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Metal contamination in sediments of dam reservoirs: A multi-facetted generic risk assessment

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Abstract

The quality of bottom sediments is a key factor for many functions of dam reservoirs, which include water supply, flood control and recreation. The aim of the study was to combine different pollution indices in a critical generic risk assessment of metal contamination of bottom sediments. Both geochemical and ecological indices reflected that sediment contamination was dominated by Zn, Pb and Cd. The ecological risk indices suggested a high riks for all three metals, whereas human health risks were high for Pb and Cd. An occasional local contamination of sediments with Cr and Ni was revealed, although at levels not expected to cause concerns about potential ecological or health risk. Sediments from the Rybnik reservoir for Cu only revealed a high potential ecological risk. EF turned to be as being the most useful, whereas TRI (∑TRI) was the most important ecological index. All multi-element indices suggested similar trends, indicating that Zn, Pb and Cd taken altogether had the greatest impact on the level of sediment contamination and posed the greatest potential ecological and health risks to organisms. The use of sequential BCR extraction and ecotoxicity analyses allowed for a multi-facetted generic risk assessment of metals in sediments of dam reservoirs.

Keywords: sediment quality, contamination indices, ecotoxicity tests , metal fractionation, ecological and human health risk

1. Introduction

The quality of bottom sediments is a key factor for many functions of dam reservoirs, which include water supply, flood control and recreation (Votruba and Broža, 1989). A comprehensive risk assessment and the appraisal of current contamination levels and effects is important for a sustainable management of these reservoirs that safeguards their long term functioning while protecting environmental and public health. Risk is defined as the probability of harmful effects on living organisms exposed to harmful factor(s) (Chapman and Wang, 2000; EPA 2007). From this definition, a variety of risk assessments procedures exist, from site-specific risk assessments to national criteria setting and ranking, which include an equal diversity of assessment tools (EPA 2007).

Currently, a number of geochemical and ecological indices are being used to assess to what extent the quality of bottom sediments might be affected by their metal contents.

Geochemical indices aim at assessing whether element accumulation is dominated by natural processes or importantly affected by anthropogenic activities (Costa-Böddeker et al., 2017; Bern et al., 2019; Castro et al., 2021). Ecological indices support the overall assessment of sediment contamination levels in generically evaluating the potential detrimental effects of metals contained in sediments to aquatic organisms (Baran et al., 2016; Nawrot et al. 2021). The contaminants present in the aquatic environment not only disturb the aquatic ecosystem: some pollutants (e.g. Cd, Pb, Hg, Zn, Cu) might readily accumulate in aquatic, benthic and pelagic organisms, and thus the trophic web and threaten environmental and human health (Jafarabadi et al., 2017; Li et al., 2020; Yüksel et al., 2022). Many of the geochemical and ecological indices, the former especially, are based on a rather traditional approach, i.e. they consider total metal content only without consideration of different reactivities between different binding forms, or biological/ecotoxicological effects. Other indices, such as the Sediment Quality Guidelines (SQG), have been supplemented with biological aspects (MacDonald et al., 2000; Kwok et al., 2014), allowing the assessment of potential risks related to the presence of substances harmful to bottom sediment-dwelling organisms. However, also these continue to be based upon total content of metals. These may inadequately reflect *in situ* conditions since the reactivity, mobility and bioavailability of trace elements depends on their chemical speciation, which in turn is strongly linked to the physicochemical environment and properties of the sediment (Tack and Verloo, 1995; Du Laing et al., 2009; Dendievel et al., 2022). Fractionation analysis through sequential chemical extractions allows to distinguish fractions of the total contents according to extractability. Easily extractable pools can be distinguished from more strongly bound forms that are less mobile and thus potentially less hazardous to the environment (Du Laing et al., 2009; Baran et al., 2019). For these reasons, fractionation is often considered as a useful method when it comes to exploring the potential availability and mobility of metals (Namieśnik and Rabajczyk, 2010; Zhang et al., 2014; Liang et al., 2017).

Nonetheless, fractionation analysis does not necessarily closely relate to the effective bioavailability of metals and their interaction with living organisms (Tack and Verloo, 1995); it rather informs about their potential bioavailability (Gao et al., 2018; Baran and Tarnawski, 2015; Al-Mur, 2020). Bioassays, in contrast, allow for a much more direct assessment of the potential hazards resulting from the presence of chemicals in bottom sediments. Many authors believe that bioassays allow to evaluate the extent to which metals in sediments negatively affect this environment, and therefore whether they are a stress factor for organisms (Jarque et al., 2016; Heise et al., 2020). In recent decades, the interest in bioassays as tools to examine metal contamination of bottom sediments has steadily been growing (Martín et al., 2010; Singh et al., 2017; Szara et al., 2020; Goksøyr et al., 2021). Nowadays, several bioassays are used as monitoring tools to assess ecotoxicity in sediments. They include representatives of all trophic levels: algae or plants as producers, invertebrates or vertebrates as consumers, and bacteria as decomposers (Keiter et al., 2010; Heise et al., 2020). They indicate an actual toxicity, but do not allow to identify the cause of observed toxic responses, hence the need to combine them with complementary risk assessment methods (Materu and Heise, 2019; Heise et al., 2020).

