

Changes in the Forms of Metal Occurrence in Bottom Sediment under Conditions of Artificial Hypolimnetic Aeration of Rybnik Reservoir, Southern Poland

K. Loska, D. Wiechula¹, J. Cebula

Silesian Technical University, Institute of Engineering of Water and Wastewater,
ul. Konarskiego 18, 44-100 Gliwice, Poland

¹ Silesian University of Medicine, Department of Toxicology,
ul. Jagiellońska 4, 41-200 Sosnowiec, Poland

Received: March 10, 2000

Accepted: June 8, 2000

Abstract

The content of metals in carbonates, sulfides, exchangeable, adsorbed and organically bound forms was determined in bottom sediment by means of a sequential chemical extraction method after Rudd et al. Cadmium, nickel and copper was found mainly in the forms of sulfides (Cd > 40%, Ni > 30%, Cu > 70%), chromium and zinc in the fraction of carbonates and sulfides. Manganese was attributed to an organically bound form (25%), carbonates and sulfides. Iron had a very small contribution of the exchangeable and adsorbed forms (<1%); sulfides contributed the most (40-45%). Lead was found mainly in the fraction of carbonates (about 35%) at all sites. Aeration of the hypolimnetic water caused only slight changes in the forms of metal occurrence in the bottom sediment.

Keywords: speciation, bottom sediment, heavy metals, artificial hypolimnetic aeration

Introduction

A constant, excessive inflow of principal food elements i.e. phosphorus and nitrate causes an excessive fertility of reservoirs, sudden growth of algae and water blooming in the upper layers of water. Deoxygenation of deeper layers of reservoirs results in reducing conditions and the production of hydrogen sulfide, ammonia nitrogen and methane from organic matter. Physico-chemical conditions prevailing in the hypolimnetic layer also influence the mobility of the compounds present in the bottom sediment.

Attempts at a complete removal or hindrance of disadvantageous phenomena concomitant with eutrophica-

tion have been made for many years. As early as in 1944, Thomas [1] suggested a number of biological and technical solutions which were intended to suppress eutrophication. In subsequent years, a number of aeration methods were applied, e.g. mechanical agitation of water in Lake Bret in Switzerland [2], and a system of complete aeration in the Wahnbach Reservoir in Germany [3, 4].

Nowadays, in order to eliminate the disadvantageous effects of eutrophication, an artificial aeration of hypolimnetic water is usually applied. The aeration causes an increase in oxygen content in the hypolimnion, and a considerable reduction in phosphates and total phosphorus in the hypolimnetic layer of water, and a decrease in iron and manganese content in water [5, 6, 7]. There are also changes in thermal conditions, a decrease of ammonia nitrogen and total nitrogen [8, 9, 10].

Preliminary research on the aeration of the bottom sediments under laboratory conditions showed a decrease in phosphate and nitrate content in the hypolimnetic water [11, 12]. It was also possible to notice negative effects of the pH drop in the hypolimnetic water which led to a leaching of metals from the bottom sediments and their increase in the water. Aeration caused an increase in copper, lead and zinc contents in the organically bound matter and carbonates, an increase in metals content in the exchangeable fraction, organically bound forms and carbonates for nickel, and an increase in the content of the adsorbed and carbonate fractions for cadmium [11], obtained from the procedure after Rudd [13]. Application of Rudd's method has been induced by the ability to determine the contents of sulphides and organically-bound metals. This method is also much easier to apply than Tessier's method (identical time of extraction carried out at room temperature).

The laboratory tests mentioned above found their continuation in the research on chemical forms of metals in the bottom sediment carried out in the Rybnik Reservoir. The content of metals in particular forms in the bottom sediment was determined prior to and during aeration of the hypolimnetic water.

