

Article

Metal Pollution Indices of Bottom Sediment and Surface Water Affected by Acid Mine Drainage

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Abstract: Sediments are normally the final pathway of both natural and anthropogenic components produced or derived from the environment. Sediment quality is a good indicator of pollution in the water column, where heavy metals and other organic pollutants tend to concentrate. Metals are introduced in aquatic systems as a result of the weathering of soils and rocks, from volcanic eruptions, and from a variety of human activities involving the mining, processing, or use of metals and/or substances that contain metal pollutants. Heavy metal concentration in the water column can be relatively low in some cases, but the concentrations in the sediment may be elevated. The presented work aimed to investigate the pollutant levels of some heavy metals (Fe, Mn, Al, Cu, Zn, As, Cd, Pb) in the water and sediments related to acid mine drainage (AMD) produced from an abandoned sulphide mine in Smolnik in Eastern Slovakia. A metal pollution index was used to compare the total content of metals at five sampling stations. The level of partitioning of the metals between the surface water and sediments in the area was calculated using Partition coefficients and the correlation coefficients between the metal pairs in both media were calculated by a Pearson coefficient.

Keywords: sediments; metals; acid mine drainage; statistical analysis

1. Introduction

Environmental pollution is a significant problem in modern society. Of the various kinds of pollution, the high contamination of aquatic systems with toxic heavy metals are of major concern since these elements are not biodegradable [1]. Heavy metals can be found in amounts several times above their natural background limits and pollute sediments and water next to industries, urban areas, and mining activities [2,3]. The main objective of this experimental work is to monitor and minimize the incidence of pollutant-oriented problems, and to provide water of sufficient quality to serve various purposes, such as drinking and irrigation [4]. The quality of water is identified in terms of its physical, chemical, and biological criteria. A particular problem that impacts water and sediment quality-checking involves the complexity associated with analysing a large number of measured variables [5–7].

The water environment is very often polluted by heavy metals due to various anthropogenic sources in the form of industrial waste water, urban surface water runoff, agricultural processes, etc. [8]. Heavy metal concentration within the water column can be relatively low in some cases, however, concentrations in the sediment may increase. The problem is to obtain representative samples to actually show accurate concentrations of contaminants in surface water [9]. Another point of view shows that sediments integrate contaminants over time and are in constant movement with the overlying water column; hence, the analysis of heavy metals in sediments permit the detection of contaminants that may be in the water column [10,11].

Low-level emission of a contaminant may meet the water quality standard, but long-term polluting of the sediments could cause the accumulation of high loads [12] that can have a negative influence on the urban and rural population that use this water for various purposes. Once heavy metals are spilled into waters, they are bound to solid particles and are integrated in the organic matter of the sediment, which impacts the adsorption of metallic elements [13–15].

They further allow for the identification of possible factors/sources impacting the system and not only provide a relevant tool for the credible management of water resources, but also provide quick solutions to pollution problems [4]. The data acquisition contains reliable information regarding the behaviour of the water resources. The classification, modelling and exposition of reviewed data are the most important points in the assessment of water quality.

Acid mine drainage (AMD) is one of the worst environmental problems associated with mining activity. In the Slovak Republic, the extensive closing of deposits using wet conservation, i.e., flooding from the middle to the end of the 20th century, caused contamination of former mining localities by these waters. The negative results of AMD activity can be observed mainly at those locations where sulphide ores and raw materials containing sulphides were mined. The classic example are deposits in Smolnik where the mine waters have a pH of 3.8, and where high concentrations of sulphates and heavy metals outflow straight into the Smolnik River. In order to propose an effective and economic method for the prevention of the negative influence of AMD at this location, it was necessary to understand the behaviour of the processes in the water environment after mixing AMD with surface water and provide a real assessment of their long-term evolution [16]. This was the reason for starting a systematic monitoring of geochemical development in acid mine drainage in order to prepare a prognosis in terms of environmental risk and the use of these sediments as an atypical source of a wide range of elements [16]. For better knowledge about migration, transformation behaviour, and rules of heavy metals in sediment, it is necessary to make an accurate assessment of the contamination level and the extent at each site.

Since geochemical surveys are multivariable studies, consideration must be made to the approaches that treat all of the variables under consideration at the same time, taking into account their relationships and the individual characteristics of each variable. Principal component analysis (PCA) is a multivariate technique that aims at studying several variables together. This type of treatment allows us to take into account the relationships (represented by the correlation matrix) that exist among all studied variables [17].

