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

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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 Goczałkowice 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
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 km² 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 30°C. 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, hydroxyammonium 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.
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\textsubscript{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\textsubscript{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\textsubscript{3}COONa in CH\textsubscript{3}COOH, pH 5 (solution II) were added to the residue from Step 1 and shaken for five hours at room temperature. The supernatant solution 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 3** (oxides fraction): 40 mL of 0.04 M NH\textsubscript{4}OH - HCl in CH\textsubscript{3}COOH (solution III) were added to the residue from Step 2 and heated for five hours at 96°C ± 2°C. After five hours, the supernatant solution was filtered off into a volumetric flask and made up to 50 mL with deionized water.
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**Step 4** (organic fraction): 4 mL of 0.02 M HNO₃ and 10 mL of 30% H₂O₂ were added to the residue from Step 3 and heated for five hours at 85°C ± 2°C. After an additional two hours, 6 mL of 30% H₂O₂ were added and heating was continued. Finally, 10 mL of 3.2 M CH₃COONH₄ in 20% HNO₃ (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% HNO₃, 3 mL of 70% HClO₄, and 4 mL of redistilled water. The flasks were placed in M-9 minilzer at 150°C and heated for 22 hours. After cooling, the solutions were quantitatively transferred into deionized water. Rinsing of residue was carried out in the same manner as described in Step 1.

**Table 1.** Measurement conditions for ICP-OES.

| Component                  | Specification          |
|---------------------------|------------------------|
| 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                      |

**Table 2.** Wavelength, limit of detection of elements.

| Element | Wavelength [nm] | in solution [µg mL⁻¹] f 1,2 | in the sample of sediments [µg g⁻¹] m=2 g V=16 mL f 3 | [µg g⁻¹] m=2 g V=50 mL f 4 | [µg g⁻¹] m=2 g V=25 mL f 5,t |
|---------|-----------------|------------------------------|---------------------------------|---------------------|--------------------------------|
| 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                           |

1 1-5 - fractions  
2 - 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% HNO₃, 3 mL of 70% HClO₄, 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 [µg g⁻¹].

| Element | S1    | S2    | S3    | S4    | S5    | S6    | S7    | S8    |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|
| Ca [µg 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 [µg g⁻¹] |       |       |       |       |       |       |       |       |
| Fraction 1 | 25.4  | 51.6  | 24.4  | 18.9  | 19.5  | 26.3  | 36.4  | 22.3  |
| Fraction 2 | 13.7  | 33.2  | 17.1  | 12.7  | 16.8  | 20.4  | 18.7  | 13.5  |
| Fraction 3 | 24.6  | 59.7  | 29.6  | 23.9  | 34.2  | 30.5  | 30.8  | 21.0  |
| Fraction 4 | 4.25  | 26.3  | 5.94  | 5.40  | 5.81  | 4.94  | 6.00  | 5.29  |
| Residue   | 37.6  | 85.8  | 32.4  | 24.5  | 33.4  | 40.3  | 42.8  | 27.4  |
| Four step+residue | 106   | 257   | 99.7  | 96.2  | 120   | 134   | 88.5  |       |
| Total     | 108   | 236   | 99.7  | 96.2  | 120   | 134   | 88.5  |       |
| Recovery (%) | 98    | 109   | 110   | 97    | 98    | 103   | 100   | 99    |
| Sr [µg 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  | 1.93  | 1.39  | 0.858 |       |
| Residue   | 12.7  | 18.3  | 12.5  | 11.2  | 3.44  | 4.93  | 12.7  | 3.31  |
| 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 [µg g⁻¹] |       |       |       |       |       |       |       |       |
| Fraction 1 | 63.0  | 71.4  | 65.4  | 97.6  | 73.7  | 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   | 37.6  | 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   | 296   | 151   | 458   | 540   | 423   |
| Recovery (%) | 116   | 123   | 114   | 95    | 115   | 105   | 101   | 110   |
| Zn [µg 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  |
### Table 3. Concentration of elements in all bottom sediment samples [µg 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 [µg 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 [µg 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 [µg 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 [µg 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  | 2606 | 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 |
### Table 3. Concentration of elements in all bottom sediment samples [µg g⁻¹].