Study Area

Rybnik Reservoir constructed in the 1970s on the River Ruda is used for surface cooling of discharge waters from power plant capacitors of the Rybnik Power Plant. It is a shallow, non-freezing reservoir of heated water, characterized by a high degree of eutrophication. Its total, usable and stable volumes are 24.3 million m³, 4.3 million m³ and 18.2 million m³ respectively [14]. The reservoir is approximately 4.5 km long. Its total area is 555 ha, 444 ha of which is used for cooling (main reservoir). The mean depth of the reservoir is about 4.5 m while the maximum depth in the area close to the dam is 10 m.

Aeration was carried out as a part of restoration works in the Rybnik Reservoir. In 1993, 3 Stratiflox aerators produced in Poland were installed in the deep water zone close to the dam.

Material and Methods

Over the 04.05.1993-20.12.1994 period there were 26 collections: 11 before the aeration i.e. from May to September 1993 and 15 during the aeration. The bottom sediment was collected at five sites: 3, 4 and 5 in the deep water zone where the water was aerated and - for comparison - at sites 1 (backwater) and 2 (in the middle zone of the reservoir). A 0-2 cm layer of the bottom sediment was collected by an Ekman-Birge apparatus. In the bottom sediments from all sites a percentage content of water, loss of ignition and the content of chosen metals were determined. The determination of total content of metals in the bottom sediments was carried out after the samples had been dried at 105°C to a stable mass and mineralized with a mixture of nitric and perchloric acids in a microwave oven. Content of metals in the bot-

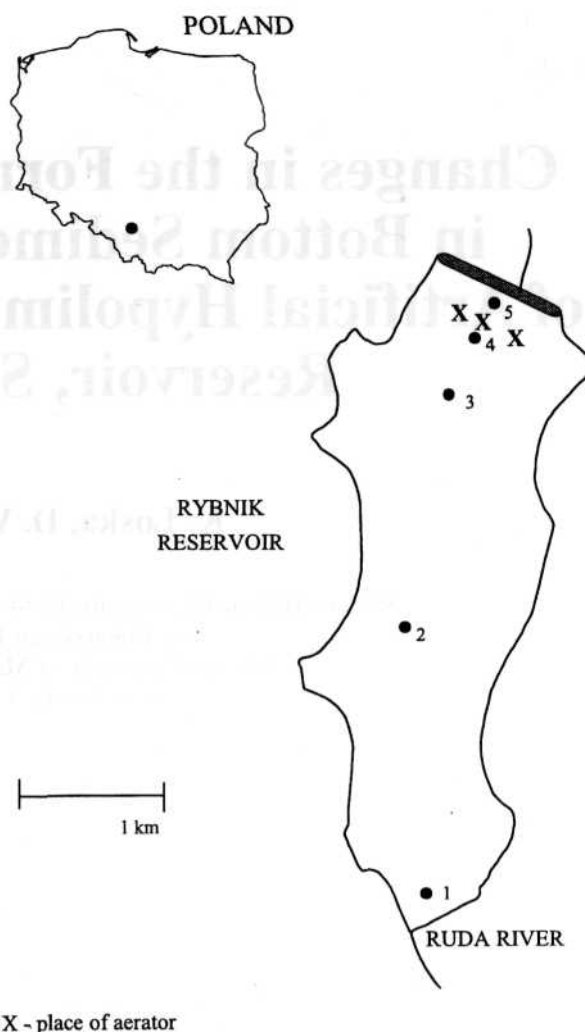


Fig. 1. Localization of the sampling points.

tom sediment was determined by means of atomic absorption spectrophotometry using the flame technique and the known addition method. An AAS-30 atomic absorption spectrophotometer produced by Carl-Zeiss-Jena and HCL lamps were used. The accuracy of analytical procedure was checked by analyzing samples of reference material (CRM 277 - Trace elements in estuarine sediment).

Apart from determining the total content of heavy metals in the bottom sediments, analysis of chemical forms of chosen metals in the bottom sediments was carried out applying the method of Rudd [13]. This method, due to the use of extractants characterized by an increasing leaching efficiency, allows determination of the mobility and accessibility of the investigated metals. The steps in the sequential extraction procedure are summarized in Table 1.