The purpose of this work is to assess the complex phenomenon of pollution of the sediment samples from old mining areas with heavy metals by the Pearson's correlation and PCA. This paper describes the consistency in the metal pollution indices of the various stations in the water and sediment of the contaminated Smolnik River. The functional relationship of how the metals will respond to a unit change in any medium has also been studied.

2. Materials and Methods

Water and sediment samples were collected from the Smolnik River during the years 2006–2016. Water and sediment sampling sites are shown in Figure 1 and GPS coordinates are in Table 1. The first two sampling sites, 1 and 2, were situated in the upper part of the Smolnik river not contaminated by acid mine water; another two sampling localities, 4 and 5, were located under the shaft. The outflow of AMD from the Pech shaft (Smolnik mine) is numbered 3. Samples were collected according to ISO 5667-6-2005 "Water quality—Sampling—Part 6: Guidance on sampling of rivers and streams". Samples were collected once a year (15 sediments and water samples per year), with triplicate sampling from each sample sites.

To determine the pH of water samples, a multifunction device MX 300 X Mate Pro (METTLER TOLLEDO, Columbus, LA, USA) was used. The concentrations of metals in the water samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Varian Vista, MPX, Victoria, Australia). The sediment samples were air-dried and ground by using a planetary mill and sieved to a fraction of 0.063 mm. The chemical composition of sediments was determined

by means of the X-ray fluorescence (XRF) method using a SPECTRO iQ II (Ametek, Klevé, Germany). The sediment samples were prepared as pressed tablets with a diameter of 32 mm by mixing 5 g of sediment and 1 g of dilution material (M-HWC) and pressed at a pressure of 0.1 MPa/m².

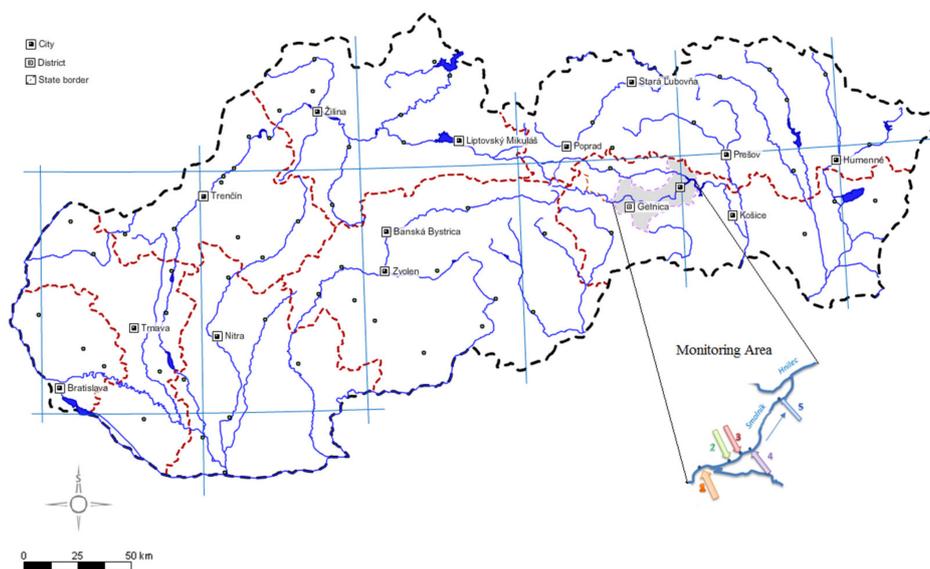


Figure 1. Location of the Smolnik River on the map of the Slovak Republic and sampling sites 1–5 in the study area.

Table 1. GPS coordinates of sampling sites.

Sample Site	GPS Coordinates	Description
1	48°43′27.6965658″ N 20°42′59.2164803″ E	Site 1: uncontaminated part; outside Smolnik village
2	48°44′21.9978463″ N 20°45′37.2264862″ E	Site 2: uncontaminated part; small bridge crossing to the Pech shaft
3	48°44′18.0496747″ N 20°45′44.9512482″ E	Site 3: source of AMD—Pech shaft
4	48°44′46.1817014″ N 20°46′28.4995937″ E	Site 4: contaminated part; 200 m downstream of the Pech shaft
5	48°45′2.2642765″ N 20°46′39.41082″ E	Site 5: contaminated part; inflow to the Hnilec River

All statistical analysis was carried out with the Data Analysis Tool pack in Microsoft Office Excell 2007 and STATISTICA 7. Differences in the levels of the metals within, and between, the media were separated by a Duncan multiple range test at a 95% level of significance [18].

