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# HEAVY METAL CONTAMINATION IN SEDIMENTS OF RZESZÓW RESERVOIR (POLAND)

Sediments of Rzeszów Reservoir were characterized by a higher content of zinc compared to other heavy metals (Cu, Cr, Ni and Cd). The strongest correlations between pairs of heavy metals were Cr–Ni, Ni–Zn, Cu–Ni and Cr–Zn, while there was also a clear relationship between the total chromium and nickel content and the pH value, as well as the percentage of organic matter in the sediments (Cr, Zn, Cu, Ni). The content of chromium and copper occurred at levels exceeding the geochemical background, and the sediments could be classified as of purity class 2 (according to the PIG criterion) or class 3 (according to the Müller's classification). Ecotoxicological criteria indicate that levels of chromium, nickel and cadmium could affect aquatic life. However, the heavy metals differ in mobility and bioavailability. The highest percentage of ion exchangeable fraction was recorded for nickel, and the lowest for chromium. This means that sediments have a greater ability to release nickel into the water column, as a result of which they are a secondary source of pollution for the aquatic ecosystem.

**Keywords:** sediments, heavy metals, bioavailable fractions

## 1. Introduction

Dam reservoirs are particularly exposed to various types of pollution introduced into the aquatic environment due to their location at the lowest points of the terrain. Therefore, sediments of these reservoirs may provide necessary knowledge about the impact of anthropopressure on the aquatic environment [5]. Heavy metals have a significant share among sediment contaminants, with specific content characterized by: harmfulness and toxicity to living organisms, durability of forms enabling their migration over considerable distances and ability to be included in food chains. Heavy metals are not biodegradable, but

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only biotransformed as a result of complex physicochemical and biological processes occurring in sediments. These processes determine the mobility and bioavailability of heavy metals. The mobility of a given element means its ability, or one of its chemical forms, to move in the environment [2, 7], which may pose a threat to living organisms. The most mobile and bioavailable fraction is the ion exchange fraction. It includes heavy metals adsorbed ion exchange on the surface of the solid phase. Metal ions, held by weak electrostatic bonds, can easily pass into the water column.

For the assessment of the contamination level of sediments, methods of their classification differ in the number of degrees, classes and a factor affecting their threshold values. In all classifications used, the highest class of heavy metals determines the contamination assessment of sediments. The methods of sediment classification can be described as follows:

- classification of sediment quality applied by the Polish Geological Institute (PIG) [1] – distinguishes three qualitative classes of sediments depending on the content of individual elements,
- geoaccumulation index classification [8],
- ecotoxicological criteria – describes indicators such as TEL (Threshold Effects Level), PEL (Probable Effects Level) and LEL (Lowest Effect Level) based on the impact of a particular pollutant on aquatic organisms [15].

The purpose of the research was to determine the content of selected heavy metals in the sediments of the dam reservoir in Rzeszów along with an assessment of their pollution. The share of the bioavailable form was determined using single extraction enabling the extraction of the ion exchange fraction.

## 2. Materials and methods

The subject of the study were sediments deposited in the dam reservoir in Rzeszów. Sediment samples were collected once in July 2016 using a gravity corer (KC Kajak). The location of 5 sampling stations are shown in Fig. 1, with morphometric parameters of the Reservoir also presented.
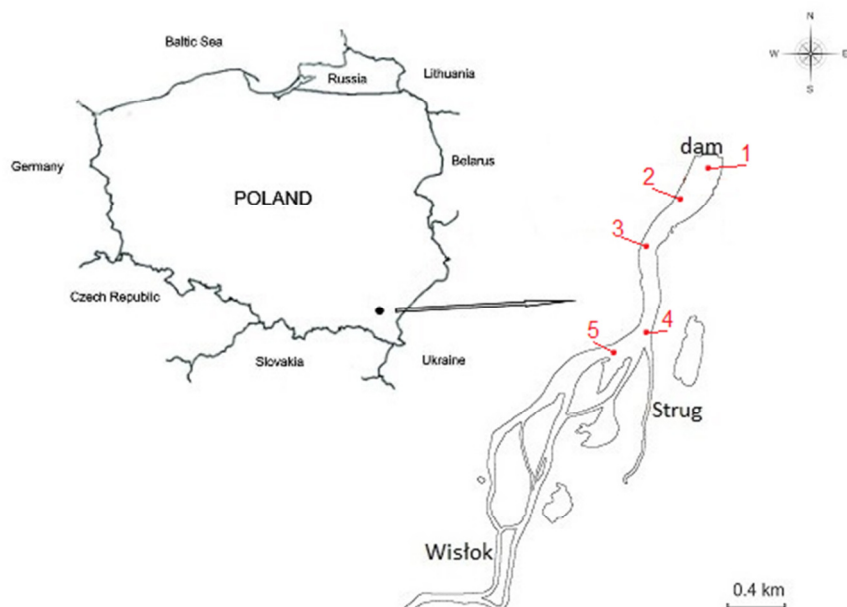
Fig. 1. Rzeszów Reservoir – location of sampling stations and morphometric parameters