The contact time of the extractant with the samples was 24 h and the ratio of the extractant to the dry mass of bottom sediment was 40:1. Between extractions, the solution was centrifuged from the sediment which was then washed with a small amount of redistilled water.

Table 1. Sequential extraction procedure.

Step	Designated form extracted	Reagent
1	Exchangeable	1 M KNO ₃
2	Adsorbed	0.5 M KF (pH = 6.5)
3	Organically bound	0.1 M Na ₄ P ₂ O ₇
4	Carbonate	0.1 M EDTA (pH = 6.5)
5	Sulfide	6.0 M HNO ₃

Table 2. The initial water contents, loss on ignition and the concentration of heavy metals in the surface (0-2 cm) layer of the bottom sediments in the Rybnik Reservoir over the 04.05.1993 - 20.12.1994 period (mean and standard deviation).

Site	Water [%]	Loss on ignition % dry wt.	Heavy metals (mg/kg)							
			Cd	Cr	Cu	Zn	Ni	Mn	Fe	Pb
1	81.3±3.1	22.2±2.7	27.7±5.1	297.5±124.9	106.3±16.7	1512.5±204.0	85.0±24.2	1290.3±167.6	55622±16901	95.7±34.3
2	88.6±1.9	26.0±2.1	25.2±4.1	101.8±19.9	628.9±82.1	1764.4±242.8	72.9±15.2	3625.2±292.0	43092±11722	108.1±30.9
3	92.5±2.1	27.9±3.2	22.3±5.0	92.7±18.1	733.1±121.1	1573.7±180.8	72.3±19.8	2763.9±822.2	42690±11817	107.1±22.4
4	94.1±0.7	30.5±1.8	22.3±4.4	106.7±17.1	770.4±69.3	1452.5±236.6	78.0±15.5	2183.7±474.1	43463±8838	112.8±24.9
5	93.6±1.8	27.9±3.6	20.5±4.7	94.0±15.3	739.9±90.3	1368.7±187.5	71.9±12.9	1993.8±521.3	38900±6383	104.4±18.4

The extract was adjusted to a specific volume and acidified with nitric acid to the content of 1% HNO₃ and then the content of chosen metals was determined.

Results

Table 2 presents a percentage content of water, loss on ignition and total content of metals in the 0-2 cm layer of the bottom sediment at particular sites.

The mean cadmium content was highest at site 1, located in the backwater area. Slightly lower contents of cadmium were found at the remaining sites. The content of chromium was also highest at site 1; the mean content of this metal at the other sites was three times lower and amounted to approx. 100 mg/kg. The lowest content of copper was found at site 1 and was 7 times lower than at the other sites. Site 1 was also characterized by the highest content of nickel; its mean content at the other sites was lower by approx. 10 mg/kg. The content of zinc showed similar values in the whole area of the reservoir; its highest mean value was found at site 2. The mean content of manganese was the lowest at site 1 - 1290.3 mg/kg; at site 2 its content was three times higher. The sites in the deep zone were characterized by the following level of manganese - 2000-2700 mg/kg. The mean iron content of 40,000 mg/kg was similar at sites 2, 3, 4 and 5, whereas at site 1 it amounted to 55,000 mg/kg. The content of lead was similar in the area of the whole reservoir.

The percentage distribution of chemical forms of the metals in the surface layer of the bottom sediment is presented in Fig. 2.

Sulfides were a predominant chemical form of cadmium and they constituted 40-45% of the total amount of this metal. Their amount in the bottom sediment was larger at sites in the backwater area where it was also possible to notice a slightly smaller fraction of the exchangeable, adsorbed and organically bound forms.

The 6 M HNO₃ teachable fraction, besides the amount obtained with EDTA pH 6.5 also constituted the predominant form of chromium - 30-35% of its total content. Site 1 was characterized by a different distribution of chromium content - 65% for 6 M HNO₃ and only 15% for EDTA pH 6.5.