The aim of the study was to combine tools detailed above in a multi-facetted generic generic risk assessment of metal contamination (Zn, Cu, Ni, Cr, Pb, Cd) of bottom sediments in dam reservoirs in Southern Poland, with emphasis on their strengths and weaknesses. The study assessed: (1) the contamination levels and associated risks according to geochemical and ecological indices; (2) the mobility and potential bioavailability of metals based on metal chemical fractionation; (3) the ecotoxicity using bioassays; and (4) the correlations between metals, sediment parameters and the different indices using Principal Component Analysis (PCA).

2. Materials and methods

2.1. Study area and sampling

Bottom sediments were collected from 11 dam reservoirs located in southern Poland (Figure 1). The reservoirs differed in size, operation time, catchment area and dominant anthropogenic pressure (Table 1).

The Rożnów dam reservoir is one of the largest water reservoirs in Poland. It serves to mitigate peak flood events, water storage, generate electricity, and develop local tourism (Szara et al., 2020). It is subject to an intensive silting process, especially in its inlet part (large shallows and islands). During 55 years of operation, the Rożnów reservoir collected all contaminants flowing in from the related catchment (industrial, agricultural and craft contaminants, especially from tanneries and tourist resort) (Szara-Bąk et al., 2021).

The other „large" reservoirs are facilities with a capacity greater than 1 million m^3. They fulfil many functions: flood control, electricity production, water supply (Besko, Rzeszów), industrial (Rybnik) and recreational applications. The Rybnik reservoir is located in Silesia, a highly industrialised part of Poland; the water of this reservoir is used by a coal-fired power plant, and the quality of the sediments has been influenced by atmospheric pollutions (Baran et al., 2019, 2020). The Rzeszów and Besko reservoirs are also located in an industrial area, in the south-eastern part of the country, which exhibits a relatively lower degree of industrialisation than Silesia (Tarnawski and Baran, 2018). Contamination of the sediments of the Rzeszów reservoir may be expected from inflows from the city of Rzeszów and from agricultural land (catchment over 1800 km^2). An important task of the Besko reservoir is to equalize low flows, water supply and recreation. The degree of capacity loss does not exceed 10-15% for the Rybnik and Besko reservoirs, while for the Rzeszów reservoir it is over 60%. The Rzeszów reservoir is very shallow, and the settlements build large islands. The reservoir is subject to limited remediation works as it is a part of the Natura 2000 protected area.

The remaining reservoirs have small to very small capacities. All these reservoirs perform important local functions, improving soil and water conditions, increasing the availability of water for plants, and enabling recreation. Located on small rivers or streams, they counteract strong bottom erosion. The process of losing the capacity of reservoirs causes them to lose their value and function. Their renovation has been frequent, and has occasionally included draining the water. Because they are located in rural areas, they are exposed to an uncontrolled inflow of nutrients (sewage) and contaminants from agriculture (Baran and Tarnawski, 2013). Many of them have a problem of eutrophication. Earlier investigation highlighted contamination of the sediments of these reservoirs with trace elements, PAHs, dioxins, and PCBs as a result of anthropogenic impacts (industry, agriculture), which constitutes a problem when considering methods of management (Baran et al., 2019, 2020, 2021). It has also been shown that increased contents in trace elements may result from natural deposits, as in the case of the Chechło reservoir which is located in the neighbourhood of Zn and Pb ores (Koniarz et al., 2022).

Sampling of sediments was described in detail in our previous studies (Baran and Tarnawski 2015; Tarnawski and Baran, 2018). Samples were collected from each reservoir using an Ekman grab, from three designated locations: inlet (backwater), middle, and outlet (near the dam) and from a sediment depth of 0-15 cm (Figure 1). Six samples were taken from each depth zone and pooled to average the sediment properties in samples representative of a given zone; approximately 2-kg-samples were separated for testing. All sediment samples were refrigerated at 4^{o}C until analysis.

2.2. Physico-chemical analyses

The following properties were determined in the air-dried bottom sediment samples: granulometric composition by Casagrande's method modified by Prószyński, pH in 1 mol

KCl/L by potentiometric method, and total organic carbon on an Elementar Vario Max Cube CNS analyser (Elementar Analysensysteme GmbH, Germany) (PN-ISO-10390, 1997; Ostrowska et al., 1991). Pseudo-total metal contents (Zn, Cd, Pb, Cu, Cr, Ni, Fe, Mn) were determined after microwave digestion of sediment samples in a mixture of concentrated HCl and HNO_3 (1:3 v/v, suprapure, MERCK), using an AntonPaar Multiwave 3000 system (Anton Paar GmbH, Austria). The digestion was carried out in accordance with the program: power: 1400 W; temperature: 240˚C; time to reach the maximum power: 5 min.; time on maximum power: 15 min.; ventilation time: 5 min.; cooling time: 40 min (A Chemist's Guide to Sample Preparation, Anton Paar).

Fractionation analysis of selected metals (Cd, Cr, Ni, Zn, Pb, Cu) was performed following a standard BCR sequential extraction procedure (Rauret et al., 1999). Four fractions of trace elements were determined: fraction F1 – exchangeable, easily soluble in acidic medium (ion exchange and carbonate, CH_3COOH at 0.11 mol/L and pH=2); fraction F2 – reducible, bound to Fe and Mn oxides (extractable with $NH_2OH.HCl$ at 0.5 mol/dm^3 and pH=1.5); fraction F3 – oxidisable, bound to organic matter (extractable with hot 30% H_2O_2, and then re-extracted with CH_3COONH_4 at 0.5 mol/dm^3 and pH=2); fraction F4 – residual, elements permanently bound to minerals (digested using a hot mixture of HNO_3 and $HClO_3$ (3:2 v/v)).