2.1. Metal Pollution Index

The metal pollution index (MPI) is a mathematical model which could solve some of the highlighted problems. MPI has been calculated to enable the presentation of all results from the metal concentrations as a single value, if possible, yet overcoming the difficulties with both application and understanding of demanding statistical analysis [19–21]. To compare the total content of metals at the different sampling stations, the MPI was used. The MPI was obtained with the equation:

$$\text{MPI} = (Cf_1 \times Cf_2 \cdots \cdots Cf_k)^{1/k}, \quad (1)$$

where Cf_1 is the concentration value of the first metal, Cf_2 is the concentration value of the second metal, and Cf_k is the concentration value of the k_{th} metal.

2.2. Partition Coefficient

The level of partitioning of metals between the surface water and sediment of the area (partition coefficients K_d) was calculated using Equation (2). K_d was transformed into a natural logarithm form to ascertain the medium that concentrates the metal more [3].

$$K_d = [\text{Metal}]_{\text{sediment}} / [\text{Metal}]_{\text{water}} \quad (2)$$

2.3. Correlation Coefficient

The correlation coefficients of the various metal pairs were calculated with the aid of the Pearson productmoment coefficients to show the association of the metal pairs in water and sediment.

2.4. Coefficient Determination

The determination coefficient (r^2) of each of the metals was carried out via regressing the values of one medium on the other to establish a functional relationship of how each metal will respond to a unit change in either of the media.

2.5. Principal Component Analysis

Principal component analysis is a technique that allows the examination of correlations between variables and the identification and elimination of those that contribute little to the overall variation [22]. PCA can be seen as an ordination technique that constructs the theoretical variable that minimizes the total residual sum of squares after fitting a straight line to the data for each species. PCA does so by choosing the best values for the site, i.e., the site scores [23].

3. Results and Discussion

Surface sediment and water pollution is considered by many regulatory agencies to be one of the largest risks to the aquatic environment. The mean levels of the total concentration of metals in the surface water and bottom sediments of the Smolnik River over 11 years, as presented in Table 2, indicated Fe to be highest in both water and in sediment. Cd is the lowest in both media. The pH of the water is shown in Table 3.

Table 2. The mean levels of the metals in the surface water and bottom sediments of the Smolnik River.

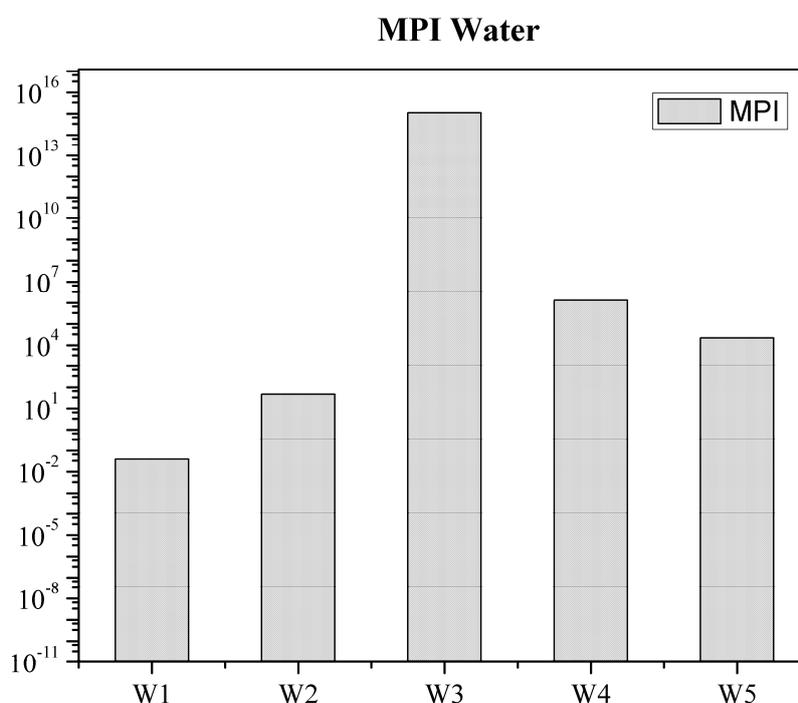
Media	Metals	Stations				
		W1	W2	W3	W4	W5
Surface water (mg·L ⁻¹)	Fe	0.058 ± 0.012	0.889 ± 0.899	332.60 ± 85.621	13.634 ± 8.789	5.919 ± 5.723
	Mn	0.011 ± 0.003	0.125 ± 0.114	25.990 ± 6.205	1.250 ± 0.726	0.976 ± 0.621
	Al	0.033 ± 0.032	0.165 ± 0.217	67.680 ± 18.431	1.283 ± 1.641	0.348 ± 0.746
	Cu	0.004 ± 0.005	0.013 ± 0.008	1.594 ± 0.722	0.105 ± 0.119	0.047 ± 0.066
	Zn	0.004 ± 0.001	0.044 ± 0.044	7.448 ± 2.271	0.372 ± 0.251	0.272 ± 0.217
	As	0.002 ± 0.001	0.001 ± 0.001	0.035 ± 0.017	0.002 ± 0.001	0.001 ± 0.001
	Cd	0.0003 *	0.0003 *	0.014 ± 0.008	0.001 ± 0.001	0.0003 *
	Pb	0.005 *	0.005 *	0.055 ± 0.008	0.005 ± 0.001	0.005 *
Media	Metals	Stations				
		S1	S2	S3	S4	S5
Sediments (mg·kg ⁻¹)	Fe	41,550.0 ± 5316.9	50,450.0 ± 18,569.4	343,600.0 ± 55,068.0	79,450.0 ± 36,415.4	97,810.0 ± 80,710.7
	Mn	900.0 ± 253.8	535.3 ± 145.3	234.0 ± 261.3	580.0 ± 145.7	584.0 ± 170.9
	Al	73,810.0 ± 6220.4	61,490.0 ± 21,764.1	21,940.0 ± 13,692.8	64,280.0 ± 3719.0	62,270.0 ± 13,105.1
	Cu	132.50 ± 44.09	266.23 ± 131.18	482.40 ± 201.60	404.10 ± 226.45	519.20 ± 158.32
	Zn	150.60 ± 26.01	180.50 ± 42.52	119.30 ± 82.13	196.80 ± 65.21	240.30 ± 49.76
	As	44.50 ± 13.18	82.30 ± 17.26	2137.90 ± 743.33	142.20 ± 73.30	97.80 ± 26.66
	Cd	0.50 *	4.850 ± 13.756	1.150 ± 2.005	0.50 *	0.50 *
	Pb	43.50 ± 10.99	91.80 ± 41.93	679.40 ± 872.20	170.90 ± 87.44	110.90 ± 44.65

