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The Impact of Anthropogenic Activity on the Quality of Bottom Sediments in the Watershed of the Delňa Creek †

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Abstract: This paper is focused on evaluating the quality of bottom sediments and water in the watershed of the Delňa creek, where gold, antimony and mercury were mined in the past. The results showed that the biggest source of pollution was a heap of mining material, where the limit values of Sb, As, Hg and Pb concentrations in the sediments were exceeded. Other sources of pollution in the river basin were the right-hand tributaries. A comparison of the dependencies of the concentrations of potentially toxic metals in the water and sediments shows that while the concentrations of pollutants in the waters react to the current state of water quality in the basin and tributaries (pH, concentration, discharge), the sediments exhibit a stable concentration character.

Keywords: potentially toxic metals; mining activity; sediment quality; water quality

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1. Introduction

Contamination of the aquatic environment with potentially toxic metals is receiving considerable attention worldwide. One of the possible sources of environmental pollution with these elements is mining activity, the consequences of which, despite the cessation of activity, persist in the environment for a long time [1]. Due to the influence of mining activity on watersheds, not only water but also sediments are contaminated. Sediments play an important role in the transport of pollutants into the water system, as they can affect water quality due to remobilization processes. Monitoring changes in the chemical composition of river sediments therefore provides important qualitative information on the overall system of water courses and their adjacent areas [2]. Changes in the pollutants' concentration in the sediment, as well as their potential risk to the aquatic environment and health [3], can be detected by monitoring the quality of sediments. Many studies have been carried out in order to determine the impact of mining activity on land quality. Many studies have been carried out with the aim of finding out the immediate or long-term impact of mining activity on the quality of the water ecosystem and its sediments [4–8]. Long-term observation revealed, for example, that increased concentrations of potentially toxic metals due to mining were detected at the beginning of mining. However, after the end of the mining, a decreasing trend in the concentrations of these pollutants in the sediments was observed [9].

2. Material and Methods

This study of the accumulation of selected pollutants in bottom sediments was carried out in the watershed of the Delňa creek, which flows through the Prešov district (Slovakia). It is a left-hand tributary of the Torysa and is 16 km long.

It springs above the Zlatá Baňa village, and above the village of Kokošovce the creek fills the Sigord water reservoir. The reservoir was built for the purpose of flood protection and, in the past, this area was a sought-after recreational location; currently the reservoir is mainly used for fishing. The area of the Zlatá Baňa village is known for its past mining activities. In the 18th century, gold mining experiments began to be carried out in the cadastre of the village. Later clay, antimony and opal were mined there. In the 1990s, geological exploration work was carried out on the Zlatá Baňa deposit, which confirmed the presence of sulfidic, mainly Pb-Zn, ores [10].

Bottom sediment and water samples were taken from 11 sampling points in the Delňa creek basin and its right-bank tributaries due to their presumed pollution (Figure 1).

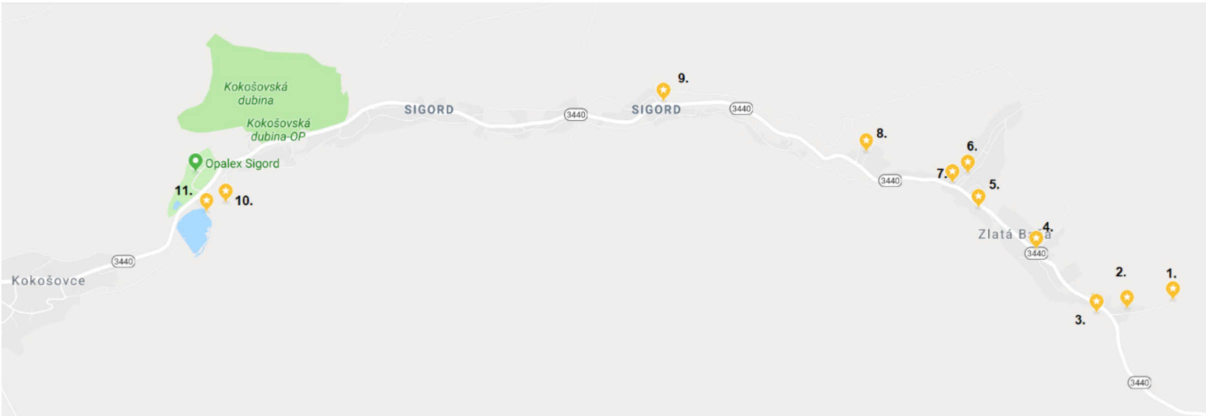

Figure 1. Sampling points in the watershed of the Sigord reservoir.