The content of elements in the obtained solutions was determined using an inductively coupled plasma optical emission spectrophotometer (ICP-OES) – Perkin Elmer Optima 7300 DV (PerkinElmer, Inc., Waltham, MA USA). Internal standards and the certified reference materials CRM023-050 (Sigma-Aldrich Chemi) and BCR-701 (fractions) (LGC Standards) were used for quality control. Recoveries with reference to the certified concentrations ranged from 80 to 119% for Zn, 79 to 122% for Cu, 91 to 124% for Pb, 79 to 118% for Cr, 85 to 112% for Cd, and 85 to 128% for Ni.

2.3. Geochemical indices

The degree of contamination of bottom sediment was evaluated using geochemical indices. Five indices were used including three single-element indices (geoaccumulation index (I_{geo}), single pollution index (PI), enrichment factor (EF)) and two multi-element indices (pollution load index (PLI), improved Nemerow pollution index (PI_N)) (Table 2 SI). The single-element indices, as the name suggests, only assess the content of single elements. However, multiple elements are present considerable spatial and time variability in any environment. Multi-element indices aim to comprehensively appraise the overall level of contamination (Birch, 2017; Kulbat and Sokołowska, 2019; Aleksander-Kwaterczak et al., 2021; Castro et al., 2021). Their common trait is that the pollution indices (PIs) of single elements are used for their calculation; they differ in the sense that the pollution load index (PLI) mainly indicates how many times the value considered as natural is exceeded, whereas the Nemerow pollution index (PI_N) value is rather strongly determined by the most polluting elements. The choice of a relevant geochemical background is a key factor when using geochemical indices in the evaluation of metal contamination (Birch, 2017). Using generic reference geochemical background (upper continental crust UCC or lower continental crust LCC) may not allow to make a region-specific distinction between natural influences and anthropogenic metal contamination (Kowalska et al., 2018). In this work, the national geochemical background as assessed by the Polish Geological Institute (Bojakowska and Sokołowska, 1998) was used, i.e., 0.5 for Cd, 6 for Cr and Ni, 7 for Cu, 15 for Pb and 73 for Zn (values in mg/kg dry soil).

2.4. Ecological risk indices

Ecological risk assessment requires the application of ecotoxicological criteria or the use of indices that take into account the level of metal toxicity (Tarnawski and Baran, 2018; Gao et al., 2018; Nawrot et al., 2021). Ecological risk indices do not assess anthropogenic changes, but the potential for biological uptake (Birch, 2017). Both single-element and multi-element indices, allowing to evaluate the total effect of metals on organisms, were used to assess the potential ecological risk of metals in bottom sediments to aquatic organisms. The indices used in this study were: Sediment Quality Guidelines (SQG) (threshold effect concentration (TEC), probable effect concentration (PEC)), toxic unit (TU), toxic risk index (TRI), risk assessment code (RAC) (single-element) and ∑TU, ∑TRI, potential ecological risk (RI) and PEC quotient (PECQ) (multi-element) (Table 2SI). TEC is a threshold value for identifying the concentrations of contaminants below which no harmful effects on benthic organisms are expected. PEC is a probable concentration value which, if exceeded, may be harmful to organisms (MacDonald et al., 2000). The following TEC values for individual elements were used: Zn 121 mg/kg; Cu 31.6 mg/kg; Pb 35.8 mg/kg; Cd 0.99 mg/kg; Ni 22.7 mg/kg; Cr 43.3 mg/kg and PEC: Zn 459 mg/kg; Cu 146 mg/kg; Pb 128 mg/kg; Cd 4.98 mg/kg; Ni 48.6 mg/kg; Cr 111 mg/kg (MacDonald et al., 2000).

2.5. Health risk indices

Health risk assessment of potential accidental exposure to the analysed metals in bottom sediments was performed according to the US EPA method (2004), Wcisło et al. (2016), and Li et al. (2020). Non-carcinogenic risk (hazard quotient, HQ) and carcinogenic risk (CR) were estimated for three exposure routes (ingestion, dermal contact, and inhalation) for adults. The following parameters were calculated for non-carcinogenic risk: HQing, HQderm, HQinh, total hazard quotient (HI =∑HQing + HQderm + HQinh), and for the carcinogenic risk: CRing, CRderm, CRinh, total carcinogenic risk (CR = ∑CRing, CRderm, CRinh), respectively (Table 2). If the HQ or HI value was less than 1.0, the potentially exposed individual was assessed unlikely to experience obvious adverse health effects. On the contrary, HQ or HI values higher than 1.0 indicated a non-carcinogenic risk (Wcisło et al., 2016; Jafarabadi et al., 2017; Li et al. 2020). If CR was between $1x10^{-4}$ and $1x10^{-6}$, this was considered an acceptable cancer risk, whereas the risk values higher than $1x10^{-4}$ were considered a carcinogenic risk to the human body (Wcisło et al., 2016; Gruszecka-Kosowska et al., 2020; Li et al., 2020).

2.6. Ecotoxicological analyses

Ecotoxicity analysis of bottom sediments was performed using three bioassays: Phytotoxkit *(Lepidium sativum)*, Ostracodtoxkit (*Heterocypris incongruens*), Microtox (*Alivibrio fischeri*). In the Phytotoxkit assay, the measured parameters were seed germination inhibition and root length inhibition of *L. sativium* after a 3-day incubation of test organisms with sediment samples. The Ostracodtoxkit assay measured the mortality and growth inhibition of *H. incongruens* after a 6-day exposure of the crustacean to sediment samples. The Microtox assay investigated luminescence inhibition of *A. fischeri.* Luminescence was measured before and after a 15-minute incubation of the bacterial suspension with the tested sediment sample using an M 500 Analyser. The toxicity of sediment samples to *A. fischeri* was tested by conducting an 81.9% screening test. The assays were conducted according to standard procedures (Ostracodtoxkit F, 2001; Phytotoxkit, 2004; Microbics Corporation, 1992).

