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Assessment of elemental contamination in the bottom sediments from a dam reservoir using a sequential extraction technique and chemometric analysis

Research Article

Marzena Dabioch*, Andrzej Kita,
Piotr Zerzucha, Katarzyna Pytlakowska

Department of Analytical Chemistry,
Institute of Chemistry, University of Silesia,
40-006 Katowice, Poland

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Abstract: The concentration of elements in sediments is an important aspect of the quality of water ecosystems. The element concentrations in bottom sediments from Goczalkowice Reservoir, Poland, were investigated to determine the levels, accumulation and distribution of elements; to understand the contamination and potential toxicity of elements; and to trace the possible source of pollution. Sediments were collected from 8 sampling points. The functional speciation, mobility and bioavailability of elements were evaluated by means of modified Tessier sequential extraction. The element contents were measured by optical emission spectrometry with inductively coupled plasma. The experimental results were analyzed using chemometric methods such as principal component analysis and cluster analysis to elucidate the metal distributions, correlations and associations. The highest concentrations of most elements were found at the center of the reservoir. The distribution of metals in the individual fractions was varied. To assess the extent of anthropogenic impact indices, contamination factor, degree of contamination, metal pollution index and risk assessment code were applied. The calculated factors showed the highest contamination factor and the ability of chromium to be released from sediments. The degree of contamination showed that the area is characterized by a very high contamination. Strontium and manganese showed high potential ecological risk for sediments.

Keywords: *Heavy metals • Sediments • Modified Tessier sequential extraction • Principal component analysis • Cluster analysis*

1. Introduction

Sediments are an important method for evaluating the status of an aquatic ecosystem with regard to metals and nutrients, because they play an important role in the circulation of elements in the surface water environment [1]. Metals are constantly moving around the reservoir. Metals which entered the water in an undissolved form sink to the bottom, adding to bottom sediment. During the descent, they may undergo partial dissolution and penetrate into water [2]. Balance between the water column and the bottom sediment is fixed. Processes occurring in water, both natural, related to the functioning of aquatic ecosystems, and those caused by human activity, may cause an imbalance. It may lead to re-release of the substance from the bottom sediment deposited by chemical and biochemical processes into the open water. This process is significantly intensified in the case of re-suspension of sediments. Release of substances accumulated in the bottom sediment into the water column is usually detrimental to the lake, because on one hand, it is a release of biogenic substances such as phosphorus and nitrogen, the elements determining the trophic state of the lake, and on the other hand, typically involves toxic substances such as heavy metals [3,4]. Therefore, the sediments in the aquatic

* *E-mail: spectro11@o2.pl*

environment play both a positive and a negative role. Adsorption and binding of toxic components of water contribute to its purification, but under certain conditions the sediments may be a source of water pollution and hazard for living organisms [5,6].

Knowledge of heavy metals in waters and bottom sediments is of great importance because of the toxicity of metals and their negative impact on the ecosystem. In the analytical environment, the total content of heavy metals in sediments is not a sufficient criterion for assessing the degree of contamination and sediment toxicity, since the proportion of biologically available forms is different for various metals. For this reason, it is necessary to obtain more comprehensive information on both the chemical form in which elements are present, and their physical characteristics, which is obtained by speciation studies [7]. Speciation of sediment is formally a functional speciation, because it is tested for bioavailability of individual elements present in the bottom sediment. Speciation analysis in sediments is carried out via one of two common procedures – one-step extraction and sequential extraction [8,9].

The first comprehensive and fundamental idea of sequential extraction of metals from bottom sediment samples to date was developed by Tessier, Campbell and Bisson in 1979 [10]. This idea links virtually all researchers interested in the subject. They modify the procedure developed by these authors in various ways. The aim of the studies carried out by Tessier *et al.* was to develop and test procedures for sequential selective extraction, enabling separation of trace metals in chemical forms that may be released into solution in a variety of environments. Tessier *et al.* distinguished and defined five basic fractions: exchangeable metals, metals associated with carbonates, metals associated with hydrated iron and manganese oxides, metals associated with organic matter and metals remaining permanently associated with minerals [11-14].

Chemometric techniques [11-13,15-20] are extremely useful in the study of similarities and differences between individual samples and the relationship between the distribution of metals in bottom sediment samples.

In this research project, sediment samples were collected from Goczalkowice Reservoir. The main objectives of the study were to apply sequential extraction based on the five-stage procedure proposed by Tessier with a novel modified residual fraction measure in combination with chemometric methods such as principal component analysis and cluster analysis to examine sediments. In order to investigate the extent of anthropogenic and natural impact, four indices were used: contamination factor, degree of contamination, metal pollution index and risk assessment code. In this way, it was possible to determine the levels, accumulation and distribution of elements in sediments and to understand the contamination and potential mobility or toxicity of elements in sediments based on the analysis of total and bioavailable metals.

2. Experimental procedure

2.1. Sample collection

Samples of bottom sediments were collected from the largest dam reservoir in southern Poland – Goczalkowice Reservoir in November 2011. The samples were taken from 8 points: Sluice of Reservoir (S1), Center of Reservoir (S2), Bajerka River (S3), Shallow 1000 (S4), Backwater of Reservoir (S5), Shallow 500 (S6), Rybaczowka (S7), Water intake „Goczalkowice" (S8). The locations of the sampling sites are shown in Fig. 1. The area of the reservoir is 32 km^2 with an average depth of 5.3 m and a maximum depth of 16 m. Although it is a human creation, we can observe a wealth of wildlife associated with this ecosystem. In the water reservoir, fishing of bream, walleye, perch, carp, eel, and pike has developed. The lakeshore is a breeding area for many bird species protected by law. Therefore both the reservoir and its surroundings were enrolled in the Nature 2000 program. Goczalkowice Reservoir is an artificial source of drinking water for the Silesian agglomeration, but it is threatened by the industry and agriculture of the region.

During collection of deposits from eight designated points in the reservoir, Global Positioning System (GPS) technology was used. The samples were taken in 5000 mL plastic containers. Large objects like stones (φ > 2 mm) were removed and the remaining material was dried in dryer at a temperature lower than 30ºC. After drying, the residue was ground and sieved through a sieve with a diameter of 2 mm. In order to homogenize the sediment samples, they were ground in a porcelain mortar. All assays were performed four times for each sediment sample and evaluated statistically.

