kowalik's paper (482.5 ppm) [6], seems to be much overestimated in comparison to the value obtained by XRF method (85.2 ppm). The mean concentration of zinc in bottom sediments of Polish lakes is 73 ppm [10].

Presented measurements were done seven years after the ones presented by Kowalik et al. [6]. Therefore, one should expect similar or higher measured values because of the accumulation of the radioactive isotopes such as other contaminations [11]. The apparent lowering of the zinc concentration in bottom sediments of Piaseczno lake is difficult to explain, even considering different methods of analysis. The average concentration of manganese, for bottom sediments of Piaseczno lake, was 183.8 ppm and it was much greater than in these ones described in the paper by Kowalik et al., equal to 98.4 ppm **[6],** The latter results can be acceptable.

From the above results, one can summarize the data of the metal concentration in bottom sediments of the lake (Tab. 1). The copper concentration does not change for the most samples of the different depth, whereas the concentrations of zinc and lead increase with the depth of the collected bottom sample. The same is for Mn, Fe, Ba and Sr (see Table 1.). For all mentioned metals the increase of their concentration is irregular.

In the examined sediments the accumulation of metal

Table 2. Maśluchowskie lake.

No.	Depth [m]	Concentration [ppm]						
		Mn	Fe	Cu	Zn	Sr	Pb	Ba
18	0.8	84	453	24	10	19	13	125
14	1	117	875	23	16	28	15	170
4	1.3	165	3132	29	41	46	20	252
16	1.5	83	1171	19	19	28	17	168
17	1.5	94	1357	18	16	25	15	145
1	3	143	2632	23	31	38	21	205
10	3	122	630	14	12	18	12	120
13	3.5	137	2973	19	28	45	22	254
2	4	188	3126	34	39	42	26	229
3	5	202	8394	25	100	72	57	362
15	5	107	1878	26	26	35	11	221
9	5.5	259	8149	23	90	68	53	354
5	6	206	8297	33	102	71	54	370
12	6	194	9421	27	115	72	65	384
7	7	221	8858	25	102	72	66	375
8	7	235	10400	32	124	75	67	383
6	7.5	293	10090	33	117	74	69	383
11	7.5	251	10350	34	123	74	66	389
Median		**176.5**	**3129**	**25.0**	**40.0**	**45.5**	**24.0**	**253.0**
Arithmetic mean		**172.3**	**5121**	**25.6**	**61.7**	**50.1**	**37.2**	**271.6**
Stand. deviation		**64.7**	**3921**	**6.0**	**45.0**	**21.8**	**23.6**	**102.2**
Geometric mean		**160.3**	**3357**	**24.9**	**44.1**	**45.0**	**29.8**	**251.4**
Minimum		**83**	**453**	**14**	**10**	**19**	**11**	**120**
Maximum		**293**	**10350**	**34**	**124**	**74**	**69**	**389**

with the depth was also observed for radioactive caesium Cs-137 [11]. These results may suggest the tendency to translocate contamination down to the deeper sites of the lake.

The concentrations of the selected metal taken from Masluchowskie lake are presented in Table 2. The sampling points were located according to isotonic lines, such as for Piaseczno lake. Masluchowskie lake has a gutter-like shape, with maximum depth equal to 8 m. From the table one can see that the amount of the metals are in the range of Piaseczno and the Pojezierze Kaszubskie lake concentrations [4]. The similar concentrations were obtained for the bottom sediments of Goreckie lake from Wielkopolski National Park [16, 17]. This lake has a shape similar to Masluchowskie lake; therefore, the results are more approximate than for other lakes. Point 15 is an exception, in spite of the sharp decrease of Zn, Sr and Pb concentration.

For Masluchowskie lake we can arrange the following order of the metal concentrations: Fe>Mn>Ba> >Zn>Sr>Pb>Cu.

In Table 3 the results for Zalew Zemborzycki are presented. The average concentrations of selected metals differ for Masluchowskie and Piaseczno lakes. That results from the type of this reservoir and the influence of the river that may carry contaminations. For Zalew Zemborzycki the metal concentrations in bottom sediments look as follows Fe>Sr>Mn>Ba>Zn>Cu>Pb.

Generally, we can say that except for copper, the concentrations of the examined metals are higher for the deeper points of Piaseczno and Masluchowskie lakes. The similar remarks are presented by Bojakowska [5] for selected lakes of the Pojezierze Mazurskie Region. This tendency is not observed for Zalew Zemborzycki because of the river and sediments are removed by water flow. The concentrations of some metals are different for both types of reservoirs. These metals that may be emitted to atmosphere by industry, (Cu, Fe, Sr) reveal higher concentrations for Zalew Zemborzycki (located in Lublin town vicinity). The concentrations of others are smaller. This confirms the influence of the industry on pollution of environment.