The results were expressed as a test reaction percentage effect (PE), and the hazard assessment system developed by Persoone et al. (2003) was used to evaluate the ecotoxicity: PE < 20% means no significant negative effect on the organism; the sample is non-toxic (class I, no acute hazard); 20% ≤PE< 50%: the sample exhibits low toxicity (class II, low acute hazard); 50% ≤PE< 100%: the sample is toxic to an organism (class III, acute hazard) ; PE = 100%: very toxic (class IV, high acute hazard).

2.7. Statistical analyses

The significance of differences among the pseudo-total metal concentrations for the different reservoirs were assessed using the non-parametric Kruskal-Wallis test (K-W, p ≤

0.05). Pearson's correlation and PCA were performed to identify potential relationships among the behaviour of metals (e.g. between metal content and granulometric composition or TOC content, or between pseudo-total content and metal fractions) as well as potential correlations among sources of metals (natural or anthropogenic) in the bottom sediments. Before starting to calculate the correlation, the data were transformed to obtain a normal distribution. Data were statistically analysed using Microsoft Excel 2016 and the Statistica 13 software package.

3. Results and Discussion

3.1. Geochemical and ecological indices

Pseudo-total metal contents in bottom sediments, except for Fe, significantly differed (K-W, $p \leq 0.05$: Cr $p = 0.008$; Ni $p = 0.041$; Zn $p = 0.029$; Pb $p = 0.012$; Cu $p = 0.004$; Cd $p = 0.001$) between the studied reservoirs (Table 3). The highest variability was found for Cu, Cd, Zn and Pb contents, for which the coefficient of variation (CV) was 135% for Pb, and more than 200% for Cu, Cd and Zn. For other metals the CV value was lower, in the range 48-65%.

3.1.1. *Geochemical indices*

An appraisal of the extent of metal contamination may differ between geochemical indexes (Table 4). The highest median I_{geo} value was found for Cr (1.15), and then for Ni > Cu > Cd > Zn = Pb. The proportion of samples assigned to class II moderately contaminated or lower were: Ni – 100%; Cr and Pb – 92%; Zn, Cu – 82%, and Cd – 73%. The highest median PI value was demonstrated for Ni (3.59), and then for Cr > Cu > Cd > Zn > Pb. For that index, unpolluted and lowly polluted samples were dominant for Zn (45% of samples) and Pb (55% of samples), strongly polluted samples for Cr (55% of samples) and Ni (55% of samples) and strongly and moderately polluted samples for Cd and Cu, which constituted 36% of the sediment samples. Due to the high similarity of the geoaccumulation index and single pollution index calculation formulas, the results obtained for both indices coincide (Table 4). Both indices showed that the most contaminated bottom sediments were these from the Chechło reservoir (Cd and Zn) and from the Rybnik reservoir (Cu). Moreover, high levels of pollution for both indices were found in bottom sediments of the Rożnów (Cr), Rybnik (Zn, Cd), Rzeszów (Cd), and Chechło (Pb, Cu) reservoirs. The lowest values of I_{geo} and PI were found for bottom sediments of the Besko, Narożniki, Brzóza Królewska, and Brzóza Stadnicka reservoirs. However, given the fact that I_{geo} is divided into a larger number of contamination classes, the presented index data show slightly more subtle information; they also allow to assess that bottom sediments are much less contaminated than it was shown in the evaluation using PI.

The enrichment factors (EF) – the last of the indices designed to assess single-metal pollution of sediments – indicated that 100% of the tested samples were enriched with Ni and Cr at a moderate or higher level (EF>3). For Cd, this was 82%, for Cu 62%, and for Zn and Pb 55%. Severe (Zn, Cd, Pb), very severe (Zn), and extremely severe (Cu, Cd) enrichments of bottom sediments were recorded in the Chechło and Rybnik reservoirs. The sediments least enriched with metals came from the Głuchów, Narożniki, and Brzóza Królewska reservoirs. The highest median EF value (3.38) was found for Cr, followed, in descending order, by Cd, Ni, Cu, Zn and Pb.

The next two geochemical indices are combined indices, accounting for the contents of all trace elements in a single index. The PLI values were ranging from 1.00 (BK) to 10.19 (Ch), with most of the sediments being classified as polluted. Only sediments from the Brzóza Królewska reservoir had a baseline level of pollution. The PLI value for sediments decreased in following order: Ch > Ry > Rz > Z > O > Ro > G > B > BS > N > BK. In contrast, the assessment of sediments based on PI_N showed that sediments with a moderate level of pollution (grades 4-5) were predominant. The PI_N values ranged between 1.00 (BK) and 37.42 (Ry) and decreased in the order: Ry > Ch > Rz > Ro > O > Z > G > N> B > BS > BK.