2.2. Reagents

All reagents used in analysis of sediments were analytically pure: magnesium chloride, sodium acetate, hydroxylammonium chloride, acetic acid 99.5%, ammonium acetate, hydrogen peroxide 30%, nitric acid 65% (POCH, Gliwice, Poland) and perchloric acid 70% (Vebjenapharm Laborchemie, Weimar, Germany). High purity double-distilled and deionized water for dilution was obtained using a Millipore Milli-Q system. All solutions of multielemental standards (Merck, Darmstadt, Germany) were prepared daily in water obtained from the Milli-Q

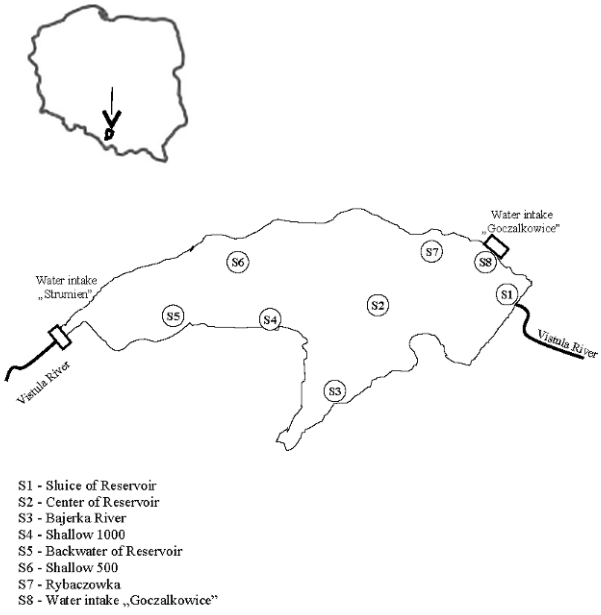

Figure 1. Location of the sampling sites in the area of Goczalkowice Reservoir.

System (Millipore, USA) and they were used for the calibration. Ultrapure concentrated nitric acid 65% (Merck, Darmstadt, Germany) was used for adjusting acidity of the standard solutions. All standards, reagent solutions and samples were kept in polyethylene containers. The plastic and glassware were cleaned by soaking in dilute HNO_3 (1+9) and they were rinsed with deionized water prior to use.

2.3. Apparatus

The concentration of elements, such as Ca, Ba, Sr, Mn, Zn, Cu, Ni, Co, Fe, Al, Cr, Ti, V, Pb and P was determined using optical emission spectrometry with excitation by argon inductively coupled plasma (SPECTROFLAME ICP-OES, Spectro Analytical Instruments, Germany). The optimum measurement conditions are shown in Table 1. The wavelengths and detection limits of the analyzed elements are shown in Table 2.

2.4. Sequential extraction

Sequential extraction was performed based on the five-stage procedure proposed by Tessier with a modified residual fraction. The extractants were prepared according to the following procedure.

Solution I (magnesium chloride, 1 M): Magnesium chloride (203.3 g) was dissolved in deionized water and made up to 1000 mL with deionized water.

Solution II (sodium acetate, 1 M): Sodium acetate (82 g) was dissolved in 900 mL of deionized water. The solution was acidified to pH 5.0 with acetic acid 99.5% and made up to 1000 mL with deionized water.

Solution III (hydroxylammonium chloride 0.04 M in acetic acid 25%): Hydroxylammonium chloride (2.78 g) was dissolved in acetic acid 25% and made up to 1000 mL with acetic acid.

Solution IV (ammonium acetate 3.2 M in nitric acid 20%): Ammonium acetate (246.4 g) was dissolved in 20% nitric acid and made up to 1000 mL with nitric acid. All assays were performed four times for each sediment sample and evaluated statistically.

The steps of the sequential extraction were as follows:

Step 1 (exchangeable fraction): 16 mL of 1 M $MgCl_2$, pH 7 (*solution I*) were added to 2 g of sample in a conical flask and shaken mechanically for one hour at room temperature. The extract was separated from the solid residue by centrifugation and the filtrate was transferred by decantation into a polyethylene container. The residue was washed by adding 16 mL of deionized water, shaken for 10 minutes on the shaker, centrifuged and decanted.

Step 2 (carbonates fraction): 16 mL of 1 M CH_3COONa in CH_3COOH, pH 5 (*solution II*) were added to the residue from Step 1 and shaken for five hours at room temperature. The supernatant solution was filtered off into a polyethylene container. The residue was washed in the same manner as described in Step 1.

Step 3 (oxides fraction): 40 mL of 0.04 M $NH_2OH{\cdot}HCl$ in CH_3COOH (*solution III*) were added to the residue from Step 2 and heated for five hours at 96ºC ± 2ºC. After five hours, the supernatant solution was filtered off into a volumetric flask and made up to 50 mL with

Table 1. Measurement conditions for ICP-OES.

Rf power, kW	1.1 kW
Frequency, MHz	27.12
Plasma torch	quartz
Plasma gas flow, L min^{-1}	14.0
Auxiliary gas flow, L min^{-1}	0.5
Nebulizer gas flow, L min^{-1}	1.0
Meinhard concentric glass nebulizer, bar	2.4
Misty Scott chamber	-
Sample uptake mL min^{-1}	1
Number of replicates	3
Read delay time, s	3
Scope of the monochromator, nm	165-460
Holographic grid, grooves mm^{-1}	2400
Reverse grid dispersion in the first row of the spectrum, nm mm^{-1}	0.55
Height above the induction coil, mm	11
Integration time, s	3

deionized water. Rinsing of residue was carried out in the same manner as described in Step 1.

Step 4 (organic fraction): 4 mL of 0.02 M HNO_3 and 10 mL of 30% H_2O_2 were added to the residue from Step 3 and heated for five hours at 85ºC ± 2ºC. After an additional two hours, 6 mL of 30% H_2O_2 were added and heating was continued. Finally, 10 mL of 3.2 M CH_3COONH_4 in 20% HNO_3 (*solution IV*) were added to the cold mixture and it was shaken for 30 minutes at room temperature. The supernatant solution was filtered off into a volumetric flask with a capacity of 25 mL. If the volume was less than 25 mL, it was filled up to 25 mL with deionized water. If the volume was larger, it was cast and measured, so that the final volume was 25 mL. Rinsing of residue was carried out in the same manner as described in Step 1.

Step 5 (residual fraction): the residue from Step 4 was dried and weighed into 0.5 g portions of sediments, which were digested in mineralization flasks using a mixture of 1 mL of 65% HNO_3, 3 mL of 70% $HClO_4$, and 4 mL of redistilled water. The flasks were placed in M-9 mineralizer at 150ºC and heated for 22 hours. After cooling, the solutions were quantitatively transferred into

Table 2. Wavelength, limit of detection of elements.

Element	Wavelength [nm]	Limit of detection in solution [$\mu g\ mL^{-1}$]	Limit of detection in the sample of sediments f 1,2 [$\mu g\ g^{-1}$] m=2 g V=16 mL	f 3 [$\mu g\ g^{-1}$] m=2 g V=50 mL	f 4 [$\mu g\ g^{-1}$] m=2 g V=25 mL	f 5,t [$\mu g\ g^{-1}$] m=0,5 g V=25 mL
Ca	445.478	1.24	9.93	31.0	15.5	62.0
Ba	455.403	0.002	0.014	0.043	0.022	0.086
Sr	407.771	0.001	0.007	0.022	0.011	0.044
Mn	293.930	0.012	0.100	0.312	0.156	0.623
Zn	213.856	0.017	0.134	0.420	0.210	0.839
Cu	324.754	0.023	0.183	0.572	0.286	1.14
Ni	352.454	0.032	0.257	0.804	0.402	1.61
Co	228.616	0.012	0.097	0.302	0.151	0.603
Fe	252.258	0.449	3.59	11.2	5.61	22.4
Al	257.510	0.490	3.92	12.2	6.12	24.5
Cr	267.716	0.020	0.156	0.488	0.244	0.976
Ti	334.941	0.006	0.050	0.156	0.078	0.312
V	268.796	0.016	0.124	0.388	0.194	0.775
Pb	220.353	0.090	0.720	2.25	1.12	4.50
P	214.914	0.491	3.93	12.3	6.14	24.6

f 1-f 5 - fractions
t - the total content of elements

volumetric flasks and made up to 25 mL with deionized water. Then, the solutions with residue were filtered off to polyethylene containers.