| Element | S1  | S2  | S3  | S4  | S5  | S6  | S7  | S8  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|
| Al [µg 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 | 18609 | 40060 | 15970 | 15429 | 2200 | 21572 | 14738 |      |
| Recovery (%) | 96 | 104 | 101 | 98 | 90 | 97 | 108 | 102 |
| Cr [µg 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 [µg 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 | 0.063 | 0.079 | 0.249 | <0.156 | <0.156 | <0.156 |
| 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 [µg g⁻¹] |     |     |     |     |     |     |     |     |
| Fraction 1 | <0.124 | <0.124 | <0.124 | <0.124 | <0.124 | <0.124 | <0.124 | <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 | 6.31 |
| 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 [µg 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.
(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); and the percentage of Ti in this fraction in comparison with the other fractions was 85.9-98.3%.

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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.

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

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:

\[ x_{ij} = \frac{(x_{ij} - \bar{x}_j)}{s_j}, \]

where \( \bar{x}_j \) 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 2. Loading plots – projection of elements on the plane spanned by: (a) PC 1 and PC 2, (b) PC 1 and PC 3.](image_url)
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 (Cf) 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. Cf is determined using the formula $C_f = C/C_n$, where C is the arithmetic mean concentration of the element in bottom sediments and $C_n$ 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.
Assessment of elemental contamination in the bottom sediments from a dam reservoir using a sequential extraction technique and chemometric analysis

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 $C_i$ 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 S9. 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:

$$\text{MPI} = \frac{M_1 \times M_2 \times M_3 \times \cdots \times M_n}{n},$$

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 environment.
Table 4. Comparison of contamination factor (C<sub>f</sub>), degree of contamination (C<sub>deg</sub>) and metal pollution index (MPI) of sediments collected from Goczałkowice Reservoir.

| Sampling sites | Ba   | Zn   | Cu   | Ni   | Co   | Cr   | Pb   | C<sub>f</sub> | C<sub>deg</sub> | MPI   |
|----------------|------|------|------|------|------|------|------|-------------|-------------|-------|
| 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 | 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  | M  | H  | M  | M  |
| Mn      | M  | L  | M  | H  | M  | L  | M  | M  |
| Zn      | L  | L  | L  | 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  | nR | 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.
Assessment of elemental contamination in the bottom sediments from a dam reservoir using a sequential extraction technique and chemometric analysis

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 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.

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References

[1] I. Bojakowska, T. Gliwicz, G. Sokolowska, Results of geochemical monitoring of bottom sediments from Poland between 1996-1997 (State Inspectorate for Environmental Protection, Environmental Monitoring Library, Warsaw, 1998) (in Polish)
[2] J. Zerbe, T. Sobczyński, J. Siepak, Ecology and Technology 15, 7 (1995) (in Polish)
[3] T. Sobczyński, J. Siepak, In: J. Siepak (Ed.),
Speciation analysis of metals in water and sediment samples (Adam Mickiewicz University Press, Poznan, 1998) 67 (in Polish)

[4] J. Zerbe, T. Sobczyński, H. Elbanowska, J. Siepak, Pol. J. Environ. Stud. 8, 331 (1999)

[5] D.J. McCauley, G.M. DeGraeve, T.K. Linton, Environ. Sci. Policy 3, 133 (2000)

[6] C.A. Atkinson, D.F. Jolley, S.L. Simpson, Chemosphere 69, 1428 (2007)

[7] J. Kwapulíński, D. Wiechula, In: L. Pawlowski, M.R. Dudzińska (Ed.), Chemistry in Environmental Protection (Lublin Polytechnic Press, Lublin, 1993) 142 (in Polish)

[8] M. Kersten, U. Förstner, In: A.M. Ure, C.M. Davidson (Ed.), Chemical Speciation in the Environment (Chapman & Hall, London, 1995) 234

[9] A. Hulanicki, In: J. Siepak (Ed.), Speciation analysis of metals in water and sediment samples (Adam Mickiewicz University Press, Poznan, 1998) 7 (in Polish)

[10] A. Tessier, P.G.C. Cambell, M. Bisson, Anal. Chem. 51, 844 (1979)

[11] J.R. Bacon, Ch.M. Davidson, Analyst 133, 25 (2008)