The uppermost 5 cm of sediments was sampled for analysis, which were then dried to constant weight at room temperature, and then at 60°C. The sediments were milled, prior to determinations being made for such parameters as: pH, percentage of organic matter (OM), organic carbon (TOC), total nitrogen (TN), carbonates ($CO_3^{2-}$), as well as metals, including heavy metals Al, Fe, Cr, Cu, Ni, Cd, Zn. Ion–exchangeable fractions within total contents were determined for Cr, Cu, Ni, Cd and Zn.

OM content was determined as loss after drying of sediments within 4 h at 550°C. Reaction was determined potentiometrically (MultiLine P4, WTW, Germany) in slurry with 1N KCl [9]. Carbonate content was measured by volume using the Scheibler apparatus, while TOC and TN contents were determined at 1020°C using a CN elemental analyzer (Flash EA 1112, ThermoQuest). Prior to determination of TOC content, the dried and ground sediment samples were placed in a desiccator with concentrated HCl vapors [19] for 24 h, to ensure the removal of carbonates. Prior to analysis, the sediment sample was again dried to constant weight at 60°C.

To mineralize sediments in order to determine total contents of some heavy metals, portions weighing about 0.5 g were placed into a Teflon vessel and 10 ml of concentrated, spectrally pure nitric acid was then added. Samples were placed into a MARS 6 Microwave Digestion System, and mineralized using microwave energy at 1600 watts for 40 min. at 180°C (temperature rise time – 15 minutes, soaking time – 25 minutes). After cooling, mineralizates were filtered through

quantitative paper filters, and additionally using syringe filters. Heavy metal contents were then determined using a plasma emission spectrometer (ICP–OES GBC Quantima E 1330).

To determine the bioavailable fraction of certain heavy metals, 6 g portions of sediment were shaken with 60 ml of 0.01 mole $CaCl_2$ at room temperature for 2 h [4]. The samples were then centrifuged and filtered through syringe filters. They were analyzed for heavy metal content by the method described above.

## 3. Results and discussion

Results for chemical parameters of Rzeszów Reservoir sediments are presented in Table 1.

Table 1. Chemical content and selected parameters in the sediments analyzed

| Parameter | Unit | Station | | | | |
|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 |
| pH | – | 7.66 | 7.75 | 7.78 | 7.83 | 7.75 |
| $CO_3^{2-}$ | % | 7.54 | 5.18 | 4.85 | 3.47 | 5.20 |
| OM | | 9.22 | 6.40 | 6.14 | 4.83 | 7.55 |
| TOC | | 2.58 | 1.56 | 1.45 | 1.35 | 2.20 |
| TN | | 0.50 | 0.28 | 0.22 | 0.23 | 0.43 |
| C:N | – | 5 | 6 | 6 | 6 | 5 |
| Fe | % | 1.87 | 1.45 | 1.45 | 1.24 | 1.73 |
| Al | | 2.37 | 1.81 | 1.68 | 1.31 | 2.48 |

Sediments from all the sampling stations were slightly alkaline, with pH values in the 7.66–7.83 range. The lowest value characterized sediments at Station 1, the highest those at Station 4. Contents of carbonate were low, ranging from 3.47% at Station 4 to 7.54% at Station 1. Slightly higher values were obtained in the Besko Reservoir (6.12–13.23%) [13]. In turn, Dobczyce Reservoir sediments are found to have lower abundance of carbonate, in the 0.42–3.18% range [18].

The sediments of Rzeszów Reservoir are also low in organic matter, with contents ranging from 4.83% at Station 4 to 9.22% at Station 1. Organic carbon content (TOC) was found to correlate strongly with OM content ($R^2 = 0.92$). Sediments were also characterized by a low total nitrogen (TN) content – in the range 0.22% (Station 3) to 0.50% (Station 1). Positive correlations were found between OM and TN content ($R^2 = 0.87$) as well as between TOC and TN ($R^2 = 0.99$). For comparison, Besko Reservoir was previously obtained to have OM and TOC in sediments in the 3.88–5.93% and 1.11–1.81% range, respectively [13]. Furthermore, sediments of Włocławek Reservoir have an OM content over twice as high – at 11.5% [16].