The distribution of the chemical forms of copper was very interesting. Almost 80% of this metal appeared as sulfides in the bottom sediment. The remaining 20% was

shared by the other forms where 10% was for the carbonates and 5% for the residual fraction.

Carbonates were the predominant form of zinc at site 1-40%. At the other sites, they constituted approx. 30% of total zinc content, whereas sulfides were the largest fraction - 40-45%. There was also a considerable fraction of organically bound forms - 20-25%.

Nickel also occurred mainly in the form of sulfides. In contrast to the other metals, there was a larger amount of the exchangeable form of this metal - approx. 15%. The amount of the adsorbed and organically bound forms was similar. The residual fraction for nickel at sites close to the dam constituted 12%, and at sites 1 and 2-17%.

Manganese was characterized by a 25% fraction of the organically bound forms, carbonates and sulfides at the sites in the deep water zone, and a much larger fraction of sulfides (35-45%) in the bottom sediment at sites 1 and 2. These two sites had a smaller fraction of the exchangeable and organically bound forms in comparison with the remaining sites.

Iron was characterized by a minimal fraction of the exchangeable and adsorbed forms (<1%). Sulfides and carbonates were the largest fractions which amounted to 40-45% and 20-25% respectively.

In the case of lead, carbonates constituted the largest fraction at all sites - approx. 35%. Sulfides made a considerable portion of the total content of lead (25-30%). The remaining forms did not exceed 15%, and the organically bound forms constituted only 3%.

Table 3 presents the content of chemical forms of the investigated metals in the bottom sediment before and during aeration.

Detailed analysis of the results obtained shows that there was a small increase in cadmium content in the adsorbed and organically bound forms at all sites. In comparison with the zone which was not aerated, there was an increase in cadmium content in the form of sul-

rides at sites 3, 4 and 5. A decrease in the content of carbonates was found at all sites.

In the case of chromium, there was a general increase in its content in all forms. At sites 1, 2, 4 and 5 a decrease in the content of carbonates compared to the period before aeration was found.

In the case of copper, there was an increase in its content in the adsorbed and organically bound forms at all sites during aeration, and a decrease in the content of copper in the forms of carbonates and sulfides.

Zinc was characterized by an increase in the form of sulfides while the content of the exchangeable and