Within row (for each medium and metal), mean ± standard deviation are significantly different at $p < 0.05$ ($n = 10$). Within column (total mean metals within a medium), mean ± standard deviation are significantly different at $p < 0.05$ ($n = 10$). * Values under the detection limits.

Table 3. The mean levels of the pH in the Smolnik River.

Sample Site	pH
1	6.19 ± 0.73
2	6.33 ± 0.82
3	3.98 ± 0.07
4	5.53 ± 0.51
5	5.80 ± 0.66

For the eight metals (Fe, Al, Mn, Cu, Zn, As, Cd, and Pb) studied in the surface water and sediments in the Smolnik River, the significant differences were not established among the station means. The pattern of the metals in the surface water at 95% significant level is $W3 > W4 > W5 > W2 > W1$ for surface water (Figure 2) and $S3 > S2 > S4 > S5 > S1$ for sediment (Figure 3). This may be due to continuous dilution of the acid mine drainage (W3) by the surface water in the Smolnik River. It influences the increase of pollutants at station W4 and W5. The MPI of the surface water at station W3 (Pech shaft) was higher than that of the other stations, while that of the sediments at station S3 (Pech shaft) was higher, too, although the differences between other stations were not significant.

**Figure 2.** Metal pollution index (MPI) for water each sampling station.

The regression analysis of the metals between both media showed some positive (Fe, Al, Cu, As) and negative (Zn, Cd, Pb) linear relationships (Table 4). As and Cu had the strongest relationship between both media ($r = 0.967$) and was closely followed by Fe ($r = 0.733$) and Al ($r = 0.718$). The determination coefficient (r^2) of the metals between the sediment and water indicated Cu and As (94%) to be more dependable to each of the mediums than in the other metals. Cadmium had the highest log-transformed partition coefficient and was followed by Pb and As, while Zn had the least.