Sampling point No. 1—a heap of mining material—is located above the built-up area of the Zlatá Baňa village and is detected as the main source of water and sediment pollution in the watershed. The sampling points No. 4, 6 and 8 are located on the right-bank tributaries of the Delňa creek in the built-up area of the village Zlatá Baňa. Other sampling locations (No. 2, 3, 5, 7, 9, 10) are situated on the Delňa creek. Sampling point No. 11 is the inlet to the Sigord reservoir. Sediment samples were taken in plastic bags, water samples were taken in small closable glass bottles. Water and sediment samples were analyzed in laboratory conditions.

Chemical composition of the sediments and water was determined via X-ray fluorescence (XRF) spectrometry using SPECTRO iQ II (Germany). To determine the pH of leachates (prepared in ratio sediment to water of 1:5) the multifunction device MX 300 Xmatepro (METTLER TOLEDO, Columbus, OH, USA) was used.

3. Results and Discussion

3.1. Chemical Composition of the Sediments and Water

To identify the mining activity's impact on the quality of sediments and surface water in the monitored area, the presence of contaminants such as Sb, As, Ni, Cu, Hg, Cr, Al, Pb, Zn, Fe and Mn was determined. The results of the chemical analysis of the monitored contaminants in the sediments and water are shown in Tables 1 and 2. The quality of the bottom sediments was evaluated according to the criteria specified in the Guideline of the Ministry of the Environment of the Slovak Republic No. 549/98-2 for the assessment of risks from polluted streams and reservoirs sediments. The quality of the surface water in the watershed was evaluated according to the Slovak Government Regulation no. 269/2010 Coll., laying down the requirements for the achievement of good water status. Sediments and water concentrations exceeding the maximum allowable values, according to the mentioned regulations, are indicated in bold in Tables 1 and 2.

Table 1. Results of chemical analysis of selected elements in sediments from the Delňa creek watershed.

Sample/Distance from the Source of Contamination	Concentrations in Sediments										
	(mg/kg)								(%)		
	Sb	As	Hg	Cr	Pb	Cu	Zn	Ni	Fe	Al	Mn
S1/0 km (heap)	**203.3**	**980.9**	**40.9**	101.7	**997.0**	51.2	114.3	31.4	3.2	7.5	<0.0010
S2/0.29 km	**21.5**	**166.4**	**14.5**	163.9	117.9	**84.0**	**1226.0**	**44.3**	4.3	5.1	0.3105
S3/0.65 km	13.2	**185.0**	4.6	104.1	110.8	**76.2**	**2378.0**	**45.3**	4.5	4.3	0.5259
S4 (tributary)	10.9	7.6	2.9	82.4	<2.0	47.4	75.4	36.0	2.6	5.0	0.1060
S5/1.72 km	13.4	**35.5**	<2.0	134.1	64.4	68.6	**621.9**	43.3	3.5	5.9	0.2831
S6 (tributary)	7.2	<1.0	<2.0	180.1	<2.0	37.1	47.4	34.5	2.5	4.6	0.1738
S7/1.92 km	**17.7**	**41.5**	<2.0	41.3	5.8	37.1	215.5	31.4	2.7	4.3	0.1022
S8 (tributary)	12.0	<1.0	<2.0	173.8	<2.0	35.9	88.8	35.5	3.4	5.6	0.1017
S9/3.88 km	**20.3**	**181.9**	<2.0	176.3	<2.0	20.5	65.9	16.8	3.8	2.3	0.2122
S10/6.86 km	10.1	<1.0	5.0	120.6	<2.0	50.4	167.6	41.8	2.9	5.5	0.1164
S11/6.96 km, inflow to the reservoir	8.7	<1.0	3.4	125.5	6.2	41.7	124.6	43.1	2.3	5.3	0.0404
Limit (Guideline No. 549/98-2)	15.0	55.0	10.0	380.0	530.0	73.0	620.0	44.0	-	-	-

Table 2. Results of chemical analysis of selected elements in surface water from the Delňa creek watershed.