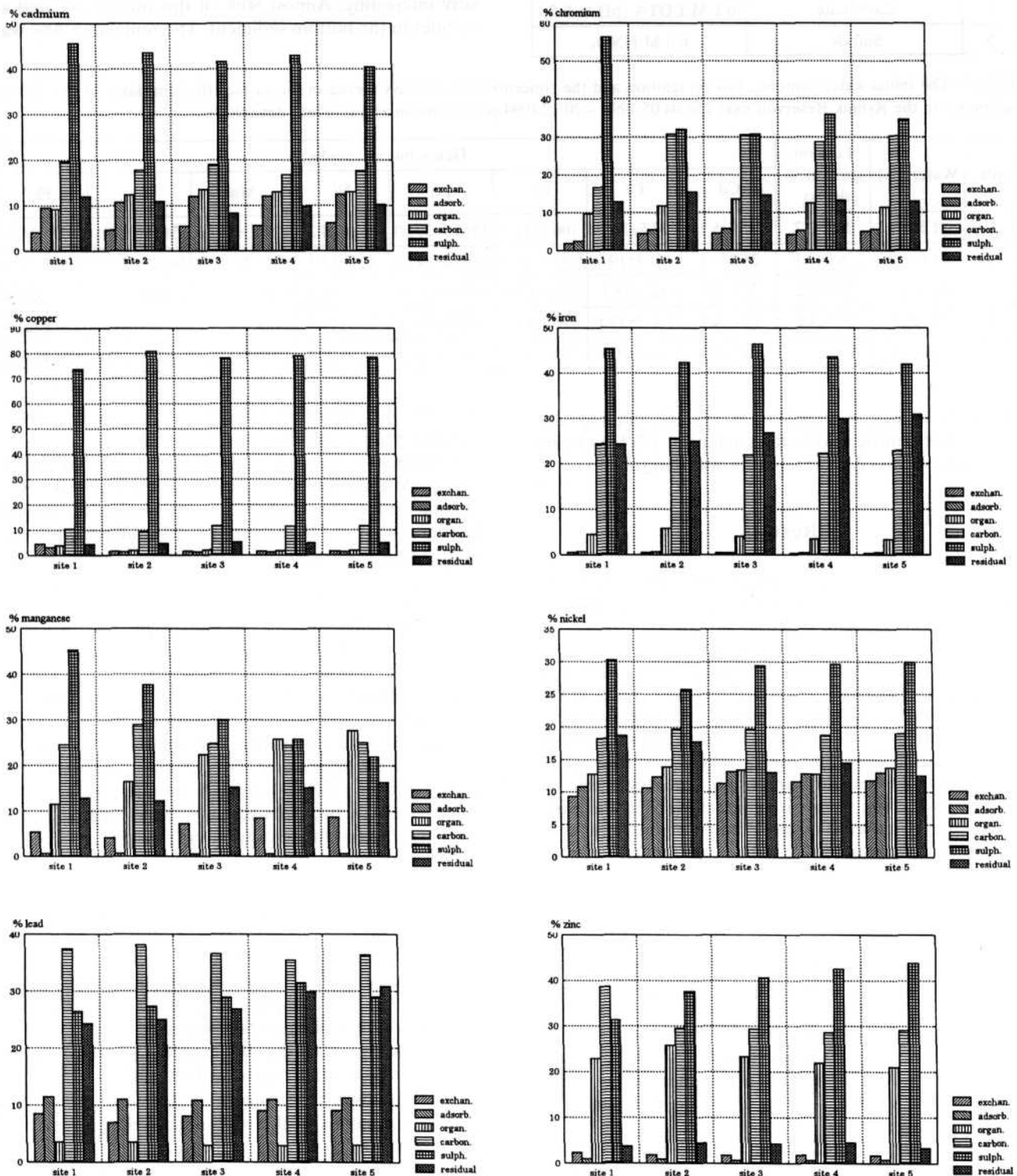


Fig. 2. The mean proportions (%) of heavy metal in the 0-2 cm layer of the bottom sediment in the Rybnik Reservoir over the 04.05.1993 - 20.12.1994 period.

Table 3. The mean content of chemical forms of heavy metals in the bottom sediment of the Rybnik Reservoir: exchan. - exchangeable form; adsorb. - adsorbed form; organ. - organically bound forms; carbon. - carbonates; sulph. - sulfides.