The total content of elements: 0.5 g each of sediment was weighed on an analytical balance and digested in mineralization flasks using a mixture of 1 mL of 65% HNO_3, 3 mL of 70% $HClO_4$, and 4 mL of redistilled water. The remainder of the procedure was the same as described for the residual fraction (Step 5).

3. Results and discussion

3.1. Elements concentrations in sediments

Fifteen elements were determined in all bottom sediment samples. Table 3 shows the element contents in different bottom sediments from various sampling sites. The total uncertainty of the signs ranged from 1.5% for Mn to 19.4% for Ti and V.

Analyzing the results obtained by the sequential extraction procedure following the Tessier method, it was noted that the highest amount of calcium occurs in the exchangeable fraction, in the concentration range of 1169 μg g^{-1} (S8) to 2888 μg g^{-1} (S2). The percentage of Ca in the exchangeable fraction in relation to the other fractions was 51.8-72.0%. Therefore, Ca was also weakly associated in this fraction and most easily removable. Calcium was also present in other fractions, of which a greater concentration was present in the residual fraction: from 116 μg g^{-1} (S5) to 732 μg g^{-1} (S4). The largest percentage of Ca in the residual fraction,27.3% in relation to the other fractions, was present at the sampling site S4. The lowest amount of Ca was present in the fraction associated with organic matter.

Barium was found in varying amounts in all fractions. Larger amounts were recorded in the following fractions: exchangeable, associated with carbonates and associated with Fe and Mn oxides and residual, in particular for sampling point S2. The percentages of Ba in the exchangeable and residual fractions were 20.1% - 26.8% and 16.4% - 35.7% in relation to the remaining fractions, respectively. The lowest concentration for Ba was present in the fraction associated with organic matter.

Strontium was present in all fractions of the sequential extraction. The largest amount of the metal was found in the residual fraction: from 8.31 μg g^{-1} (S8) to 18.3 μg g^{-1} (S2). The exception in this fraction was point S5, for which the concentration of Sr was only 3.44 μg g^{-1}. A significant amount of Sr was also present in the exchangeable fraction: from 5.49 μg g^{-1} (S1) to 13.9 μg g^{-1} (S2). The percentages of Sr in the exchangeable and residual fractions were 22.4% - 40.4% and 19.7% - 52.0% in relation to the remaining fractions, respectively. However, its concentration was lowest in the fraction associated with carbonates and organic matter.

Manganese was found in all fractions. Its largest amount occurs in the fraction associated with Fe and Mn oxides: from 87.3 μg g^{-1} (S5) to 656 μg g^{-1} (S2); the percentage of Mn in this fraction was 38.3% - 67.8%. The lowest concentration of Mn was present in the fraction associated with organic matter.

The presence of zinc was observed in all fractions of the sequential extraction by the Tessier method. The highest concentration was present in the fraction associated with Fe and Mn oxides (ranging from 42.0 μg g^{-1} (S8) to 123 μg g^{-1} (S2)) and in the residual fraction in concentrations of 14.5 μg g^{-1} (S5) to 83.0 μg g^{-1} (S2). The percentages of Zn in the fraction associated with Fe and Mn oxides and residual fractions were 44.3% - 57.3% and 14.1% - 34.6% in relation to the remaining fractions, respectively. The smallest amount of Zn was present in the fraction associated with organic matter.

Copper was found in all fractions. The largest amount of the metal occurred in the residual fraction: from 4.80 μg g^{-1} (S5) to 18.7 μg g^{-1} (S2), wherein the percentage of Cu in this fraction was 32.8% - 63.2%. The smallest concentration of Cu was obtained in the exchangeable fraction.

Nickel was present in all fractions of the sequential extraction. A large amount of this metal occurred in the fraction associated with Fe and Mn oxides: from 1.88 μg g^{-1} (S8) to 11.8 μg g^{-1} (S2); and in the residual fraction: from 3.61 μg g^{-1} (S3) to 16.0 μg g^{-1} (S2). The percentages of Ni in both fractions were 13.7% - 54.8% and 20.6% - 65.1% in relation to the remaining fractions, respectively. The lowest concentration of this element was present in the exchangeable fraction.

Large amounts of cobalt were present in the fraction associated with Fe and Mn oxides: from 2.28 μg g^{-1} (S4) to 6.54 μg g^{-1} (S2) and in the residual fraction: from 0.962 μg g^{-1} (S5) to 5.62 μg g^{-1} (S2). The percentages of Co in the fraction associated with Fe and Mn oxides and the residual fractions were 43.2% - 62.1% and 17.2% - 41.9% in relation to the remaining fractions, respectively. The lowest concentrations of Co were observed in the exchangeable fraction and in the fraction associated with carbonates.

No iron above the detection limit was found in the exchangeable fraction for all sampling sites. However, high levels of iron ranging from 6669 μg g^{-1} (S8) to 17700 μg g^{-1} (S2) were present in the fraction associated with Fe and Mn oxides and from 6506 μg g^{-1}

Table 3. Concentration of elements in all bottom sediment samples [$\mu g\ g^{-1}$].