[12] C.R.M. Rao, A. Sahuquillo, J.F. Lopez Sanchez, Water Air Soil Pollut. 189, 291 (2008)

[13] M.S. Masoud, T.O. Said, G. El Zokm, M.A. Shreadah, AJBAS 6, 44 (2012)

[14] C.K. Jain, Water Res. 38, 569 (2004)

[15] A.N.M. Pappoe, E.K.A. Afrifa, F.A. Armah, IJAST 1, 37 (2011)

[16] V. Simeonov, L. Wolska, A. Kuczynska, J. Gurwin, S. Tsakovski, M. Protasowicki, J. Namiesnik, TrAC 26, 323 (2007)

[17] H. Zeng, J. Wu, Int. J. Environ. Res. Public Health 10, 793 (2013)

[18] S. Tsakovski, B. Kudlak, V. Simeonov, L. Wolska, G. Garcia, J. Namiesnik, Anal. Chim. Acta 719, 16 (2012)

[19] S. Tsakovski, V. Simeonov, J. Chemomet. 25, 254 (2011)

[20] S. Tsakovski, B. Kudlak, V. Simeonov, L. Wolska, J. Namiesnik, Anal. Chim. Acta 631, 142 (2009)

[21] S. Wolf, K. Ebbensen, P. Geladi, Chemomet. Intell. Lab. Syst. 2, 37 (1987)

[22] I.T. Jollife, Principal Component Analysis (Springer-Verlag, New York, 2002)

[23] H. Abdi, L.J. Williams, Wiley Interdisciplinary Reviews: Computational Statistics 2, 433 (2010)

[24] B.M.G. Vandeginste, D.L. Massart, L.M.C. Buydens, S. de Jong, P.J. Lewi, J. Smeyers-Verbeke, Handbook of Chemometrics and Qualimetrics (Elsevier, Amsterdam, 1998) Part B

[25] W. Wu, D.L. Massart, S. de Jong, Chemomet. Intell. Lab. Syst. 36, 165 (1997)

[26] W. Wu, D.L. Massart, S. de Jong, Chemomet. Intell. Lab. Syst. 37, 271 (1997)

[27] K. Loska, D. Wiechula, Chemosphere 51, 723 (2003)

[28] E. de Andrade Passos, J.C. Alves, I.S. dos Santos, J. do Patrocínio H. Alves, C.A.B. Garcia, A.C. Spinola Costa, Microchem. J. 96, 50 (2010)

[29] W. Sun, L. Sang, B. Jiang, J. Soil Sediment 12, 1649 (2012)

[30] I. Stanimirova, M. Polowniak, R. Skorek, A. Kita, E. John, F. Buhl, B. Walczak, Talanta 74, 153 (2007)

[31] D.L. Massart, L. Kaufman, The Interpretation of Analytical Data by the Use of Cluster Analysis (Wiley, New York, 1983)

[32] W. Vogt, D. Nagel, H. Sator, Cluster Analysis in Clinical Chemistry; A Model (Wiley, New York, 1987)

[33] J. Morillo, J. Usero, I. Gracia, Environ. Int. 28, 263 (2002)

[34] A. Smoliński, B. Walczak, J.W. Einax, Chemomet. Intell. Lab. Syst. 64, 45 (2002)

[35] L. Kaufman, P. Rousseuw, Finding Groups in Data (Wiley & Sons, New York, 1990)

[36] J. Abonyi, B. Feil, Cluster analysis for data mining and system identification (Birkhäuser, Basel, 2007)

[37] L. Hakanson, Water Res. 14, 975 (1980)

[38] H.H.H. Ahdy, A. Khaleed, Aust. J. Basic & Appl. Sci. 3, 3330 (2009)

[39] G. Perin, L. Craboldd, M. Lucchese, R. Cirillo, L. Dotta, M.L. Zanette, A.A. Orio, In: T.D. Lekkas (Ed.), Heavy Metal in the Environment (CEP Consultants, Edinburg, 1985) vol. 2, 454

[40] K.P. Singh, D. Mohan, V. Singh, A. Malik, J. Hydrol. 312, 14 (2005)

[41] K. Nemati, N.K. Abu Bakar, M.R. Abas, E. Sobhanzadeh, J. Hazard. Mater. 192, 402 (2011)