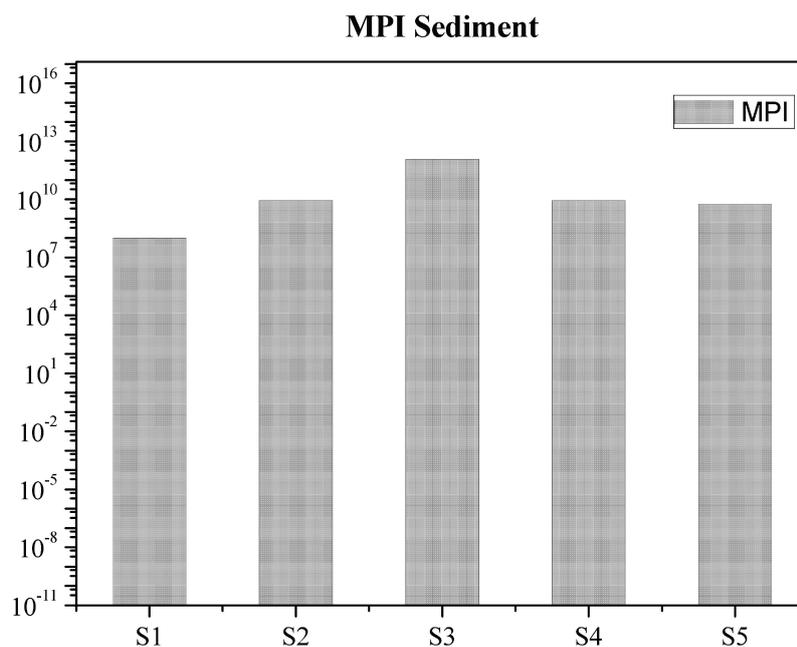


Figure 3. Metal pollution index (MPI) of sediment for each sampling station.

Table 4. Various relationships of the metals in the media.

Metals	Relationship [Sediment (Y) and Surface Water (x)]	Determination Coefficient r^2	Correlation Coefficient r	Partition Coefficient k_d	$\log K_d$
Fe	$Y = 69.705x - 136.28$	54%	0.733	1735.7	3.24
Al	$Y = 14.044x - 27.792$	52%	0.718	4082.7	3.61
Cu	$Y = 100,541x + 62,517$	94%	0.967	1023.5	3.01
Zn	$Y = -3599.6x + 189,842$	2%	0.372	21.91	1.34
As	$Y = 392,156x - 706,648$	94%	0.967	61,090	4.79
Cd	$Y = -339.3x - 2628.5$	7%	0.255	305,198.1	5.48
Pb	$Y = -88,068x - 35,118$	26%	0.506	68,962.3	4.84

The data were subjected to a Pearson correlation matrix and principal component analysis (PCA) to select the studied characteristics that best represented the Smolnik River. The Pearson correlation was made separately for sample sites 1 and 2 (uncontaminated samples), for the source of AMD (sample site 3) and sample sites contaminated by the source of heavy metals (AMD) 4 and 5. The variables must have a substantial number of correlations equal to, or higher than, 0.30 to ensure the existence of true factors [24]. The Pearson product-moment correlation coefficients of heavy metals in both media at different sediment sites showed several metal pair correlations ($p < 0.05$) (Table 5). The very high positive (>0.9) correlations between sediment sites 1 and 2 were among Fe-Mn (0.92) and Mn-Zn (0.98) in water, and Mn-Zn (0.93), Al-Zn (0.97), and Mn-Al (0.93) in bottom sediment. In sediment site numbers 4 and 5, the very high correlations were observed between Fe-Mn (0.90) and Mn-Zn (0.95) in water. The highest correlation of 0.89 was found between As-Pb. Sediment site 3 shows a very high correlation in water between Fe-Mn, Fe-Al, Mn-Al, and Al-Zn. The highest negative correlation in sediment was among Fe-Zn (-0.93). The high negative correlations were between Zn-As and Cu-Al in sediment. The comparison of all evaluated sources showed a high dependence among Fe, Mn, Zn, Cu, and Al in water (Figure 4).

Table 5. Pearson product moment correlation coefficients between metal levels in the media.