C:N ratios in the sediments of Rzeszów Reservoir range from 5 to 6. Values for the C:N ratio indicate a greater share of autochthonous matter in sediments.

Rzeszów Reservoir sediments were characterized by iron contents in the range 1.24–1.87% and by aluminum in the range 1.31–2.48%. The sediment contents of these heavy metals are lowest at Station 4, while the highest values noted for iron and aluminum are at Station 1 and 5, respectively. These values were similar to those obtained in sediments of Besko Reservoir (Fe: 1.88–2.23%, Al: 1.34–1.85%) [13] and Solina Reservoir (Fe: 0.88–1.81%, Al: 0.92–1.86%) [12].

The sediments of Rzeszów Reservoir were also analyzed for their contents of the heavy metals Cr, Cu, Ni, Cd and Zn. The results of this analysis are presented in Fig. 2.
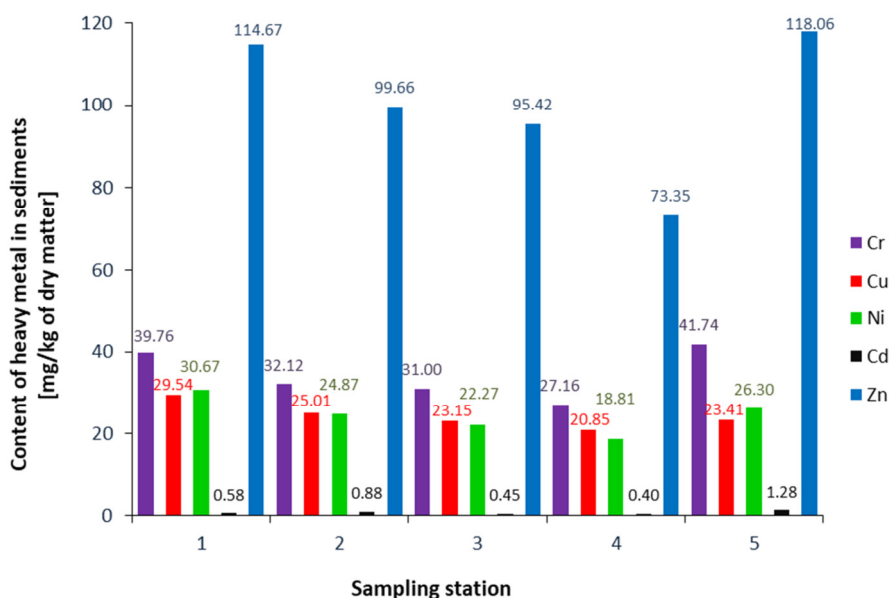


Fig. 2. Contents of heavy metals in sediments of Rzeszów Reservoir

Sediments of Rzeszów Reservoir are characterized by significant contamination by heavy metals, considering the content of zinc (73.35–118.06 mg·kg$^{-1}$ of dry matter). In terms of total content, this element was clearly predominant over the other heavy metals. A similar content of zinc was found in sediments of Solina Reservoir (28.68–144.85 mg·kg$^{-1}$ of dry matter) [12], while lower values were noted for sediments of Zesławice Reservoir (55.0–72.6 mg·kg$^{-1}$ of dry matter) and Krempna Reservoir (39.7–79.5 mg·kg$^{-1}$ of dry matter) [6].

The highest values for $R^2$ determination coefficients concern the Cr–Ni relationship (0.74), the Ni–Zn relationship (0.81), the Cu–Ni relationship (0.86) and the Cr–Zn relationship (0.92). High correlations between total contents of different heavy metals have also been confirmed by other authors [3, 14]. There was also

a clear relationship between total contents of copper and nickel, and the pH value (pH–Cu: 0.96, pH–Ni: 0.97), as well as the percentage of organic matter in sediments (OM–Cr: 0.78, OM–Zn: 0.79, OM–Cu: 0.81, OM–Ni: 0.97).

According to the classification of river and lake sediments prepared by the Polish Geological Institute (PIG) [1], sediments of Rzeszów Reservoir can be classified as of purity class 2 (medium contamination), mainly due to the highest exceedances of the geochemical background value for chromium and copper. In turn, the application of Müller's criterion [8] evidenced the $3^{th}$ purity class (i.e. moderately to heavily contaminated sediments), with this again confirmed by observed values for the geoaccumulation index in respect of chromium (2<Igeo<3). Taking into account ecotoxicological criteria, it has been observed that chromium, nickel and cadmium may all be regarded as potentially toxic to living organisms (>LEL, TEL). Possible toxic effects due to zinc do not occur, however (<PEL; no TEL).