When analysing the results of multi-element index calculations with respect to the size of the reservoirs, a considerable difference was observed between the level of contamination of sediments from very small reservoirs on one side and small and large reservoirs on the other side, for both parameters. However, the literature on contamination of reservoir bottom sediments shows that the content of metals depends of a wide number of factors such as the age of the reservoir, its location, allocation, the nature of the catchment area and hydrodynamic conditions, rather than by the size of the reservoir solely (Wang et al., 2018; Sojka et al., 2019; Michalec and Cupak, 2022). Sojka et al. (2019) found that reservoirs with a shorter water retention time are more likely to be impacted by metals. Moreover, shape and morphology of the reservoir modify the metal deposition (Sojka et al., 2018). Czaplicka et al. (2017) determined that reservoir depth may significantly influence the spatial distribution of metal content in the reservoir bottom sediments. According to many authors, sediment contamination with trace element is generally an effect of intensive human impact on the area where reservoirs are located (Wu et al., 2014; Baran and Tarnwaski 2015; Wang et al., 2018). Despite significant differences in the degree of contamination with metals in the bottom sediments of large, small and very small reservoirs, we conclude that the content of metals in sediments are probably more affected by catchment characteristics and anthropogenic conditions that exist in the catchments.

3.1.2. Ecological risk assessment

In the risk assessment related to the presence of metals in bottom sediments based on SQG indices, TEC threshold values were exceeded for Cd (Ry, Rz, Ch, O, G, BS), Cu (Ro, Ry, Ch), Zn (Ry, Ch, Z), Ni (Ro, Ry, Rz), and Cr (Ro). Values above TEC and below PEC are believed to indicate a low toxicity of sediments to benthic organisms (MacDonald et al., 2000) In our case, PEC values were exceeded for Zn, Pb (Ry, Ch), Cu (Ry), Cd (Ch), which suggests a high risk to aquatic organisms due to the above metals. For bottom sediments of the Besko, Brzóza Królewska, and Narożniki reservoirs, TEC values were not exceeded for any element, and in the case of sediments from the Głuchów and Brzóza Stadnicka reservoirs, only the Cd content was above TEC.

TU, ∑TU, TRI, and ∑TRI indices were used to assess the potential toxicity of trace metals contained in bottom sediments based on chemical models (Gao et al., 2018; Zhang et al., 2016) (Table 5). Among the metals, importantly higher median values for TU were found for Ni (0.44) > Cd > Cr > Cu = Zn > Pb. ∑TU values differed significantly depending on the studied sediment and were between 0.70 (BK) and 12.68 (Ch). The ∑TU values for the studied sediments decreased in the following order: Ch > Ry > Rz > Ro > Z > O > G > B > BS > N > BK. Nickel accounted for the largest share in ∑TU for 6 reservoirs (Ro, B, N, BK, G), Cd for 4 reservoirs (Rz, Ch, O, BS), and Cu and Pb for 1 reservoir (Ry, Z) each, illustrating the relative importance of these elements in the potential toxicity of sediment.

The parameter ∑TU may underestimate the potential toxicity of bottom sediments, because it only considers the PEC effects; therefore, the TRI was used to assess the integrated toxic risk based on both the TEC and PEC effects of metals (Zhang et al. 2016, Gao et al. 2018). Aquatic organisms exposed to TECs of trace metals in sediments are likely to suffer only limited acute toxic effects; however, the possibility of chronic toxic effects cannot be dismissed if the duration of exposure is long enough (Gao et al. 2018). Therefore, the TRI and ∑TRI indices, integrating TEC and PEC, were used to assess the potential toxic risk for both acute and chronic effects. In general, the toxicity of bottom sediments was higher when assessed using TRI values rather than TU values, because, when using TRI, chronic toxic effects are taken into consideration**.** Furthermore, Cd was in this case linked with the highest median TRI value (0.74), and the hierarchy among metals was slightly different: Cd > Zn > Ni > Cr > Cu > Pb. The ∑TRI values ranged from 1.46 (BK) to 39.56 (Ch) and formed the following series: Ch

> Ry > Rz > O > Z > Ro > G > BS > B > N > BK (Table 5). The analysis of the % share of individual elements in ∑TRI showed slightly different relationships than for ∑TU, especially for Cr, Zn, and Ni; Cr had the highest % share in ∑TRI in 2 sediments (Ro, N), Zn in 2 sediments (B, BK), Pb in 1 sediments (Z), Cu in 1 sediments (R), and Cd in 5 sediments (Rz, Ch, O, G, BS), which shows that those elements can be considered the most largely responsible for the potential toxicity of these sediments. The ∑TRI values of the analysed bottom sediments indicated no toxic risk for sediments from the Rożnów, Besko, Narożniki, Zesławice, Ożanna, Brzóza Królewska, Głóchów, and Brzóza Stadnicka reservoirs, low toxic risk for bottom sediments from the Rzeszów reservoir, considerable toxic risk associated with sediments from the Rybnik reservoir, and very high toxic risk for sediments from the Chechło reservoirs.

The mean PEC quotient (PECQ), similarly to ∑TU and ∑TRI, was used to assess the potential effect of a complex mixture of metals in sediments (Geo et al. 2018). The values of PECQ ranged from 0.12 (BK) to 2.11 (Ch) for bottom sediments and were ranked as follows: Ch > Ry > Rz > Ro > O > Z > G> B > BS > N > BK (Table 5). The PECQ values showed a slight ecological risk for sediments from the Rożnów, Besko, Zesławice, Ożanna, Narożniki, Brzóza Królewska, Głochów, and Brzóza Stadnicka reservoirs, and potenctial heavy effect for samples from the Rybnik and Chechło reservoirs.