Couple of Elements	1 2 *		4 5 *		3 **	
	Water	Sediment	Water	Sediment	Water	Sediment
Fe-Mn	0.92	-0.67	0.90	-0.44	0.98	-0.77
Fe-Al	0.44	0.67	0.45	-0.78	0.90	-0.69
Fe-Cu	0.53	0.64	0.45	0.67	0.55	-0.46
Fe-Zn	0.85	0.54	0.87	0.09	0.89	-0.93
Fe-As	-0.26	0.49	0.08	0.15	-0.34	0.39
Fe-Cd	0.79	-0.66	0.39	0.00	0.78	0.26
Fe-Pb	-0.13	0.70	0.26	-0.18	0.83	-0.45
Mn-Al	0.59	0.93	0.49	0.33	0.93	0.23
Mn-Cu	0.67	0.57	0.52	-0.04	0.57	0.08
Mn-Zn	0.98	0.93	0.95	0.28	0.93	0.88
Mn-As	-0.30	-0.32	0.04	0.15	-0.32	-0.57
Mn-Cd	0.51	0.74	0.30	-0.16	0.74	-0.05
Mn-Pb	-0.14	0.85	0.25	0.35	0.85	-0.04
Al-Cu	0.82	0.77	0.79	-0.41	0.77	0.81
Al-Zn	0.50	0.97	0.48	0.04	0.97	0.59
Al-As	-0.26	-0.53	0.09	0.05	-0.53	0.11
Al-Cd	0.12	0.58	0.10	0.13	0.58	-0.18
Al-Pb	-0.11	0.82	0.59	0.28	0.82	0.84
Cu-Zn	0.62	0.73	0.66	0.75	0.73	0.43
Cu-As	-0.05	-0.49	-0.16	0.52	-0.49	0.23
Cu-Cd	0.17	0.12	0.22	-0.20	0.12	-0.09
Cu-Pb	-0.14	0.73	0.05	0.23	0.73	0.66
Zn-As	-0.27	-0.44	-0.10	0.49	-0.44	-0.48
Zn-Cd	0.38	0.60	0.32	-0.18	0.60	-0.27
Zn-Pb	-0.14	0.86	0.06	0.38	0.86	0.24
As-Cd	-0.12	-0.40	0.19	0.17	-0.40	0.22
As-Pb	0.08	-0.18	0.43	0.89	-0.18	0.23
Cd-Pb	-0.05	0.53	0.05	0.18	0.53	-0.11

* Correlation is significant at the 0.05 level ($n = 20$). ** Correlation is significant at the 0.05 level ($n = 10$).

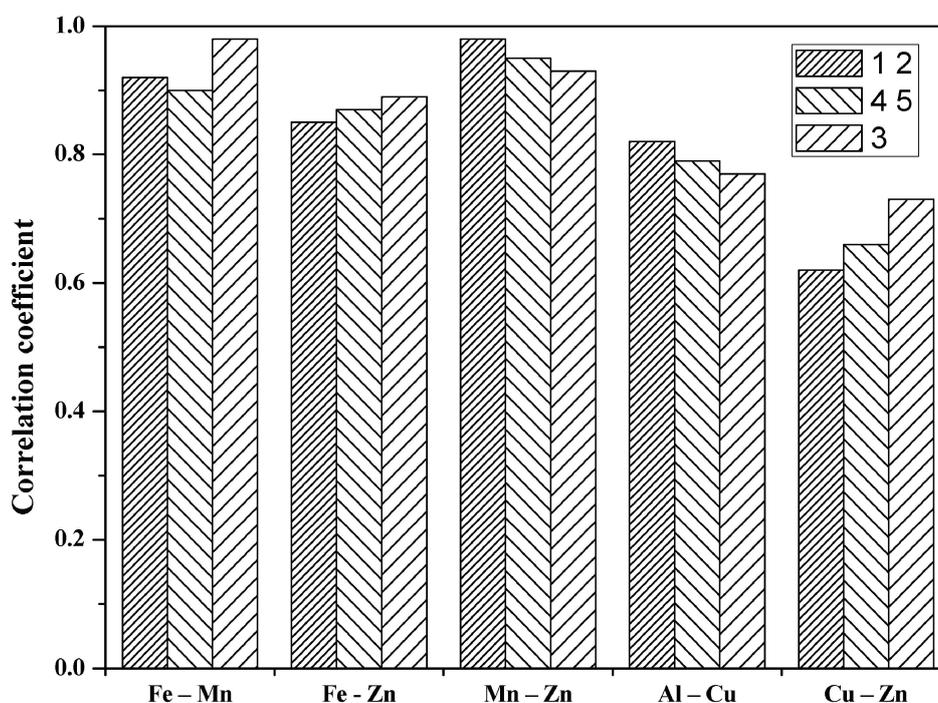


Figure 4. The highest correlation coefficients for water at all sampled sites.

The principal component analysis (PCA), applied to the data matrix, showed a differentiation between the samples according to their sampling sites (1–2; 3; 4–5). The number of significant principal components was selected on the basis of the Kaiser criterion with an eigenvalue higher than 1 [25]. According to this criterion, only the first three principal components were retained because subsequent eigenvalues were all less than one; hence, the reduced dimensionality of the descriptor space is three.