Element	S1	S2	S3	S4	S5	S6	S7	S8
Ca [$\mu g\ g^{-1}$]								
Fraction 1	1216	2888	1991	1389	1628	1710	1676	1169
Fraction 2	191	350	265	206	198	232	193	161
Fraction 3	259	399	265	235	191	267	235	188
Fraction 4	129	312	118	121	128	234	145	76.0
Residue	418	472	713	732	116	356	504	389
Four step+residue	2213	4421	3352	2683	2261	2799	2753	1983
Total	2038	4094	3026	2475	1662	2547	2577	1925
Recovery (%)	109	108	111	108	136	110	107	103
Ba [$\mu g\ g^{-1}$]								
Fraction 1	25.4	51.6	24.4	18.9	19.6	26.4	36.0	22.3
Fraction 2	13.7	33.2	17.1	13.8	16.8	20.4	18.7	12.8
Fraction 3	24.6	59.7	29.6	23.5	32.4	29.7	30.8	21.3
Fraction 4	4.35	26.4	5.90	4.30	5.44	6.86	6.13	3.46
Residue	37.6	85.8	32.5	32.8	14.5	40.3	42.8	27.7
Four step+residue	106	257	110	93.3	88.7	124	134	87.6
Total	108	236	99.7	96.2	91.1	120	134	88.5
Recovery (%)	98	109	110	97	98	103	100	99
Sr [$\mu g\ g^{-1}$]								
Fraction 1	5.49	13.9	8.13	5.60	7.04	7.39	7.79	5.72
Fraction 2	1.36	2.26	1.79	1.18	1.54	1.72	1.22	1.11
Fraction 3	3.57	5.25	3.82	3.49	3.90	3.92	3.50	2.81
Fraction 4	1.35	2.53	1.31	1.31	1.52	1.93	1.39	0.858
Residue	12.7	18.3	12.4	11.2	3.44	8.35	12.7	8.31
Four step+residue	24.5	42.2	27.4	22.8	17.4	23.3	26.6	18.8
Total	22.9	38.9	24.2	21.7	16.4	21.5	24.1	17.5
Recovery (%)	107	109	113	105	106	109	110	108
Mn [$\mu g\ g^{-1}$]								
Fraction 1	63.0	71.4	65.4	97.2	33.7	50.8	134	63.6
Fraction 2	61.1	119	51.4	35.4	35.4	64.6	80.2	55.4
Fraction 3	351	656	277	108	87.3	293	258	305
Fraction 4	7.87	41.1	7.95	4.78	2.39	11.8	11.5	6.27
Residue	35.0	103	37.8	36.6	15.9	61.4	59.8	34.5
Four step+residue	518	991	440	282	175	482	544	465
Total	446	806	385	298	151	458	540	423
Recovery (%)	116	123	114	95	115	105	101	110
Zn [$\mu g\ g^{-1}$]								
Fraction 1	7.05	7.84	14.9	16.0	18.2	7.14	7.53	4.69
Fraction 2	10.4	15.1	11.8	7.35	8.31	9.28	8.40	7.33
Fraction 3	50.2	123	57.1	44.8	59.0	72.7	60.3	42.0
Fraction 4	5.52	19.8	5.59	4.54	3.02	8.04	7.30	3.36

Continued **Table 3.** Concentration of elements in all bottom sediment samples [$\mu g\ g^{-1}$].

Element	S1	S2	S3	S4	S5	S6	S7	S8
Residue	24.4	83.0	24.9	28.5	14.5	50.6	44.2	22.9
Four step+residue	97.6	249	114	101	103	148	128	80.3
Total	81.5	208	100	95.3	105	147	119	74.9
Recovery (%)	120	120	114	106	98	101	108	107
Cu [$\mu g\ g^{-1}$]								
Fraction 1	0.637	0.785	0.785	0.806	0.857	0.778	0.791	0.553
Fraction 2	1.83	2.09	1.35	1.94	1.76	2.16	1.57	1.51
Fraction 3	2.77	1.39	0.854	2.69	1.39	3.60	2.02	1.88
Fraction 4	4.74	12.1	5.86	5.56	5.82	6.01	6.14	3.30
Residue	8.22	18.7	15.2	11.2	4.80	13.1	11.6	8.18
Four step+residue	18.2	35.0	24.0	22.2	14.6	25.6	22.1	15.4
Total	12.5	29.9	19.4	17.0	15.7	20.1	16.2	13.0
Recovery (%)	146	117	124	130	93	128	137	118
Ni [$\mu g\ g^{-1}$]								
Fraction 1	1.02	1.80	1.45	1.35	2.35	1.43	1.46	0.711
Fraction 2	1.29	1.88	1.28	1.12	1.53	2.28	0.791	0.668
Fraction 3	8.61	11.8	9.12	10.1	7.54	4.06	2.82	1.88
Fraction 4	1.93	2.80	2.07	1.53	1.29	4.05	2.13	0.862
Residue	8.46	16.0	3.61	4.36	9.88	15.8	13.4	5.91
Four step+residue	21.3	34.3	17.5	18.5	22.6	27.6	20.6	10.0
Total	12.1	22.7	9.40	20.3	22.6	24.9	19.4	8.42
Recovery (%)	177	151	187	91	100	111	106	119
Co [$\mu g\ g^{-1}$]								
Fraction 1	0.140	0.130	0.155	0.462	0.40	<0.097	0.262	<0.097
Fraction 2	<0.097	0.207	0.123	0.257	0.422	0.237	0.225	<0.097
Fraction 3	3.88	6.54	2.63	2.28	3.48	4.60	3.81	2.84
Fraction 4	0.328	0.929	0.389	0.341	0.346	0.533	0.375	0.286
Residue	1.96	5.62	2.06	1.94	0.962	3.68	3.32	1.85
Four step+residue	6.41	13.4	5.36	5.28	5.61	9.15	7.99	5.17
Total	5.86	11.9	4.94	5.05	4.84	9.66	7.76	4.78
Recovery (%)	109	113	108	105	116	95	103	108
Fe [$\mu g\ g^{-1}$]								
Fraction 1	<3.59	<3.59	<3.59	<3.59	<3.59	<3.59	<3.59	<3.59
Fraction 2	268	360	216	243	384	259	265	172
Fraction 3	8948	17700	8161	7793	12709	10433	9347	6669
Fraction 4	587	2608	871	674	882	905	853	357
Residue	9303	28099	7365	7194	6506	15981	15031	7728
Four step+residue	19110	48771	16617	15908	20485	27582	25500	14930
Total	17493	43038	15415	15230	22855	27595	23432	14535
Recovery (%)	109	113	108	104	90	100	109	103

Continued **Table 3.** Concentration of elements in all bottom sediment samples [$\mu g\ g^{-1}$].

Element	S1	S2	S3	S4	S5	S6	S7	S8
Al [$\mu g\ g^{-1}$]								
Fraction 1	<3.92	<3.92	<3.92	11.6	9.02	<3.92	9.11	<3.92
Fraction 2	21.1	25.9	18.1	24.1	27.8	26.5	22.1	15.8
Fraction 3	1349	1190	1194	1184	999	1311	1197	1113
Fraction 4	1054	2598	1254	995	719	1273	1426	706
Residue	15456	37686	13613	13223	9148	19005	20695	13137
Four step+residue	17884	41504	16083	15438	10903	21619	23349	14976
Total	18639	40060	15970	15749	12142	22200	21572	14738
Recovery (%)	96	104	101	98	90	97	108	102
Cr [$\mu g\ g^{-1}$]								
Fraction 1	<0.156	<0.156	<0.156	<0.156	<0.156	<0.156	<0.156	<0.156
Fraction 2	0.224	0.347	0.663	0.279	0.249	<0.156	<0.156	<0.156
Fraction 3	4.88	10.8	4.00	5.86	4.04	8.36	4.31	3.68
Fraction 4	3.21	7.82	7.05	6.59	2.62	3.32	3.87	2.06
Residue	25.6	63.8	23.5	26.6	13.8	34.6	29.4	19.5
Four step+residue	34.1	82.9	35.4	39.5	20.8	46.6	37.9	25.6
Total	29.4	82.3	28.0	34.0	27.8	42.0	40.6	23.5
Recovery (%)	116	101	126	116	75	111	93	109
Ti [$\mu g\ g^{-1}$]								
Fraction 1	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
Fraction 2	<0.050	0.068	<0.050	<0.050	<0.050	<0.050	0.075	<0.050
Fraction 3	0.398	0.221	0.334	0.340	0.167	0.290	0.298	0.377
Fraction 4	9.00	5.53	18.2	29.7	3.33	5.46	27.7	19.9
Residue	225	328	238	206	50.0	99.5	171	134
Four step+residue	235	334	257	236	53.6	105	199	154
Total	246	332	257	245	57.2	105	219	157
Recovery (%)	95	101	100	96	94	101	91	98
V [$\mu g\ g^{-1}$]								
Fraction 1	<0.124	<0.124	<0.124	<0.124	<0.124	<0.124	0.131	<0.124
Fraction 2	<0.124	<0.124	<0.124	<0.124	<0.124	<0.124	<0.124	<0.124
Fraction 3	4.65	8.60	3.03	3.55	3.28	8.02	9.79	6.81
Fraction 4	0.693	1.64	0.947	0.878	0.491	1.59	1.88	2.60
Residue	12.6	31.5	9.28	9.28	6.23	35.2	32.1	18.1
Four step+residue	18.2	42.0	13.5	14.0	10.2	45.1	44.0	27.8
Total	17.6	36.4	12.5	13.2	10.3	45.2	40.6	27.4
Recovery (%)	103	115	108	106	99	100	108	101
Pb [$\mu g\ g^{-1}$]								
Fraction 1	<0.720	<0.720	<0.720	0.845	<0.720	<0.720	<0.720	<0.720
Fraction 2	1.41	2.19	2.18	1.76	1.17	2.05	1.38	<0.720
Fraction 3	22.6	47.0	21.2	19.8	17.0	23.2	22.9	17.2
Fraction 4	<1.12	<1.12	<1.12	<1.12	<1.12	<1.12	<1.12	<1.12
Residue	15.3	42.2	12.7	13.1	5.3	25.1	22.7	13.6

