Effects of pH and Aeration on Copper Migration in Above-Sediment Water

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Abstract

This research analyzed the influence of pH and aeration of the above-sediment water on the amount of copper released from contaminated bottom sediments of Rybnik Reservoir. Leaching of copper from the bottom sediment in the non-aerated systems was the highest when pH reached 2.0-3.5. For the aerated systems, the range was from 2.0 to 4.5. A dependence of the amounts of leached water on leaching time was also observed. Sulfides were a predominant form of copper occurrence in the bottom sediment (60%). The remaining forms were as follows: organically bound, carbonates > residual > adsorbed > exchangeable.

Keywords: copper, speciation, migration, influence of pH and aeration

Introduction

Metals deposited in contaminated bottom sediments can be released to the water column with changes in different hydrobiological and physico-chemical conditions such as pH, redox potential, salinity [1, 2, 3, 4]. Mobility and bioavailability of metals in sediments depend also on their chemical form. Therefore, it is necessary to determine metal speciation while evaluating the amounts of metals leached into water from the bottom sediments under changing environmental conditions.

There are numerous studies on the effect of physico-chemical conditions on the forms of metal occurrence in bottom sediments. Most of them are based on laboratory experiments carried out under specific pH, redox or salinity conditions [5, 6, 7, 8, 9].

Our research aimed at determining the effect of pH and aeration on copper migration into water from the contaminated bottom sediments of Rybnik Reservoir. Research prior to this showed a high level of copper in the bottom sediments of Rybnik Reservoir resulting from the impact of the Upper-Silesian Industrial Region and the Rybnik Industrial District [10, 11, 12]. Since 1993, a restoration process involving aeration of the above-sediment water has been carried out in the reservoir.

Materials and Methods

Two types of bottom sediment sample were taken from Rybnik Reservoir. The first type of sediment (A) was taken from the dam area (8-10 m), and the second (B) from the backwater (depth 1-1.5 m). The selection of these sites was determined by different levels of copper in the water and sediments of the reservoir.

The samples of the bottom sediments were averaged by passing them through a 0.43 mm sieve. Twelve systems were investigated:
- A series - systems with the sediment sampled from the dam area
  A1 - non-aerated system, initial pH = 5,
  A2 - non-aerated system, initial pH = 3,

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A3 - non-aerated system, initial pH = 2,
A4 - aerated system, initial pH = 5,
A5 - aerated system, initial pH = 3,
A6 - aerated system, initial pH = 2, - B series - systems with the sediments sampled from the backwater
B1 - non-aerated system, initial pH = 5,
B2 - non-aerated system, initial pH = 3,
B3 - non-aerated system, initial pH = 2,
B4 - aerated system, initial pH = 5,
B5 - aerated system, initial pH = 3,
B6 - aerated system, initial pH = 2.

The experiment was carried out in 10 dm^3 closed containers at a constant temperature. The ratio between the sediment and water was 1:10. The pH of water was lowered in particular containers with specpure HNO$_3$.

Water samples were taken after 0.5 hour, and then every 2 hours for the first 12 hours, and then every 12 hours for 7 days. The samples were filtered through 0.45 m membranes (cellulose nitrate) and acidified with specpure HNO$_3$.

The pH of the above-sediment water was measured at each sample collection.

The amount of copper in the bottom sediments was determined before and after the experiment. The upper layer of the sediment was dried to a constant weight (105°C), and subsequently mineralized with a mixture of nitric and perchloric acids in a microwave oven.

A chemical analysis of copper forms was made by Rudd's method [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 sample was treated in turn with the following extractants: 1 M KNO$_3$, 0.5 M KF (pH = 6.5), 0.1 M Na$_4$P$_2$O$_7$, 0.1 M EDTA (pH = 6.5), 6.0 M HNO$_3$. The contact time of the extractant with the sample was 24 hours, and the ratio of the extractant to the dry mass of the sediment was 50:1. Between successive extractions, the extractant was centrifuged from the sediment and the sediment was washed with a small amount of redistilled water. The supernatant liquid was brought to a specific volume, acidified with nitric acid to obtain 1% HNO$_3$ and then the amount of copper was determined. The extractants applied enabled an isolation of copper in the following forms: exchangeable, adsorbed, organically bound, carbonates and sulfides.

The amount of copper in the samples was determined by means of the atomic absorption spectrophotometry using the flame and flameless techniques. An AAS-30 atomic absorption spectrophotometer (Carl-Zeiss-Jena) and HCL lamps were applied. The instrumental conditions for copper were following: wavelength 324.8 nm, bandpass 0.2 nm, lamp current 5 mA, flame air/acetylene. The accuracy of procedure was checked by analyzing

Table 1. Changes in the amounts of dissolved copper in above-sediment water [µg/dm^3].