Site	Form	Heavy metals (mg/kg)							
		Cd	Cr	Cu	Zn	Ni	Mn	Fe	Pb
1	2	3	4	5	6	7	8	9	10
Before the aeration (04.05.1993 – 09.09.1993)									
1	exchan.	1.3	3.7	4.6	35.3	12.0	67.1	205.8	9.9
	adsorb.	2.2	5.2	3.3	13.5	10.9	5.4	221.8	8.4
	organ.	2.0	25.1	3.7	404.8	9.9	153.2	1906.8	3.4
	carbon.	6.3	43.7	10.9	582.0	19.2	335.8	10721.4	40.5
	sulph.	13.1	92.3	80.9	470.7	27.9	611.3	18489.6	25.5
2	exchan.	1.4	3.6	11.4	39.1	14.1	178.4	166.6	11.2
	adsorb.	2.5	5.1	9.2	14.7	12.2	16.1	139.4	9.9
	organ.	3.2	7.5	11.7	571.7	10.6	648.4	2172.7	4.2
	carbon.	5.6	31.0	61.9	517.0	20.4	1082.0	9735.1	46.5
	sulph.	10.3	30.6	519.3	670.2	21.9	1493.4	15069.9	27.6
3	exchan.	1.3	3.2	12.0	31.9	11.9	213.6	137.1	10.3
	adsorb.	2.3	4.6	9.6	11.2	11.6	13.5	98.2	8.8
	organ.	2.6	6.2	10.8	403.9	8.2	707.6	1698.9	3.3
	carbon.	4.3	25.0	69.8	409.1	14.7	855.7	8604.9	36.2
	sulph.	7.4	25.1	473.2	574.4	19.9	1274.4	15143.8	25.2
4	exchan.	1.3	3.8	12.6	35.0	14.4	213.9	132.2	11.2
	adsorb.	2.4	4.9	9.1	10.5	12.7	9.9	82.2	9.5
	organ.	2.5	11.3	9.6	402.6	9.6	609.5	1380.1	3.3
	carbon.	4.7	29.3	97.5	442.6	20.3	586.8	10852.0	42.7
	sulph.	8.5	36.7	601.4	556.6	26.0	747.1	14639.4	32.3
5	exchan.	1.4	4.6	13.6	29.7	13.7	195.2	128.6	12.1
	adsorb.	2.3	4.5	10.4	11.1	11.7	12.2	112.2	9.7
	organ.	2.3	8.6	10.2	363.5	9.8	622.8	1330.2	3.2
	carbon.	4.0	26.7	79.5	399.0	17.8	544.7	8865.5	37.7
	sulph.	7.0	30.9	547.8	612.3	25.8	543.3	14961.8	29.7
During the aeration (22.10.1993 – 20.12.1994)									
1	exchan.	1.0	5.4	4.7	34.0	9.6	69.5	365.3	6.8
	adsorb.	2.7	6.9	3.3	15.4	10.4	8.9	482.6	11.3
	organ.	2.7	27.4	4.2	317.7	10.5	145.0	2502.0	2.8
	carbon.	5.0	42.6	10.9	581.6	22.8	307.7	13562.7	33.9
	sulph.	12.2	215.4	77.9	510.7	32.7	570.5	27106.8	23.9
2	exchan.	1.0	4.6	9.7	28.8	9.0	137.2	234.5	5.9
	adsorb.	2.7	5.5	9.4	17.0	10.1	27.9	378.1	11.9
	organ.	3.0	14.3	12.0	407.8	9.5	570.2	2433.5	3.2
	carbon.	3.9	30.6	57.8	517.1	20.0	1023.7	10399.7	39.2
	sulph.	11.0	34.1	504.9	694.8	23.2	1317.3	18836.4	28.4
3	exchan.	1.1	4.5	11.2	24.0	10.2	176.1	175.1	7.5
	adsorb.	2.8	5.6	10.3	10.8	11.0	15.5	198.5	12.5
	organ.	3.2	16.3	17.3	347.1	9.8	547.1	1520.2	3.0
	carbon.	3.9	29.3	92.1	482.7	22.9	601.8	8898.4	40.1
	sulph.	10.0	29.7	617.9	717.8	28.4	709.7	20898.2	33.5

cont. Table 3

1	2	3	4	5	6	7	8	9	10
4	exchan.	1.1	4.6	12.7	22.9	11.3	166.1	169.7	9.3
	adsorb.	2.7	5.6	10.4	9.9	11.6	13.1	207.6	13.2
	organ.	3.0	14.6	15.6	287.9	9.8	517.3	1461.4	3.1
	carbon.	3.2	30.8	83.4	394.3	20.7	508.0	8462.4	39.3
	sulph.	9.9	39.2	613.8	672.6	29.7	520.8	20522.2	35.6
5	exchan.	1.1	4.6	11.9	21.7	10.7	160.6	147.0	8.4
	adsorb.	2.6	5.3	11.1	11.2	11.2	15.1	229.6	12.5
	organ.	2.8	12.2	16.7	263.9	9.6	510.6	1231.4	3.1
	carbon.	3.2	29.0	86.8	390.5	19.8	488.2	8482.7	37.6
	sulph.	8.6	32.8	595.1	627.4	26.9	404.2	16793.1	30.4

organically bound forms decreased. Those changes took place both in the aerated and comparative areas.