Therefore, the heavy metals for sediment sites 1 and 2 could be grouped into a model of three components that explained 72.32% of the total variability of the data (Figure 5).

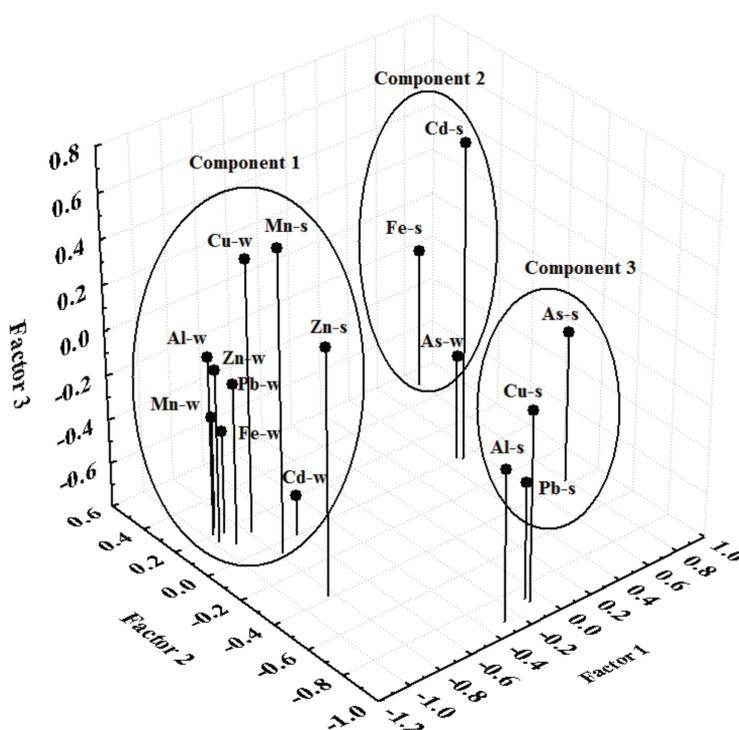


Figure 5. Graphical display of the principal components influencing the heavy metal concentration in sediment and water between sediment sites 1 and 2.

This matrix demonstrates that Mn, Fe, Zn, Al, Cd, Cu, and Pb in water, and Zn and Mn in bottom sediment, were associated with the first component (PC1); the second component (PC2) included only Cd and Fe in sediment and As in water, and the third component (PC3) grouped the metals Pb, As, Cu, and Al in sediment.

The heavy metals at sediment site 3 were grouped into a model of four components explained 83.62% (Figure 6). The first component grouped Mn and Al in sediment. Pb, As, Al, and Cd in water belong to component 2. Component 3 grouped Fe, Cd, Cu, in sediment and Zn, Mn, Fe, Cu, in water. The last component grouped Zn, As, and Pb in sediment.

Figure 7 shows the four components for sediment sites 4–5, which explains 73.35%. The first component explains 27.67% and belong to Mn, Fe, Zn, Cu, Al, and Cd in water and As, Zn, Pb, Cu, and Fe in sediment. Pb, Cd, and Mn in water belong to component 2 (18.14%). Group 3 explains 16.67% (As and Pb in water). The last component explains 10.87% and belongs to Al in the bottom sediment.

Figures 5–7 show comparable behaviour of metals Fe, Zn, Al, Mn, and Cu in water (they are always in the same component), which is in accordance with the results presented in Table 4. The behaviour of metals in sediments is probably related to the change of pH and, thus, the possibility of their precipitation [26,27].