Time [h]	A1	A2	A3	A4	A5	A6	B1	B2	B3	B4	B5	B6
0.5	6.9	200.2	1230.9	37.1	145.0	674.3	6.2	3.0	140.4	29.8	2.1	97.6
2.0	3.4	59.2	402.5	19.6	113.7	607.5	5.7	10.7	8.1	6.2	5.7	112.5
4.0	4.6	41.8	490.0	11.1	88.8	650.9	5.3	10.1	20.2	1.7	6.9	143.2
6.0	8.7	163.5	507.0	10.9	68.3	608.1	10.3	6.7	21.8	2.0	27.1	222.6
8.0	5.4	85.7	604.2	9.1	186.9	683.4	4.5	12.5	9.1	4.0	11.2	253.5
10.0	2.5	62.9	543.5	19.3	126.1	1395.5	4.6	12.2	91.9	5.3	6.8	17.9
12.0	5.9	132.7	557.9	10.5	61.1	696.2	5.3	13.6	41.1	5.9	8.4	10.5
24.0	7.3	87.4	598.0	13.4	11.5	753.3	5.9	12.5	210.1	69.3	119.6	91.0
36.0	2.6	34.5	542.5	47.8	15.3	431.3	1.4	6.9	684.8	41.4	122.4	515.4
48.0	8.6	43.2	531.8	14.9	3.8	214.2	8.2	7.5	766.3	5.9	13.3	47.2
60.0	13.4	17.8	466.9	32.0	9.4	139.1	33.3	40.0	1095.1	34.0	94.4	355.0
72.0	4.2	8.0	459.5	40.6	6.0	66.7	15.0	64.6	704.8	11.5	29.6	66.3
84.0	5.2	6.7	399.6	56.5	5.1	75.1	6.2	10.1	837.5	4.9	10.3	80.7
96.0	8.6	3.3	594.2	29.9	25.7	274.3	5.1	8.8	688.8	2.2	9.0	48.8
108.0	27.2	70.5	808.1	58.7	16.5	275.2	4.8	12.4	908.4	13.9	4.5	38.5
120.0	31.3	34.5	764.5	56.0	53.9	248.3	6.7	83.6	930.8	3.2	11.3	68.4
132.0	19.4	64.0	860.3	52.7	35.9	278.5	61.9	27.6	746.1	3.4	2.5	54.3
144.0	35.0	35.5	925.0	48.5	27.2	292.5	11.3	10.6	423.8	109.0	8.7	61.2
156.0	43.2	43.6	920.1	37.6	27.9	327.2	5.6	10.5	496.2	65.9	4.7	62.0
168.0	53.7	64.0	936.6	59.0	20.0	341.8	46.6	9.5	348.5	4.3	2.8	41.9

samples of reference material (CRM 277 - Trace elements in estuarine sediment). These standards were treated and analyzed for copper in a similar manner to those of the sediment with each batch of sediment studies.

The effects of water pH, aeration and type of sediment on migration of copper from the bottom sediment into water, and on the forms of copper occurrence in the sediment was determined applying the method of multidirectional analysis of variance and linear regression.

Results

Changes of pH of the above-sediment water for the systems examined are presented in Fig. 1. There is a considerable increase in the pH of the above-sediment water in all the examined systems. In the case of the Al, A2, A4, A5 and Bl, B2, B4, B5 systems, pH reached the values of 7 - 7.5. Stabilization of the pH level occurred after 50 hours for the initial pH = 5, after 100 hours for pH = 3 (for A series) and after 50 hours for B series. In the case of the initial pH = 2, there was also an increase in pH which stabilized after 50 hours for A3, A6 as well as B3 and B6. However, the final pH did not exceed the value of 4.6 for A6, 3.7 for B6 and 2.8 for A3 and B3.

The amount of copper dissolved in the water is presented in Table 1. Its amount in the water before the experiment started was three times higher for A series (1.4 µg/dm^3) than B (0.5 µg/dm^3).