Sample/Distance from Source of Contamination	Concentrations in Water (mg/L)										
	Sb	As	Hg	Cr	Pb	Cu	Zn	Ni	Fe	Al	Mn
W1/0 km (heap)	10.6	<1.0	<2.0	104.9	<2.0	16.2	<1	17.3	**89.2**	**37.8**	<5.1
W2/0.29 km	8.4	<1.0	<2.0	126.1	<2.0	12.4	<1	13.4	**47.2**	**27.0**	<5.1
W3/0.65 km	<2.4	<1.0	<2.0	124.9	<2.0	18.8	<1	16.5	**52.1**	**14.4**	<5.1
W4 (tributary)	7.7	<1.0	<2.0	107.7	<2.0	9.1	<1	15.5	**47.3**	**32.1**	<5.1
W5/1.72 km	7.2	<1.0	<2.0	114.4	<2.0	17.8	<1	16.1	**51.1**	**67.3**	<5.1
W6 (tributary)	10.1	<1.0	<2.0	110.8	<2.0	16.3	<1	14.0	**48.5**	**16.4**	<5.1
W7/1.92 km	7.2	<1.0	<2.0	178.7	<2.0	14.9	<1	14.9	**49.2**	**48.9**	<5.1
W8 (tributary)	5.4	<1.0	<2.0	113.6	<2.0	9.0	<1	15.7	**51.9**	**72.5**	<5.1
W9/3.88 km	9.9	<1.0	<2.0	125.2	<2.0	10.9	<1	14.9	**49.5**	**37.6**	<5.1
W10/6.86 km	4.9	<1.0	<2.0	116.2	<2.0	15.7	<1	14.2	**49.4**	**20.3**	<5.1
W11/6.96 km, inflow to the reservoir	8.0	<1.0	<2.0	155.1	<2.0	8.9	<1	8.1	**49.4**	**44.8**	<5.1
Limit values (Reg. No. 269/2010)	-	0.0075	0.00007	-	-	-	-	-	2.0	0.2	0.3

The results showed that the heap of mining material was a very significant source of pollution in the studied basin, where the maximum allowable concentrations in sediments and surface water were significantly exceeded for some elements (Sb, As, Hg, Pb, Cu and Zn for sediments, and Fe and Al for surface water).

Due to the influence of pH on the mobilization of contaminants at the sediment/water interface, the pH values of the sediments were determined in the leachates (Table 3).

Table 3. The pH values of sediments.

Sample	pH
S1	3.39
S2	8.72
S3	7.45
S4	7.63
S5	8.23
S6	8.11
S7	8.17
S8	8.51
S9	7.72
S10	7.80
S11	6.77

The lowest pH value was found in S1 sample, which was also assumed to be due to the presence of sulfidic mining material deposited on the heap.

3.2. Accumulation of the Selected Pollutants in the Sediments

Because the increased concentration of potentially toxic metals in waters usually has a direct impact on the concentrations of metals in the sediments [11], in the next part of our study we focused on studying the mobilization of Fe, Al and Sb between the sediment and water. The dependence of the mobilization of these elements on pH values and their distance from the pollution source is shown in Figure 2.

The highest concentrations of iron in the surface water were recorded in sampling point S1—the heap of mining material—which is considered the most significant source of pollution in the studied area (Figure 2). The subsequent decrease in the concentration of Fe in surface water is caused by an increase in the pH value of the water above 3.5 [12,13], which leads to the precipitation of iron cations and their accumulation in the sediment.

The concentrations of aluminum in the water and sediment increased or decreased in direct proportion in all monitored sampling points. An exception was observed in sampling point S10, where there was a decrease in the aluminum concentration in the surface water and a significant increase in the Al in the sediment due to accumulation.

Regarding antimony concentrations, the highest values in the water and sediment were recorded in sampling point 1 (the heap). With the increasing distance from the source of pollution, the concentration of Sb in the sediment decreased. But the right-hand tributaries had the effect of increasing the concentration of antimony in the water due to the presence of dissolved antimony in the tributaries.

A comparison of the dependences of the concentrations of potentially toxic metals in the water and sediments shows that while the concentrations of pollutants in the waters react to the current state of water quality in the basin and tributaries (pH, concentration, discharge), the sediments exhibit a stable concentration character. And with increasing distance from the source of pollution, the accumulation of toxic substances in the sediment occurs to a large extent.

On the other hand, the change in pH due to inflows causes the leaching of heavy metals from the sediments and their subsequent mobility in the watershed. However, it is necessary to add that the concentration of heavy metals is also significantly influenced by their concentration in the tributaries, as was observed in the case of antimony and aluminum.