Nickel's characteristic feature was an increase in sulfides at all sites. At sites 1, 2 and 3 there was also an increase in nickel in the form of carbonates. The content of the remaining forms decreased, particularly the exchangeable and adsorbed ones.

Manganese was characterized by its increase in the adsorbed form at all sites. The content of the remaining forms decreased slightly.

During aeration, there was an increase in iron content in all examined chemical forms at sites 1 and 2. In the aerated area, it was possible to observe an increase in iron content of the exchangeable and adsorbed forms, and sulfides.

At all sites, there was an increase in lead content of the adsorbed forms. An increase of sulfides at all sites but 1 was also observed. The level of the remaining forms of lead did not decrease significantly.

A dependence of particular chemical forms of metals on the total content of a given metal in the bottom sediment was also analyzed (Table 4).

At sites in the aerated zone, the content of sulfides, adsorbed and organically bound forms increased with increasing total content of cadmium. At sites 1 and 2, there was an increase in the content of carbonates and sulfides with increasing cadmium content in the sediment.

An increase of the total content of chromium in the bottom sediment was correlated with an increase in carbonates, sulfides, adsorbed, organically bound forms at sites 3, 4 and 5, and an increase in all examined forms at sites 1 and 2.

It was possible to notice a significant correlation of the content of sulfides on total copper content in the bottom sediment ($r = 0.93-1.00$) at all sites. Only the content of the exchangeable form did not increase with increasing total copper content at the sites in the aerated zone. At sites 1 and 2, there was an increase in content of all examined forms with increasing total copper content.

An increase of zinc content correlated with the content of organically bound forms and zinc sulfides at all sites. There was also a proportional increase in the content of the remaining forms with increasing content of zinc in the bottom sediment at sites in the aerated zone.

Table 4. Correlation coefficients between various metal fractions and the total content of heavy metals in the bottom sediment of the Rybnik Reservoir over the 04.05.1993 - 20.12.1994 period: exchan. - exchangeable form; adsorb. - adsorbed form; organ. - organically bound forms; carbon. - carbonates; sulph. - sulfides.

Zone of the reservoir	form	Cd	Cr	Cu	Zn	Ni	Mn	Fe	Pb
aerated (site 3. 4. 5)	exchan.	0.06	0.22	0.17	0.56	-0.34	0.51	0.28	0.26
	adsorb.	0.58	0.26	0.26	0.23	-0.12	0.37	0.33	0.29
	organ.	0.68	0.43	0.35	0.77	0.57	0.68	-0.08	0.27
	carbon.	0.06	0.55	0.38	0.36	0.70	0.83	-0.16	0.83
	sulph.	0.75	0.66	0.93	0.36	0.63	0.83	0.64	0.56
non aerated (site 1. 2)	exchan.	0.11	0.42	0.77	0.14	-0.34	0.85	0.43	0.65
	adsorb.	-0.02	0.45	0.88	0.16	-0.38	0.61	0.40	0.32
	organ.	-0.03	0.59	0.78	0.74	0.58	0.88	0.42	0.57
	carbon.	0.32	0.60	0.92	0.18	0.68	0.89	0.23	0.91
	sulph.	0.62	0.98	1.00	0.56	0.66	0.77	0.78	0.66

In the area of the whole reservoir, there was a decrease in the content of the exchangeable and adsorbed forms of nickel with increasing total content of nickel in the bottom sediment. The content of the remaining forms increased at all sites.

The content of manganese in the whole area of the reservoir showed a significant correlation with the level of particular chemical forms ($r = 0.37-0.83$ in the aerated area, $r = 0.61-0.89$ in the not aerated area).

At sites 1 and 2, the content of iron in all chemical forms increased with its increasing total content. It was possible to notice an increase in the sulfides, exchangeable and adsorbed forms in the aeration zone. The change of the content of the other forms was characterized by an insignificant, negative dependence.

In the case of lead, there was a proportional increase in all chemical forms with increasing total content of this metal in the bottom sediment.