Continued **Table 3.** Concentration of elements in all bottom sediment samples [$\mu g\ g^{-1}$].

Element	S1	S2	S3	S4	S5	S6	S7	S8
Four step+residue	41.2	93.2	38.0	36.6	25.3	52.2	48.8	33.4
Total	39.0	89.0	39.5	36.2	13.5	54.9	48.0	31.8
Recovery (%)	106	105	97	102	190	95	102	105
P [$\mu g\ g^{-1}$]								
Fraction 1	<3.93	<3.93	<3.93	<3.93	<3.93	<3.93	<3.93	<3.93
Fraction 2	11.4	9.43	8.49	7.50	5.83	4.40	10.8	9.49
Fraction 3	269	314	266	229	166	123	238	195
Fraction 4	191	729	263	233	155	275	322	144
Residue	168	506	164	156	84.7	269	260	175
Four step+residue	644	1562	705	629	416	675	835	527
Total	617	1405	645	589	397	733	781	529
Recovery (%)	104	111	109	107	105	92	107	100

(S5) to 28099 μg g^{-1} (S2) in the residual fraction. The percentages of Fe in both fractions were 36.3% - 62.1% and 31.8% - 59.0% in relation to the remaining fractions, respectively. This element was also present in other fractions.

The concentration of aluminum in the exchangeable fraction was below the detection limit at all sampling sites with the exception of points S4, S5, and S7. The metal was also present in other fractions. The amount of Al in the residual fraction was an order of magnitude higher than the ones in the fraction associated with Fe and Mn oxides and in the fraction associated with organic matter. It ranged from 9148 μg g^{-1} (S5) to 37686 μg g^{-1} (S2). The percentage of Al in the residual fraction in comparison with the other fractions was 83.9% - 90.8%.

The contents of chromium in the exchangeable fraction were below the limit of detection for all sampling sites, and this was also the case for the fraction associated with carbonates at sampling sites S6-S8. The concentration of Cr was highest in the residual fraction: from 13.8 μg g^{-1} (S5) to 63.8 μg g^{-1} (S2), wherein the percentage of Cr was 66.6% - 78.2% in relation to the remaining fractions. In the fraction associated with Fe and Mn oxides and in the fraction associated with organic matter, contents of Cr were an order of magnitude lower in comparison with the residual fraction.

The titanium amount in the exchangeable fraction was below the detection limit in all sampling sites, and this was also the case for the fraction associated with carbonates with the exception of points S2 and S7. The highest concentration of Ti was found in the residual fraction: from 50.0 μg g^{-1} (S5) to 328 μg g^{-1} (S2), while the percentage of Ti in this fraction in comparison with the other fractions was 85.9-98.3%.

The concentration of vanadium in the fraction associated with carbonates was below the detection limit for all sampling sites, and this was also the case for the exchangeable fraction (except at S7). The greatest concentration of the metal was found in the residual fraction: from 6.23 μg g^{-1} (S5) to 35.2 μg g^{-1} (S6), and in the fraction associated with Fe and Mn oxides: from 3.03 μg g^{-1} (S3) to 9.79 μg g^{-1} (S7). The percentages of V in the fraction associated with Fe and Mn oxides and in the residual fraction were 17.9-32.8% and 62.3-78.6% in relation to the remaining fractions, respectively.

The contents of lead in the fraction associated with organic matter and in the exchangeable fraction (with the exception of S4) were below the detection limit. The highest concentration of the metal was found in the fraction associated with Fe and Mn oxides: from 17.0 μg g^{-1} (S5) to 47.0 μg g^{-1} (S2) and in the residual fraction: from 5.3 μg g^{-1} (S5) to 42.2 μg g^{-1} (S2). The percentages of Pb in both fraction were 46.0-72.3% and 22.7-49.9% in relation to the other fractions, respectively.

The contents of phosphorus were below the limit of detection in the exchangeable fraction. Large amounts of this element were found in the fraction associated with Fe and Mn oxides: from 123 μg g^{-1} (S6) to 314 μg g^{-1} (S2); in the fraction associated with organic matter: from 144 μg g^{-1} (S8) to 729 μg g^{-1} (S2); as well as in the residual fraction: from 84.7 μg g^{-1} (S5) to 506 μg g^{-1} (S2). The percentages of P in these fractions were 18.3-42.1%, 27.6-46.8% and 20.6-40.1% in relation to the remaining fractions, respectively.

The highest total content of elements in the bottom sediments was observed for Ca, Ba, Sr, Mn, Zn, Cu, Co,

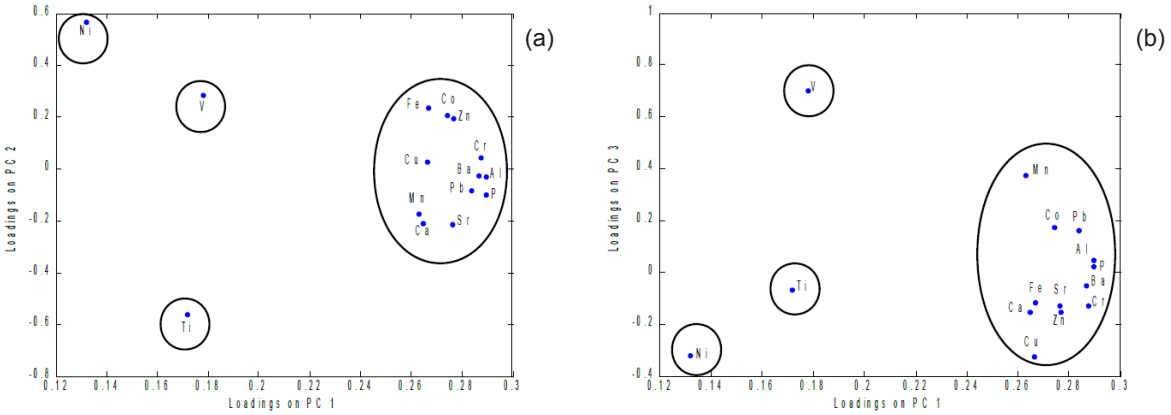

Figure 2. Loading plots – projection of elements on the plane spanned by: (a) PC 1 and PC 2, (b) PC 1 and PC 3.