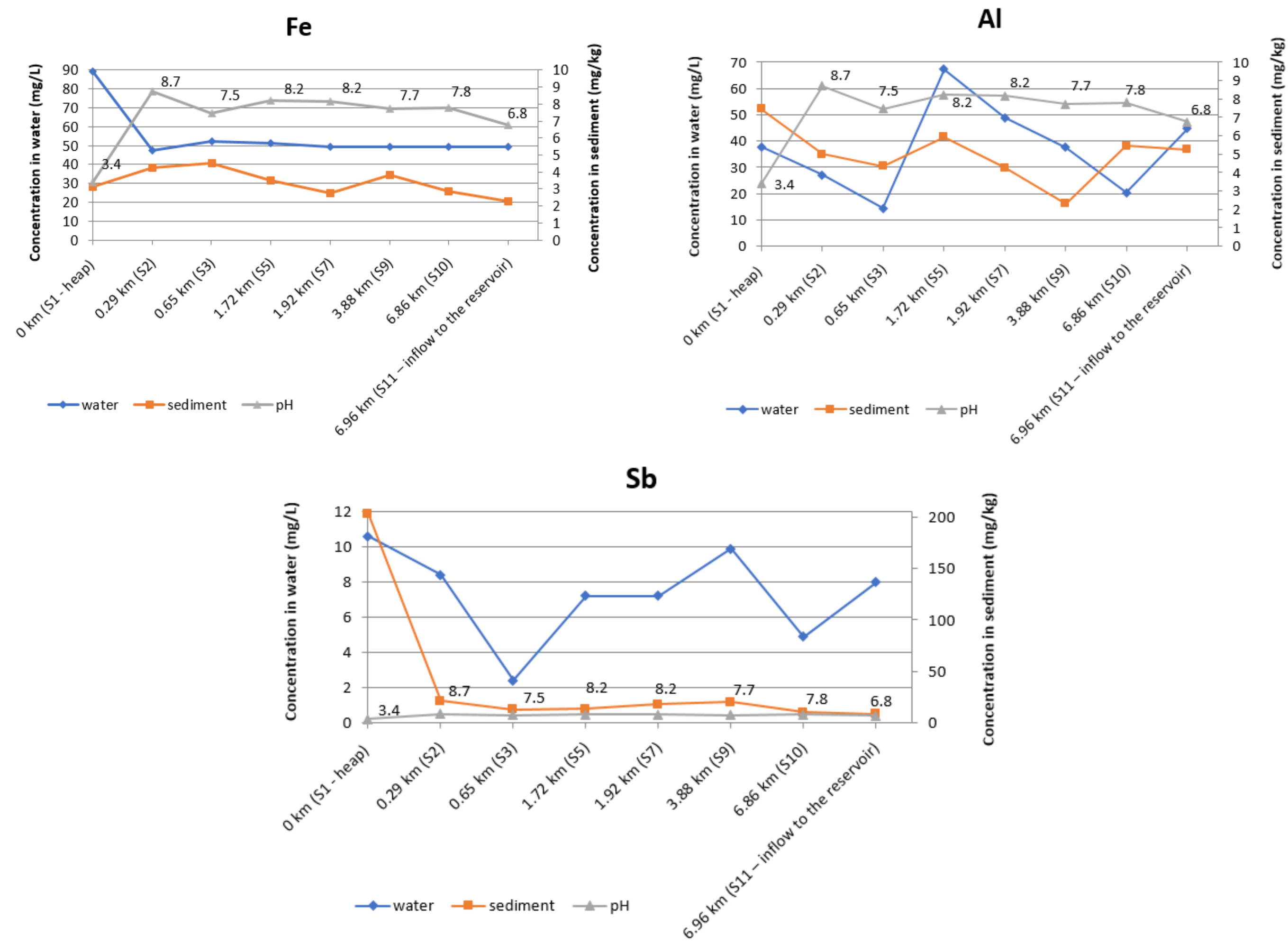

Figure 2. The dependence of the mobilization of Fe, Al and Sb between water and sediment on pH values and their distance from the pollution source.

4. Conclusions

Sediments are a priority source of pollutants in the environment of contaminated areas. They are a reliable indicator of the state of the polluted environment. This work studied the quality of bottom sediments in the Delňa creek watershed, which is affected by mining activity. The results showed that the heap of mining material is a very significant source of pollution in the studied river basin, where the maximum allowable concentrations in the sediments and surface water were significantly exceeded for some potentially toxic elements (Sb, As, Hg, Pb, Cu and Zn for sediments, and Fe and Al for the surface water). In addition to other parameters (discharge, concentration, proportion of clay particles, etc.), the mobilization of contaminants at the interface between the sediment and water is also influenced by the water's pH values, which directly affect the accumulation of heavy metals in sediments, or their release into the surface water. Based on the study of the dependencies between sediment and water in the Delňa creek basins, we can state that increasing the concentration of heavy metals in the water will also increase their concentration in the sediment, but only up to the particular capacity to which the sediment is able to absorb them. However, long-term monitoring is necessary to predict the contamination of water and sediments in the monitored basin.

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