The last index assessing the potential ecological risk, RI, is a slightly different index. The pollution indexes (PIs) of individual elements were used for its calculation and, additionally, the toxicity of individual metals were taken into account. RI values ranged from 43.4 to 2109. In a similar manner as for ∑TU and ∑TRI, the lowest RI values were observed for bottom sediments collected from the Brzóza Królewska reservoir and the highest for sediments from the Chechło reservoir. RI values for sediments formed the following series: Ch > Ry > Rz > O > Z > G > BS > Ro > B > N > BK. Mean values of RI indicated a low ecological risk (RI <150) related to the presence of metals in sediments of the Ro, B, N, Z, BK, BS;

medium risk (150≤ RI <300) in the O, high risk (300≤ RI <600) in the R, and a very high risk (RI > 600) in the Ry and Ch reservoir sediments.

Statistically significant differences in ∑TU, ∑TIR, and PECQ (K-W, $p \leq 0.05$: ∑TU $p = 0.004$; ∑TIR $p = 0.003$: PECQ $p = 0.001$) were found between sediments of very small reservoirs on one hand and small as well as large reservoirs on the other hand, the highest multi-element risk index values being found for small reservoirs and the lowest for very small ones. As explained in chapter 3.1.1. the location of the reservoir and the intensity of anthroporesia in the catchment have a greater influence on the obtained results than its size.

3.1.3. Human health risk assessment

The non-carcinogenic and carcinogenic risks were assessed for the bottom sediments from each reservoir (Figure 2). The highest HQs for Cd, Pb, Zn were determined for bottom sediments from the Chechło reservoir; for Ni, Cr from the Rożnów reservoir, and for Cu from the Rybnik reservoir. The calculated total HI values ranged from 1.30×10^{-4} (Cu, Narożniki) to 8.8×10^{-2} (Cd, Chechło). Total HI values for trace elements followed the order: Ni > Cd > Pb > Cr > Zn, and for bottom sediments: Ch > Ry > Rz > Ro >Z > O > G > N > BS > B >BK. The calculated HQ values are in the following descending order: Pb > Cr > Cd > Cu > Ni > Zn (HQing); Ni > Cd > Pb > Cr > Cu > Zn (HQderm); and Pb > Cr > Ni > Cd (HQinh). In most cases, the non-carcinogenic risk decreased for all exposure routes in adults, according to the following series: ingestion > dermal contact > inhalation of bottom sediments. HQing, HQderm, HQinh, and total HI calculated for individual trace elements in bottom sediments did not exceed the acceptable level of 1, indicating negligible non-carcinogenic toxic risk. Lead, although its level in most sediments was not high, showed a relatively higher non-carcinogenic risk than other elements because of its low RfD values (Li et al., 2020).

The total carcinogenic risk (CR) ranged from 5.52 x10^{-10} (BK) to 1.87 x 10^{-9} (Ro) for Ni and from 7.19 x 10^{-7} (Ro) to 9.47 x 10^{-5} (Ch) for Cd. To a similar extent as for the total non-carcinogenic risk, the highest total CR value was observed in bottom sediment from the Chechło reservoir and the lowest in bottom sediment from the Rożnów reservoir (Ch > Rz > Ry > O> Bs > G > Z > B > N > BK = Ro). Moreover, carcinogenic risk indices were lower than 1x10^{-4}, suggesting that no obvious carcinogenic risk would be associated with metal exposure. In the study of Li et al. (2020), the HQ values for trace elements in the Xiangjiang River sediment samples ranged from 3.59 x 10^{-5} to 7.1 x 10^{-1}, and the HI values for adults followed the order: Pb > As > Cr > V > Zn > Mn > Cu > Cd > Be > Co. The study of Yüksel et al. (2022) also proved that, according to the results of hazard quotient (HQ), total hazard index (HI), and carcinogenic risk (CR), metals did not pose a significant health risk for adults exposed to sediments in the Çavuşlu stream in Giresun (Turkey).

3.2. Fractionation of metals

In most sediments, the residual fraction F4 of Zn was dominant, except for the O and BS reservoirs where the exchangeable fraction F1 was the highest (Figure 3). In most of the studied sediments, Cu was similarly mainly present in the F4 (residual) fraction, and in Ry and Rz sediments in the F3 (oxidisable) fraction. Also for Cr the residual fraction F4 dominated, except for the Rybnik and Chechło reservoirs, where it was mainly bound to F3. Cr bound to fractions F1 and F2 accounted for respectively 0 to 2% and 1 to 5% of the pseudo-total metal content. The highest Ni content was also found in fractions F3 and F4. Cd was bound to different fractions depending on the sediment. F1 was notably dominant in Ro, Z, and O sediments, F3 in B, Rz, N, and BK sediments, and F4 in Ry, Ch, G, and BS sediments. In contrast with other elements, Pb was found mainly in the reducible fraction F2 (6-55%), residual fraction F4 (1-65%), and oxidisable fraction F3 (10-52%). Smaller amounts of Pb – up to 9% – were bound to the exchangeable fraction F1. The presence of metals in the potentially mobile fraction (PMF = ∑F1-F3) probably indicates their anthropogenic source, whereas in the fourth fraction (F4), the elements are generally lithogenic, immobile, and poorly available (Gao et al. 2018). The PMF of metals exceeded 50% of the pseudo-total content in most bottom sediments (Cd – all sediments; Pb and Zn – Rz, Ry, O, BK, BS, G, N, Ch, B, Z (only Zn); Ni - Rz, O, BK, BS, G, Z; Cu – Rz, Ry, N; Cr - Ry, Ch) suggesting that these elements usually originate from anthropogenic sources.