Analysis related to overall contents of heavy metals was augmented by considerations of their mobile fractions. The results are as shown in Fig. 3.
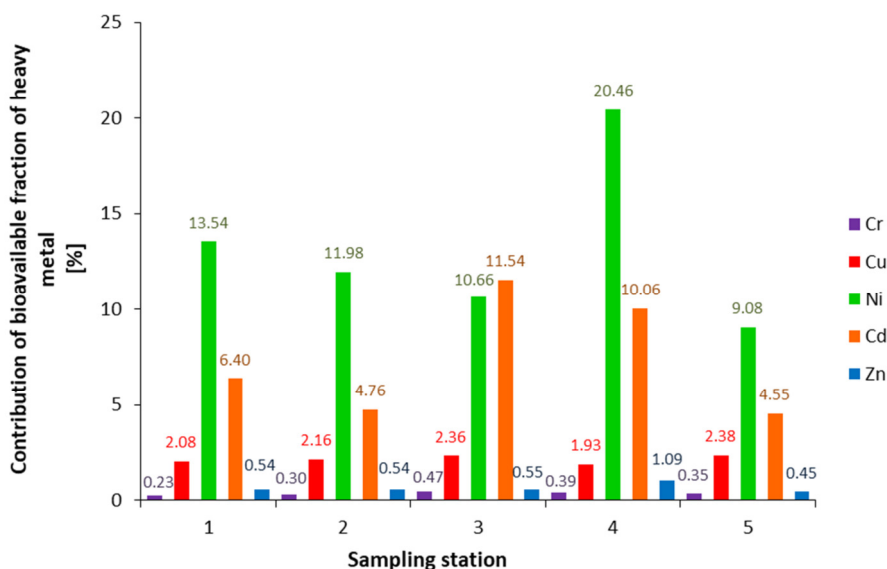


Fig. 3. Bioavailable fractions of heavy metals in sediments of Rzeszów Reservoir

Based on the procedure of extraction of the mobile fraction, it was found that the following hierarchy for the mobility of heavy metals (and hence for the possibility of secondary water contamination in a reservoir) is arranged: Ni>Cd>Cu>Zn>Cr. This order arises percentage amounts of heavy metals in the ion–exchangeable fraction. This fraction is considered the most mobile and the most sensitive to changes in environmental condition in the benthic zone. When quantified contents of the heavy metals are concerned (in mg·kg$^{-1}$), the ordering is: Zn>Cr>Cu>Ni>Cd.

Largest percentage of the ion–exchangeable fraction was obtained in the case of nickel (in the range 9.08–20.46%). Sediments of River Liwiec has also been characterized by high nickel mobility (15.6%) [10].

The ion–exchangeable fractions within the total contents of chromium, copper and zinc are similar to those in the sediments of Solina Reservoir (Cr, Cu, Zn) [12], the Łasica Canal (Cr, Zn) [11] and the River Utrata (Cu, Zn) [17]. Accurate comparisons with results for other water reservoirs are not entirely possible due to varying methods and extractants used. Most of the previous research [10, 11, 17] has applied extractants other than used in our work ($CaCl_2$).

## 4. Conclusions

Analysis of sediments from Rzeszów Reservoir in terms of contamination with heavy metals and assessment of potential toxicity to living organisms yields the following conclusions:

- Compared with other heavy metals studied, it was zinc that achieved highest values (73.35–118.06 mg·$kg^{-1}$ of dry matter).
- According to the criteria from the Polish Geological Institute (PIG), sediments at Rzeszów can be classified as of purity class 2 (medium contamination). Where Müller's classification is taken into account, sediments are found to be in the 3th purity class (denoting moderate to strong contamination). While based on ecotoxicity criteria, contents of chromium, copper, nickel and cadmium indicate potential toxicity to living organisms.
- Mobility data for the heavy metals is arranged in a hierarchy Ni>Cd>Cu>Zn>Cr, which means that nickel has the highest mobility than any other heavy metal studied. This element has a greater capacity for release from sediment into the water column and thus – there is a possibility of secondary contamination.
- While results for heavy–metal bioavailability in Rzeszów Reservoir have been compared loosely with those for other aquatic ecosystems. However, an accurate and reliable comparison of these results was not possible due to differences in research procedures applied.

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