Obtained results are compared with those for other examined Polish lakes [4, 5, 10, 12]. Often, comparison is

Table 3. Zalew Zemborzycki.

No.	Depth [m]	Concentration [ppm]						
		Mn	Fe	Cu	Zn	Sr	Pb	Ba
28	0.5	149	1376	37	13	19	13	97
30	0.5	–	2658	–	–	72	14	106
12	0.7	184	5194	39	29	127	20	249
21	0.7	147	1029	22	12	64	12	115
25	0.8	110	3547	20	20	80	13	207
27	1	–	3379	32	32	67	15	140
29	1.1	101	844	23	17	27	10	99
24	1.2	91	1470	20	17	44	16	121
2	1.3	143	3000	30	28	223	15	128
15	1.4	155	12310	25	63	461	33	233
19	1.4	194	11160	27	85	191	31	299
3	1.5	242	8683	47	66	706	41	138
16	1.5	266	13650	47	89	529	36	221
18	1.7	189	13190	47	92	342	26	290
20	1.7	238	11350	39	90	545	31	192
17	1.8	217	15260	31	51	352	29	281
4	2	143	3000	30	28	223	17	128
14	2	282	11090	27	37	148	29	248
5	2.3	208	10750	42	64	587	31	169
13	2.3	195	10670	33	40	276	29	243
6	2.5	439	13230	52	88	737	50	136
11	2.6	153	12490	51	65	572	32	195
9	3.1	205	9077	32	53	406	24	176
10	3.1	244	14830	35	77	494	33	220
7	3.4	157	11230	19	74	500	36	170
8	3.8	184	12390	43	74	511	36	187
Median		**186.5**	**10710**	**32.0**	**53.0**	**309.0**	**29.0**	**181.5**
Arithmetic mean		**178.3**	**8341**	**32.7**	**50.2**	**319.3**	**25.8**	**184.2**
Stand. Deviation		**72.6**	**4948**	**10.1**	**27.4**	**226.7**	**10.5**	**61.4**
Geometric Mean		**182.0**	**6190**	**32.5**	**43.7**	**214.1**	**23.7**	**174.2**
Minimum		**91**	**844**	**19**	**12**	**27**	**10**	**97**
Maximum		**439**	**15260**	**52**	**92**	**737**	**50**	**299**

difficult because of the different procedures applied for sample collection. The results obtained by Bojanowska et. al. [4, 5, 12] concern samples collected from the deepest sites of the lakes. This method may be justified by the assumption of the contamination concentration in these sites. These results are not representative for the contamination of the whole reservoir. They also do not reflect different physicochemical properties of the sediments from various sites (shallow near the bank and the deepest at the center) [16, 17]. The data presented in Table 4 concern the bottom sediments from the lakes: Piaseczno, Masluchowskie and Zalew Zemborzycki, taken from the deepest sites. There are mean values of the measurements of the sediments collected from 16-38 m for Piaseczno, 5-7.5 m Masluchowskie and 2 - 3.8 m for Zalew Zemborzycki. Observed difference in the concentrations may be explained by the different geochemical background of the investigated reservoirs. The most surprising are results for Piaseczno and Masluchowskie lakes, both from the Pojezierze L^czyfisko-Wlodawskie territory administered by Zarz^d Gospodarki Wodnej Warszawa. The concentration of Cu, Sr and Pb are the most approximate to the results obtained for other Polish lakes [10].

Table 4. Average values of the concentrations (in ppm) of some metals in bottom sediments of Poland.

Metal	Piaseczno	Maśluchowskie	Zalew Zemborzycki	Z.G.W. Warszawa [12]	Pojezierze Kaszubskie [4]	Pojezierze Mazurskie [5]	Average for Poland [10]
Mn	208	217	221	–	–	786	506
Fe	7599	8426	10876	–	–	10010	11800
Cu	26	29	36	18	11	10	21
Zn	126	100	60	88	126	83	247
Sr	63	68	445	112	103	88	40
Pb	81	56	32	33	36	34	68
Ba	247	358	187	73	108	53	80

The obtained data allow to state as follows:

- The lower and higher concentrations of the exam ined metals are similar to those of other Polish lakes.
- The concentration of the examined metals increases with the depth of the lake.
- The sequences of metal concentrations are very similar.

Piaseczno lake Fe>Ba>Mn>Zn>Sr>Ph»Cu
Masluchowskie lake Fe>Mn>Ba>Zn>Sr>Pt»Cu
Zalew Zemborzycki Fe>Sr>Mn>Ba>Zn>Cu>Pb.

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