The elements determined in F1 are considered to be the most mobile and potentially bioavailable (Baran et al. 2019, Gao et al. 2018). Here, the Risk Assessment Code (RAC) was used to assess the risk related to the release of metals from sediments (Singh et al., 2005; Liang et al., 2017). This classification takes into account the percentage of metals bound to the exchangeable fraction: F1 < 1 no risk, F1: 1-10 low risk, F1: 11-30 medium risk, F1: 31-50 high risk, F > 50 very high risk. Metal contents in the fraction F1 were notably contrasted: Cd (31%) > Zn (22%) > Ni (13%) > Pb (7%) > Cu (3%) > Cr (1%). A higher concentration in F1 (for Cd and Zn here) suggests a higher mobility and a probable higher assimilation by benthic organisms, or a higher environmental threats to aquatic ecological systems. Szara-Bąk et al. (2021) discovered for example that the F1 of Cd and Cu contents in sediments significantly correlated with the content of these metals in mussel tissues. This requires to be nuanced, however, as illustrated by Gao et al. (2018), who demonstrated that the potential bioavailability of metals derived from F1 by the BCR method was probably overestimated. Additionally, when evaluating the risk related to the mobility of metals, their total content must be considered (Nag et al., 2022). In our case, a high value of RAC coincided with a metal mobility that was low in absolute terms because of the low pseudo-total metal concentration, such as for Cd and Zn in bottom sediments. Most of the bottom sediments contained less than 1 mg/kg Cd and less than

150 mg/kg Zn. A serious risk related to high mobility of these elements can only be observed in sediments of the Rybnik and Chechło reservoirs (Table 3).

Total contents of metals tend to be correlated with the physicochemical properties of the bottom sediments (Rinklebe and Shaheen, 2014; Liang et al., 2017; Klink et al., 2019). Correlations between metals in sediments may result from their geochemical relationships and also may reflect similar sources. Significantly positive correlations were found between the pseudo-total concentrations of the following metal pairs: Zn with Cd and Pb ($r = 0.97$, $r = 0.88$, $p \leq 0.05$); Cr with Ni and Mn ($r = 0.83$, $r = 0.58$, $p \leq 0.05$); Ni with Mn ($r = 0.51$, $p \leq 0.05$); Pb with Cd ($r = 0.90$, $p \leq 0.05$) (Table 6SI). The correlations among the contents of elements suggest that their partly natural and anthropogenic sources and routes of distribution to bottom sediments are similar. When analysing the interrelationships among the metal contents, Fe was treated in a separate way, because the correlation between the content of iron and the content of another trace element may make it possible to distinguish sediments with natural element contents from those enriched with trace elements because of human activity. It is believed that a lack of significant correlations between iron and other trace elements in these studies may indicate their anthropogenic origin (Wieczorek and Baran 2022). In the present study, a significantly positive correlation was found between Fe and Cr ($r = 0.41$, $p \leq 0.05$), and Ni ($r = 0.56$, $p \leq 0.05$), suggesting their rather natural origin in most of the studied sediments.

No significant correlations were found between TOC or pH and the content of most of the metals (except for pH and Mn, and F2 of Cr), despite two sites having a markedly low pH (<5.5). The absence of a more significant correlation suggests that the pH and TOC do not play a dominant role in the content and mobility of metals. However, the correlations with the silt and clay fraction were significant, and especially strong for Ni and Cr. The largest silt fractions was found in bottom sediments of the Rożnów, Zesławice and Głuchów reservoirs, and the largest clay fractions in bottom sediments of the Besko and Rzeszów (Table 3). The correlation of sediment texture and metal content is well established (Windom et al. 1984; Boguta et al., 2022). The Rożnów, Rzeszów, Zesławice reservoirs are intensively silting (Baran and Tarnawski, 2013; Tarnawski and Baran, 2018; Szara-Bąk et al. 2021). Silting is results on the inflow of small mineral particles whose origin is both natural and anthropogenic. The fine fraction, especially the clay fraction, has a large sorption area for metals. A significant correlation was also found between Fe and Mn contents with F2 of Ni, F4 of Ni (only Mn), and F2 of Cr (only Fe). As highlighted recently by Zhou et al. (2020), it is well known that Fe and Mn can significantly influence the behaviour of metals in bottom sediments. Under reducing conditions, metals adsorbed on the surface hydrated iron and manganese oxides (F2) may be released from the sediment. Similarly, Wang et al. (2019) found that Fe-Mn oxyhydrooxides play a role in controlling Cd mobilization in paddy systems, whereas sulfate reduction was important in immobilizing Cd in reduced conditions but had little or no impact on the mobilization of cadmium upon oxidation.