Fe, Al, Cr, Ti, Pb, and P at sampling point S2. Ni and V are exceptions, and the highest concentration of these two metals was found at sampling point S6. The lowest total content of elements in the sediments was observed for Ca, Sr, Mn, Al, Ti, V, Pb, and P at point S5, and for Cu at S1, as well as for Ba, Zn, Ni, Co, Fe, Cr at S8.

3.2. Principal component analysis

Principal component analysis (PCA) [21-23] has been widely applied in data mining to investigate data structure. In PCA, new orthogonal variables (latent variables or principal components) are obtained by maximizing variance of the data. The number of the latent variables (factors) is much lower than the number of original variables, so that the data may be visualized in a low-dimensional PC space. Several algorithms may be used to perform PCA, such as, *e.g.* the singular value decomposition (SVD) approach [24] and the non-linear iterative partial least squares (NIPALS) algorithm [25]. In recent years, the so-called kernel PCA approach has gained a lot of attention in chemometrics, due to its computational efficiency [26]. PCA reveals similarities and differences between individual samples and the relationship among the measured parameters [27-29].

In this study, principal component analysis allowed us to find the relationship among all measured elements and bottom sediment samples. All analytical results were put together in one 8×15 matrix (samples×elements) and were autoscaled according to the equation:

$$x_{ij} = \frac{\left(x_{ij} - \overline{x}_j\right)}{s_j},$$

where $\overline{x}_j$ denote the mean of the j-th column, and s_j denote the standard deviation. Then, the singular value decomposition (SVD) algorithm was adopted. After calculating the cumulative percentage of the variance, it was possible to see the percentage of the variability, described by all principal components. The first principal component (PC1) describes about 78% of the total variance, the first two PCs – above 90.4% and the first three PCs – above 96.4% of the total variance. Subsequent factors explain less and less variability. Therefore, data analysis was carried out based on the first three main factors.

In order to examine the interactions between the analyzed elements, projections of weights of selected pairs of the main factors (PC 1 to PC 2 and PC 1 to PC 3) were subsequently drawn (Fig. 2). Elements characterized by high absolute values of weights for the main component contribute substantially to the creation of this factor. Analyzing the projection of elements on the plane spanned by PC 1 and PC 2, one may conclude that the variables that make the greatest contribution to the creation of the first principal component (PC 1) are the contents of Al, P, Cr, Ba, Pb, Sr, Zn, and Co. The greatest contribution in the second principal component (PC 2) include the contents of Ni and Ti. In the formation of the third factor (PC 3), the content of V and the contents of Ni and Cu have the greatest contribution. Additionally, the lack of correlation between the contents of Ni, V and Ti may be seen.

The projection of the main components scores (PC 1 to PC 2 and PC 1 to PC 3) has also been plotted (Fig. 3). This projection shows the relations between all the analyzed bottom sediment samples. When two data points on the plot are closer together, they are more similar to each other. The differences are larger when the distance increases [30].

The score plots of PC1 to PC2 and PC1 to PC3 show that the bottom sediment S2 differs significantly from the other bottom sediments with respect to the first factor, which includes the contents of elements such as Al, P, Cr, Ba, Pb, Sr, Zn, and Co. Sediment collection point

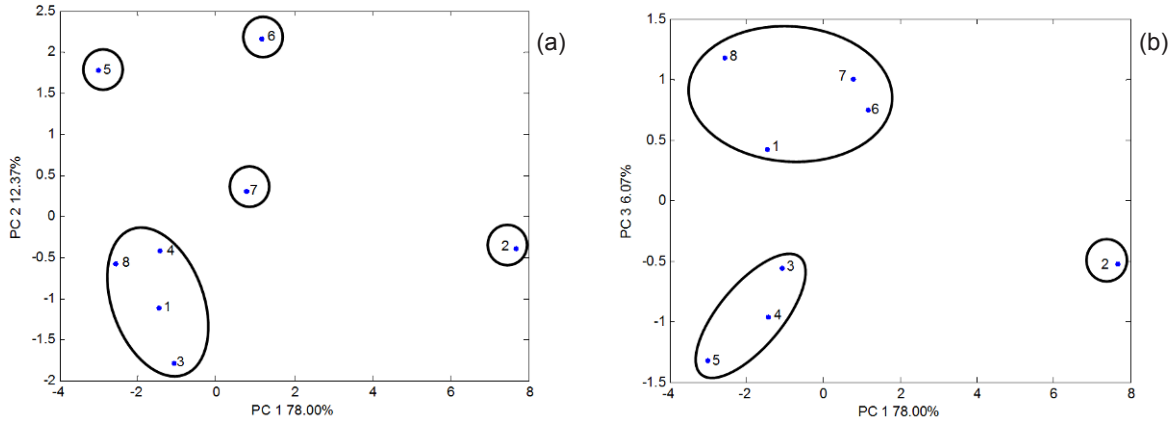

Figure 3. PCA score plots – projection of bottom sediment samples on the plane spanned by: (a) PC 1 and PC 2, (b) PC 1 and PC 3.

S2 is located in an oxbow of the Vistula River, which leads to high concentrations of most of the analyzed elements in the sediment. The second factor indicates that bottom sediments S5 and S6 are different from the rest with regard to the contents of nickel and titanium. However, the third factor indicates the breakdown of bottom sediments into two groups which vary in terms of the vanadium content.

3.3. Cluster analysis

Hierarchical clustering analysis [31-36] may be applied to multidimensional data sets, in order to study (dis) similarities of objects in the variable space, or similarities of variables in the object space. Any agglomerative hierarchical clustering method is characterized by the similarity measure used, and the way resulting subclusters are merged (linked). This method usually produces a dendrogram, or other types of tree diagrams, as the final output. On the x-axis of the dendrogram, the indices of clustered objects (or variables) are displayed, whereas the y-axis represents the corresponding linkage distances (or an adequate measure of similarity) between the two objects or clusters which are merged.

The results of the cluster analysis are based on the Euclidean distance as a measure of similarity between the individual samples (variables) and the 'Ward' linkage algorithm. Dendrograms depict the degree of similarity between the individual samples (Fig. 4), and between variables (Fig. 5).