series A

series B
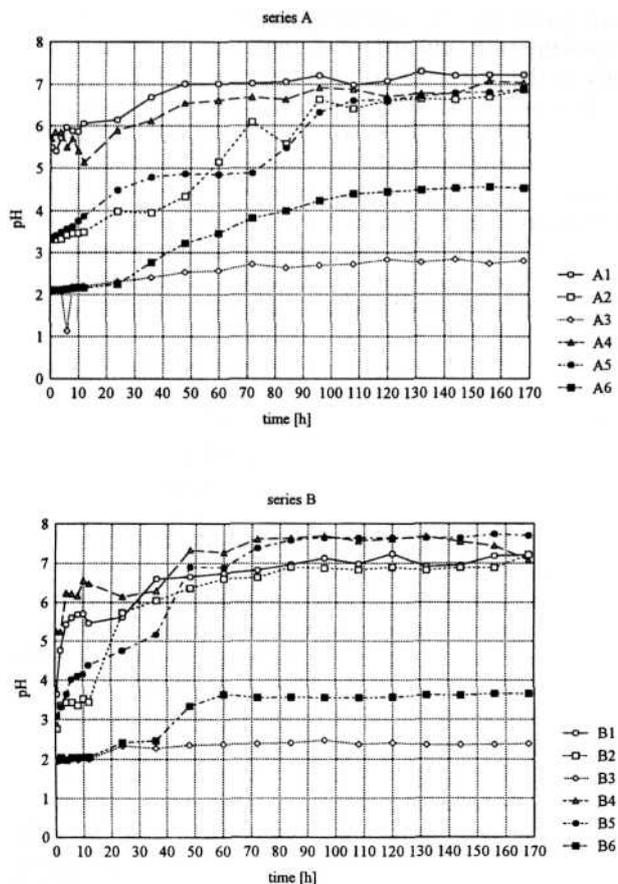
Fig. 1. Changes in the pH of the above-sediment water.

Lowering the initial pH to 2 for the A systems caused migration of 1230.9 µg/dm^3 of copper into the above-sediment water (A3). The level of copper in the A6 non-aerated system was even higher and amounted to 1395.5 µg/dm^3. Similarly, B series showed maximum concentration of dissolved copper at the lowest pH values - 1095.1 µg/dm^3 (B3).

In the system with the initial pH = 5, the amount of copper increased with increasing pH. The correlation coefficient which describes this dependence was r = 0.59. Introduction of aeration did not affect the dependence between pH and copper amount - in the A4 system, the correlation coefficient was r = 0.74. In the system with the initial pH = 3, the amount of copper in the water increased with decreasing pH. Correlation coefficients for those dependences were -0.52 for A2 and -0.63 for A5. For the system with pH = 2, there was not a significant correlation between pH and the amount of copper in the water - r = 0.29 (A3 system). Introduction of aeration to the system with the initial pH = 2 caused an increase in copper amount with decreasing pH (r = -0.73). Analyzing the changes in the amount of copper in the whole pH range, it is possible to state that the highest leaching of copper from the bottom sediment took place at pH = 2.0-3.5. Slightly higher copper values occurred also in the water with neutral pH. Aeration of the above-sediment water caused widening of the pH range characteristic of the strongest leaching of copper. For the aerated system the range is from 2.0 to 4.5. For pH = 7 there was also a slight increase in copper amount leached from the bottom sediment to water.

The amount of copper in the above-sediment water depended also on leaching time. Correlation coefficients for this dependence were as follows:

Al system	0.86	A4 system	0.77
A2 system	-0.46	A5 system	-0.58
A3 system	0.46	A6 system	-0.61

In the case of the bottom sediments from backwater, the dependences between the amount of copper in water, leaching time and the pH of water occurred only for B3 system. The correlation coefficients obtained in the remaining systems were low.

The amount of copper leached to the water was the highest for B series at the pH range of 2.0 - 2.5. In the range from 2.5 to 6.5, it remained at a low level but it slightly increased for pH = 6.5 - 7.5. In the aerated system, high amounts of copper in the water occurred in the pH range from 2.0 to 4.0. For higher pH values, apart from generally low levels of copper, its single higher amounts were observed.

The amount of copper in the bottom sediment differed depending on a collection site of the sediment. The copper concentration in bottom sediment from the dam area was 842.2 µgCu/g dry weight, from the backwater 93.6 µg/g dry weight.

Most of the copper was found as sulfides (60%) for both A and B series - Fig. 2. The amount of organically bound copper in the bottom sediment of A series amounted to 150 µg/g on average (approximately 20%) and for B series - 7 µg/g (approximately 8%). Copper found as carbonates was approximately 80 µg/g (A series) and 15 µg/g (B series). The most mobile forms i.e.

Table 2. Determination of the influence of sediments origin, aeration and initial pH on the occurrence of particular forms of copper in bottom sediment.