Discussion

Cadmium was much less mobile in the bottom sediments of the Rybnik Reservoir than in other reservoirs [15, 16, 17]. However, even a 5% contribution of the exchangeable fraction and a 10% contribution of the adsorbed form, characterized by the highest mobility, makes it possible for cadmium to diffuse to the hypolimnetic layer of water. This is due to a higher content of this metal in bottom sediments than in other reservoirs and an increase of the adsorbed form with increasing total content of cadmium in the bottom sediment. The research carried out under conditions of artificial aeration of the reservoir did not confirm the increase in the content of carbonates and the adsorbed form which took place under laboratory conditions. The content of cadmium in the adsorbed form increased slightly in the whole area of the reservoir, whereas the content of carbonates decreased insignificantly. The content of cadmium sulfides under conditions of artificial aeration increased slightly in the area of deep water.

Literature data, as well as the results obtained, show that there is a very small possibility of copper's migration deposited in the bottom sediment [18, 19]. It is also expressed by copper's deposition mainly in the form of sulfides characterized by a high correlation coefficient (0.93-1.00). The results obtained did not confirm the decrease of sulfides resulting from the aeration of the hypolimnetic layer [11, 12].

During research on the changes in chemical forms of zinc after aeration, it was possible to observe a larger fraction of carbonates and a significant decrease in sulfides from 34% to 2.4% [11]. Under conditions of artificial aeration of the reservoir, the qualitative changes of particular chemical forms were insignificant and took place in the whole area of the reservoir.

The largest part of nickel in the bottom sediment occurred as sulfides and organically bound forms - approx. 50% [16, 17, 20] and residual fraction [18, 19, 21]. The residual fraction (40%) and sulfides (35%) of nickel had the largest contribution in the bottom sediment examined under laboratory conditions. Aeration caused only a slight decrease in sulfides and an increase in the organi-

cally bound and exchangeable forms [11]. The changes observed under laboratory conditions were not confirmed by the tests carried out in the reservoir. The level of sulfides increased slowly in the whole area of the reservoir after aeration, whereas the content of the exchangeable form decreased.

Manganese was characterized by a higher proportion of potentially mobile form than other metals [20, 22, 23, 24]. Its release or deposition in the bottom sediment is strongly linked with aerobic conditions prevailing in the hypolimnetic zone. An increase of the hypolimnetic water reaction also causes an intensified precipitation of manganese in the sediments. It was very characteristic that an increase in total manganese content caused a proportional increase in all its distinguished forms.

The contribution of iron in particular chemical forms enables the assumption that in spite of its high total content in bottom sediment its bioaccessibility is low. The exchange of iron between the sediment and water is, similarly to manganese, under the influence of conditions prevailing in the reservoir. Steinberg and Hogel [22] found that there was a negative correlation between the reaction and the total content of iron in the bottom sediment. A similar phenomenon was found in the Rybnik Reservoir. The aeration of the hypolimnetic layer causes iron precipitation in the form of oxides and hydroxides, which leads to an increase in the content of iron in the bottom sediment. This phenomenon was not found during aeration at sites in the deep zone.

Aeration in research under laboratory conditions caused a decrease of lead in the form of sulfides; however, there was an increase in carbonates and organically bound forms [11]. The artificial aeration of the Rybnik Reservoir did not cause any significant changes in the distribution of particular forms in the bottom sediment.

The research did not show a clear effect of the artificial aeration of the hypolimnetic water on the changes in the distribution of particular chemical forms of metals occurring in the bottom sediment. The fact that the laboratory results were not confirmed was due to the low efficiency of aeration because the tests showed neither an increase in oxygen content in the hypolimnetic water nor an increase in the degree of water oxygenation. The changes of other parameters e.g. the decrease in iron and manganese content in the hypolimnetic water were not explicit and may have been the result of aeration or a number of other processes caused by certain hydrobiological and weather conditions.

Acknowledgements

Financial support by the State Committee for Scientific Research (KBN), Poland. Grant No. PB 0834/S4/93/04.

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