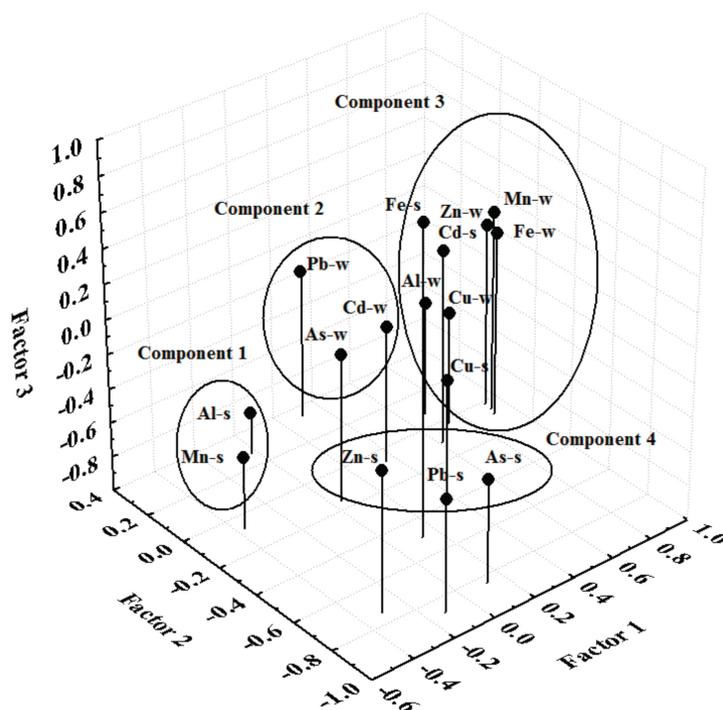


Figure 6. Graphical display of the principal components influencing the heavy metal concentration in sediment and water in sediment site 3.

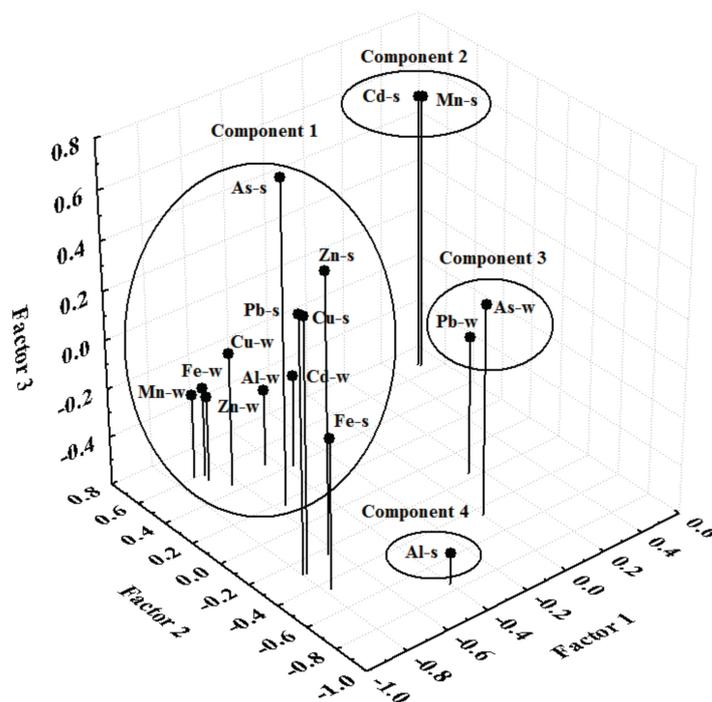


Figure 7. Graphical display of the principal components influencing the heavy metal concentration in sediment and water between sediment sites 4 and 5.

4. Conclusions

The data obtained in this study has shown interdependence in the metal pollution indices of the five stations of the Smolnik area (Slovakia). This may be due to the similarity of the geological

background of the locality, continuous dilution of the acid mine water in the Smolnik River, and similarity of the physical and chemical composition of the sediments. The stations with higher pollution indices are related to areas of intense activities, such as the S4 and S5 for the surface water and for the sediments.

The pattern of the metal levels at all the stations studied followed $W3 > W4 > W5 > W2 > W1$ for surface water and $S3 > S2 > S4 > S5 > S1$ for sediment.

Significant correlations were between As-Pb, As-Fe, and Fe-Pb in bottom sediment. Pearson product moment correlation coefficients for all metal pairs in water showed significant positive correlation.

Principal component analysis was shown to be a very important tool to extract information from a complex trace element dataset. The comparison of the graphical display of the principal components influencing the heavy metal concentration in sediment and water for all sampled sites shows the same behaviour of metals Fe, Zn, Al, Mn, and Cu, which are in accordance with the results presented by the Pearson product moment correlation coefficients between metal levels in both media.

The present study suggests that these indices are useful tools for the identification of different sources of contamination of the bottom sediment. This paper will hopefully contribute to the development of a water and sediment pollution prevention strategy. The main topics that may need to be investigated are the control of industrial and domestic discharge, regular observation of pollutants, and evaluating the effects of pollutants on the ecosystem over the long term, coordinating the pollution source and preventing inflow of pollutants to the water and sediment.

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Author Contributions: Eva Singovszka conceived and designed the experiments and wrote the paper. Magdalena Balintova supervised and controlled the chemical contribution of the manuscript. Eva Singovszka and Stefan Demcak contributed to the statistical analysis. Stefan Demcak supervised the graphical portion of the paper. Petra Pavlikova participated on sampling and treatment of the sediment and water samples.

Conflicts of Interest: The authors declare no conflict of interest.

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