Series	Variable	p						
		total	exchangeable	adsorbed	organically bound	carbonates	sulfides	residual
A	Initial pH	0.517	0.699	0.829	0.838	0.847	0.625	0.784
	Aeration	0.187	0.524	0.651	0.282	0.061	0.004	0.707
B	Initial pH	0.006	0.776	0.048	0.522	0.983	0.669	0.445
	Aeration	0.318	0.132	0.940	0.099	0.089	0.024	0.293

Fig. 2. Copper amounts in particular forms of occurrence.
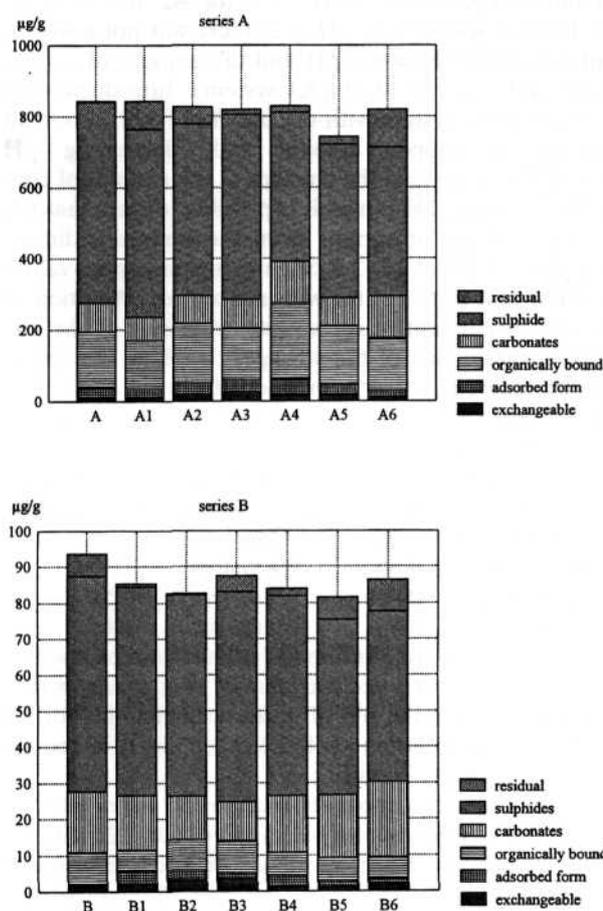
Discussion

Copper is relatively difficult to leach from bottom sediments. Migration of copper is limited by the presence of $CaCO_3$, adsorption by hydrated ferric and manganese oxides, silt minerals and organic substances. Copper is much more mobile in the oxidizing than reduction environment due to the limited solubility of the compounds of monovalent copper in comparison with the diversified solubility of the bivalent compounds. According to most researchers, copper occurs in the bottom sediments mainly in the sulfide-organic fraction [6, 14, 15, 16, 17] and in residual form [18]. In the Rybnik Reservoir, copper also occurred mainly in the form of sulfides (approximately 60%), and in the organically bound forms and carbonates [9]. The contribution of the mobile fractions - exchangeable and adsorbed ones, was the smallest similarly to the researches of other authors [14, 15, 16].

The factor which causes mobilization of copper from the bottom sediments to water is first of all pH. Depending on aerobic or anaerobic conditions prevailing in the above-sediment water, the pH value below which there was a considerable mobilization of copper was between 3-5 [1, 6, 14, 19]. In our research in the non-aerated A series (Al, A2, A3), the amount of leached copper decreased when pH exceeded 3.5. For the non-aerated B series (Bl, B2, B3), the value was pH = 2.5. In the aerated A and B series, the pH boundary value increased in comparison with the non-aerated systems and amounted to 4.5 for A series and 3.5 for B series. The amount of copper leached at lower pH indicate that it is a predominant factor in leaching copper from bottom sediments. When pH was lower, the amount of copper in the above-sediment water increased 900 times for A series and 2000 times for B series.

The impact of the aerobic conditions on the forms of copper occurrence and consequently on the possibility of copper mobilization from the bottom sediments to water is also high. According to Hakanson et al. [1], under anaerobic conditions the amount of the carbonate and exchangeable forms of copper increases and the amount of residual fractions decreases. Aeration causes an increase in the amount of copper easily released from organically bound forms (labile organic material) and a decrease in the organic-sulfide fraction (stable organic, humic and fulvic acid) [20]. In our research, the aeration of the above-sediment water caused a considerable de-

exchangeable and adsorbed copper, as well as the residual fraction were the form found in the smallest amount. The effect of pH and aeration on the forms of copper occurrence in the bottom sediment was analyzed by means of the multidirectional analysis of variance (Table 2). The forms of occurrence were affected by a given type of the bottom sediment. In the A series, pH did not affect the amount of copper in particular forms of occurrence. In the B series, pH influenced the decrease in the total amount of copper and the amount of the adsorbed form. Aeration caused a considerable decrease in the amounts of sulfides in all systems.

crease in the sulfide form of copper in the all examined systems. At the same time, there was a slight increase in the adsorbed form of copper in the bottom sediments for A and B series, and organically bound form for A and carbonates for B.

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