Fig. 4 shows that there are two clearly distinct groups. The first group contains samples S1, S3, S4, S8, and the second group contains samples S6 and S7. Samples S2 and S5 have characteristics very different from the rest. Bottom sediment from sampling site S2 differs from the remaining samples, in that it has the highest content of the elements. This is caused by the fact that this point corresponds to the old river bed of the Vistula. Fig. 5 shows that elements are split into three groups: the first group contains Al, P, Ba, Cr, Mn, and Pb; the second group contains Ca, Sr, and Cu; and third group contains Fe, Zn, and Co. Elements such as Ti, Ni, and V have characteristics very different from the rest.

3.4. Software

All chemometric calculations were performed on a PC equipped with an Intel Core i5 M 520 and a 2.40 GHZ processor with 4 GB RAM using MATLAB (version R2012a) running under Windows 7 Professional (64-bit system). All figures were prepared in Matlab 2012a.

3.5. Environmental implications

To study heavy metal retention in bottom sediments, the contamination factor, degree of contamination of elements, metal pollution index and risk assessment code in Goczalkowice Reservoir samples were calculated.

3.5.1. Contamination factor and degree of contamination

The contamination factor (C_f) is used to evaluate the degree of contamination of the sediment based on the current content of an element relative to its content from pre-industrial times. C_f is determined using the formula $C_f = C/Cn$, where C is the arithmetic mean concentration of the element in bottom sediments and Cn is the concentration of the element from the pre-industrial period, in this case the geochemical background (Ba-50 mg kg^{-1}, Zn-73 mg kg^{-1}, Cu-7 mg kg^{-1}, Ni-5 mg kg^{-1}, Co-3 mg kg^{-1}, Cr-6 mg kg^{-1}, Pb-15 mg kg^{-1}) [37].

On the basis of the values of C_f, it is possible to allocate the sediment to one of four categories of contamination. A contamination factor $C_f < 1$ refers to low contamination, $1 \leq C_f < 3$ means moderate contamination, $3 \leq C_f < 6$ indicates considerable contamination, $C_f \geq 6$ means very high contamination.

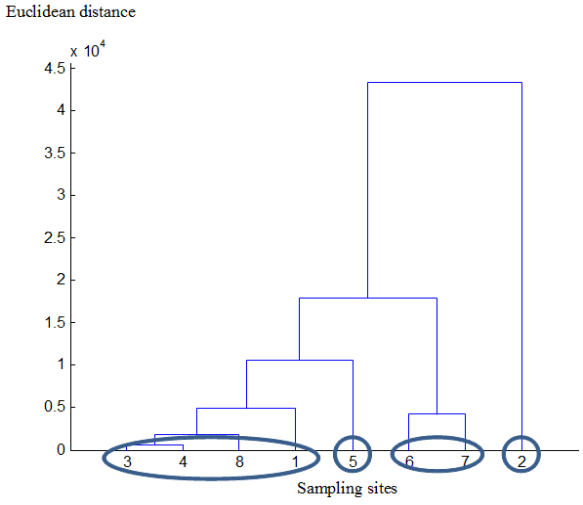

Figure 4. Diagram of hierarchical clustering analysis for all bottom sediment samples.

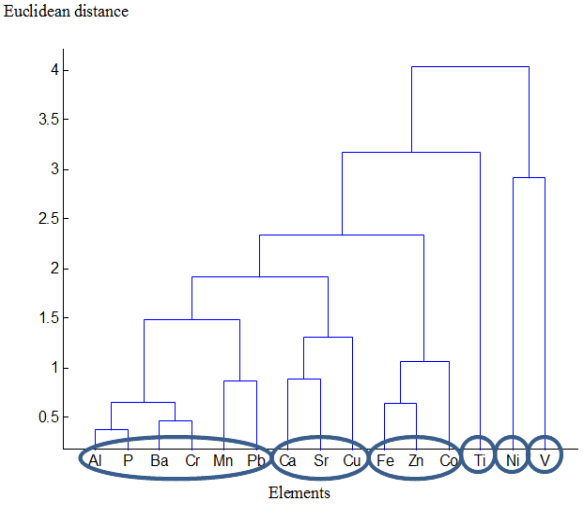

Figure 5. Diagram of hierarchical clustering analysis for the elements studied.

Summing up the contamination factors for all the analyzed elements, we can obtain a geochemical indicator called the degree of contamination (C_{deg}). On the basis of the values of C_{deg}, it is possible to allocate the studied area (Goczalkowice Reservoir) to one of four categories of contamination: $C_{deg} < 8$ low contamination, $8 \leq C_{deg} < 16$ moderate contamination, $16 \leq C_{deg} < 32$ considerable contamination, $C_{deg} \geq 32$ very high contamination indicating serious anthropogenic pollution [38].

Fig. 6 shows the estimated contamination factors of Ba, Zn, Cu, Ni, Co, Cr, Pb in the samples at all sampling sites. The calculated factors in sediments show the highest C_f and the ability of Cr to be released from sampling sites S2, S6, and S7, whereas the values for S1, S3-S5, and S8 show considerable contamination. The residual concentration of any heavy metal is considered a non-mobile fraction and it is an important part in influencing the mobility of the heavy metal. The effect of Cr in high concentration and with high mobility potential shows the increased possible risk of emission of this metal to the environment. Considerable contamination factors were obtained also for Ba at S2, Cu at S2, Ni at S2 and S4-S7, Co at S2 and S6 or Pb at S2 and S6-S7, while the lowest value was found only for Pb in sediment from sampling site S5. Other heavy metals show a moderate value of contamination factors calculated for the rest of the sediments (Table 4).

The degree of contamination (C_{deg}) for seven selected heavy metals reaches a value of 173.7, so it can be concluded that the area of Goczalkowice Reservoir, as a whole, is characterized by a very high contamination (Table 4).

3.5.2. Metal pollution index

The metal contents in bottom sediments from Goczalkowice Reservoir were compared using the metal pollution index (MPI). The MPI was calculated using the following formula:

$MPI = (M_1 \times M_2 \times M_3 \times \cdots \times M_n)^{1/n}$, where M_n is the concentration of metal n expressed in mg kg^{-1}. In this case the number of metals n was 7. When MPI > 1, the sediment ecosystem is considered to be polluted, and when MPI < 1, it is regarded as unpolluted [13,15]. The metal pollution index for the investigated sampling sites is shown in Table 4. Sampling sites S1 to S8 must be classified as considerable contamination areas, where MPI > 1.

3.5.3. Risk assessment code

Metals are bound to various sediment fractions, with the binding strength determining their bioavailability and the risk associated with their presence in aquatic ecosystems. In order to assess the potential risks associated with the presence of heavy metals in the first sediment fraction (exchangeable), the risk assessment code (RAC) is evaluated. The RAC coefficient is the percentage content of heavy metals in the first fraction (% F1) in relation to the sum of these metals in the individual fractions (exchangeable fraction, carbonates fraction, oxides fraction, organic fraction and residual fraction). This indicates that the metals are weakly bound to the solid phase. From here, the metals pose a greater hazard to the aquatic environment due to their greater potential. This classification is <1% (no risk), 1-10% (low risk), 11-30% (medium risk), 31-50% (high risk) and >50% (very high risk) [13,14,28,39-41].

Table 5 shows the results of the comparison of RAC values for elements and all sampling sites. In general, all studied sediments pose no risk to the aquatic

Table 4. Comparison of contamination factor (C_f), degree of contamination (C_{deg}) and metal pollution index (MPI) of sediments collected from Goczalkowice Reservoir.

Sampling sites	C_f Element							C_{deg}	MPI
	Ba	Zn	Cu	Ni	Co	Cr	Pb		
S1	2.17	1.12	1.78	2.41	1.95	4.90	2.60	16.93	2.212
S2	4.72	2.85	4.28	4.53	3.96	13.71	5.93	39.99	5.052
S3	1.99	1.37	2.77	1.88	1.65	4.67	2.63	16.96	2.245
S4	1.92	1.31	2.43	4.05	1.68	5.66	2.42	19.48	2.475
S5	1.82	1.44	2.24	4.52	1.61	4.63	0.90	17.16	2.097
S6	2.40	2.01	2.88	4.98	3.22	6.99	3.66	26.13	3.440
S7	2.68	1.63	2.31	3.88	2.59	6.77	3.20	23.04	3.002
S8	1.77	1.03	1.86	1.68	1.59	3.92	2.12	13.97	1.854

Table 5. Comparison of RAC values for elements and all sampling sites.

Element	Sampling sites							
	S1	S2	S3	S4	S5	S6	S7	S8
Ca	vH	vH	vH	vH	vH	vH	vH	vH
Ba	M	M	M	M	M	M	M	M
Sr	M	H	M	M	H	H	M	M
Mn	M	L	M	H	M	L	M	M
Zn	L	L	M	M	M	L	L	L
Cu	L	L	L	L	L	L	L	L
Ni	L	L	L	L	L	L	L	L
Co	L	nR	L	L	L	nR	L	nR
Fe	nR	nR	nR	nR	nR	nR	nR	nR
Al	nR	nR	nR	nR	nR	nR	nR	nR
Cr	nR	nR	nR	nR	nR	nR	nR	nR
Ti	nR	nR	nR	nR	nR	nR	nR	nR
V	nR	nR	nR	nR	nR	nR	nR	nR
Pb	nR	nR	nR	L	nR	nR	nR	nR
P	nR	nR	nR	nR	nR	nR	nR	nR

nR - no risk, L - low risk, M - medium risk, H - high risk, vH - very high risk

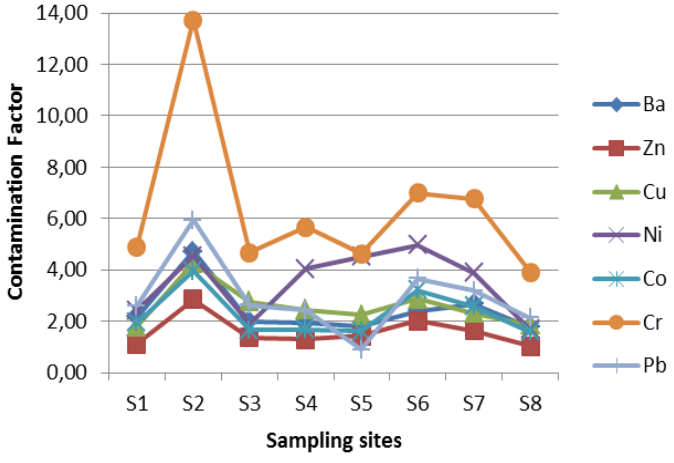

Figure 6. Estimated contamination factor of each metal in the samples at all stations.

environment only for elements such as Fe, Al, Cr, Ti, V, P, Pb (except at S4) and Co at S2, S6 and S8. The sediments show low risk for Cu, Ni, Co and Zn (except at S3-S5), and Mn at S2 and S6 with RAC values less than 11%, so there is no significant metal mobility for these elements. Medium risk is indicated for Ba, Sr (except at S2, S5, S6), Mn (except at S4) and Zn, which may be noticeable in the near future. Sr at S2, S5, S6, and Mn at S4 show high risk for sediment samples. Therefore, a significant remediation must be applied, especially for Sr and Mn emission as soon as possible. Among all samples, only Ca is an element of very high risk, but it is not dangerous to the environment.

4. Conclusions

The results of this study show clear evidence of sediment contamination by heavy metals in Goczalkowice Reservoir. Due to the fact that Goczalkowice Reservoir is an important part of the water supply system of the Upper Silesia and a natural habitat for fish and waterfowl, the problem of pollution of these waters with heavy metals is of great importance in the region. Contamination of sediments with heavy metals depends on the location. PCA confirmed the conclusions drawn from dendrogram analysis. The highest concentration for most elements of the total content in the bottom sediment is found at sampling site S2, where high accumulation is found, which is related to the fact that the Vistula River bed runs through this site. Ni and V are exceptions, and the highest concentration of these two metals is found at S6. The lowest total content of elements in the sediments is observed at sampling points S5, S1, and S8.

To study heavy metal retention in bottom sediments, the contamination factor, degree of contamination of elements, metal pollution index and risk assessment code were used. The calculated factors in sediments showed the highest contamination factor and the ability of chromium to be released from sampling sites S2, S6, and S7, whereas the values for S1, S3-S5, and S8 pointed to considerable contamination. The high content of Cr may be derived from natural geological contamination. The degree of contamination showed that the area of Goczalkowice Reservoir, as a whole, is characterized by very high contamination. The metal pollution index indicated that sampling sites from S1 to S8 must be classified as considerable contamination areas. The sediments indicated low risk for Cu, Ni, Co and Zn (except at S3-S5), and Mn at S2 and S6, but medium risk is shown for Ba, Sr (except at S2, S5, S6), Mn (except at S4) and Zn. Strontium at S2, S5, S6, and manganese at S4 showed high risk for sediment samples, so a significant remediation must be applied, especially for Sr and Mn emission.

The highest content of individual metals in sediments is mainly associated with anthropogenic sources located in the catchment of the reservoir, such as run-off from areas used for agriculture and industry or ponds for fish farming. Municipal wastewater and agricultural run-off enter the reservoir primarily through pumping stations of drainage areas south and west of the lake basin. However, pollution from fish farms is introduced mainly by the Vistula River and Bajerka River, and industrial wastewaters are introduced into the reservoir primarily with water from the Vistula River, which also has a significant share of the pollution load from municipal wastewater. The content of heavy metals in the sediments indicates a serious toxicological threat for benthic organisms. However, due to the fact that most of the sludge is retained in the pumping stations before discharge into Goczalkowice Reservoir, they are not a direct threat to this water reservoir. But only a part of the load of heavy metals is accumulated in sediments from the pumping station. The exceptions are iron and manganese, the presence of which is a result of both industrial pollution and enrichment of surface water as a result of leaching from the peat bog and the contact of surface water with artesian water, which feed the reservoir. In the case of copper, the increase in the amount of metal is associated with the introduction of this element into the water in the past to destroy cyanobacteria. In addition, the toxicity of copper increases in the presence of zinc, which occurs in Goczalkowice Reservoir.

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