3.3. Ecotoxicity of bottom sediments

In the Phytotoxkit test, the mean percentage inhibition of *L. sativum* seed germination ranged from 0 (N) to 61% (BK), and the inhibition of the test plant root growth ranged from -12 (Z) to 57% (Rz), indicating that most of the sediments showed low toxicity (Ch, O, BS) or were non-toxic (Ro, Ry, B, N, Z, G) to *L. sativum*. The Rz and BK sediments showed the highest phytotoxicity. In the Ostracodtoxkit test, the mortality of *H. incongruens* ranged from 0 (G) to 67% (Ch), and the growth inhibition of the crustacean ranged from 20 (Z) to 76% (Ch). The tested sediment samples generally had low toxic effects to *H. incongruens* (Ro, B, Rz, N, O, BK, G, Z). The sediments from the Chechło, Rybnik, and Brzóza Stadnicka reservoirs were the most toxic to *H. incongruens* (Table 3). *A. fischeri* luminescence inhibition ranged from 12 (Rz) to 91% (O). Five out of eleven tested sediments were found to be toxic (Ry, Ch, O, BK, BS) to the bacteria. The sediments from the Rożnów and Głuchów reservoirs turned out to have low toxicity, while the sediments from the Besko, Rzeszów, and Zesławice reservoirs were non-toxic to *A. fischeri*. The study determined significantly positive correlations between sediment toxicity to *A. fischeri* and *L. sativum* as well as *H. incongruens*, indicating similar sensitivity of the test organisms to contaminants present in the tested sediments (Table 6 SI).

Statistical analysis showed significant correlations between the pseudo-total content of Zn or Pb and the response of *H. incongruens*, as well as between the pseudo-total content of Cd and the toxicity of sediments to *L. sativum* and *H. incongruens* (Table 6SM). A positive correlation was also found between all fractions of Zn, Cd, Pb (except F4 of Cd and Pb) and mortality and growth inhibition of *H. incongruens*, as well as between Cd (F2, F3) and Pb (F2) and root growth inhibition of *L. sativium*. It indicates that the metal content in bottom sediments affect their toxicity to the test organisms. Positive correlations were also shown for Cd, Zn, Pb, and Cu contents and *A. fischeri* luminescence inhibition, but these were not significant.

The higher correlations between the *H. incongruens* response and the metal content in sediments are related to the fact that in the Ostracodtoxkit test crustaceans are exposed to both soluble contaminants and contaminants absorbed on sediment particles, while the exposure of bacteria and plants is limited to dissolved and thus more mobile substances (Boguta et al., 2022). Chial and Persoone (2002) indicated that the *H. incongruens* mortality in Zn-polluted soils was a result of the substances bound to the solid-phase particles, rather than dissolved forms in the water phase. The less or lack of significant relationships between the metals content in individual fractions and the response of test organisms would indicat their relatively low mobility and bioavailability (Cr, Ni, Cu). Our previous studies showed that the relationship between the total content of trace element and *A. fischeri* response was insignificant in sediments from the Rybnik reservoir (Baran et al., 2019). However, in the same study, a positive correlation was found between all fractions of the trace element and inhibition of luminescence in *A. fischeri* (Baran et al., 2019). Tarnawski and Baran (2018) highlighted that *L. sativum* in the sediments correlated significantly, positively with Cr, Ni, Zn, Pb, Cu, however most relations of *H. incongruens* and *V. fischeri* with metals were negative. Rosado et al. (2016) observed that mobile fractions of metals have a significant influence on toxicity. Gao et al. (2018) found that the acid-soluble forms of metals caused significant toxicity towards *A. fischeri*. Szara et al. (2020) and Szara-Bąk et al. (2021) found that the trace element content in the Rożnów reservoir bottom sediments was not responsible for the ecotoxicity of sediments to plants, but significantly correlated with *H. incongruens* growth inhibition. Gao et al. (2018) reported that the sediment toxicity observed for *A. fischeri* showed a positive correlation with the estimated toxic effect based on chemical models. From the literature, it appears that the lack of significant relationships between the ecotoxicity of bottom sediments and the content of trace metals could be explained by the fact that ecotoxicological analyses allow for a summary assessment of the toxicity of all substances present in the tested sample, in many cases acting synergistically or antagonistically (Heise et al., 2020). The toxicity of bottom sediments could also be due to other contaminants such as ammonia, pesticide residues, PAHs, dioxins, biogens present in the studied sediments (Baran et al., 2019; Baran et al. 2020, 2021).

Other authors observed that clay, TOC content and pH have a significant influence on the toxicity of metals (Chial and Persoone, 2003; Baran et al., 2019). In this studies, analysis of correlation revealed the influence of the physicochemical properties of the sediments (sand, silt, clay, TOC, pH) on the sediment ecotoxicity for test organisms. There were significant correlations between the toxicity to *H. incongruens* and either silt or clay content or pH (negative), or sand content (positive). The response of *L. sativum* was negatively correlated with pH and positively correlated with TOC content. Response of *A. fischeri* was positively correlated with sand and TOC and negatively with pH, clay and silt content. The above environmental factors determine the conditions for the growth of organisms in sediments and have a significant impact on the mobility and bioavailability of metals. Son et al. (2007) found lower cadmium toxicity to *Paronychiurus kimi* (Lee) in soils with high content of organic matter content and high pH. García-Lorenzo et al. (2009) indicated a negative correlation between pH and response of the plants, suggesting that acidic pH increases the sediment toxicity to plants. Wieczorek and Baran (2022) also found that the bioavailability and toxicity of Cd and Pb in soils to test organisms (*H. incongruens, S. saccharatum, L. sativum)* increased at pH lower than 5.5. In our study, the high pH value of most bottom sediments would rather limit the mobility of metals and thus their toxicity. *H. incongruens* is very sensitivity to the acidic pH of soils/bottom sediments (Ruiz et al., 2013), which may explain the higher toxicity of the sediments from Chechło to that crustacean (Table 3). Furthermore, the positive correlation of sediment ecotoxicity with organic matter content may suggest the effect of other substances accumulated in sediments on the response of test organisms, although earlier studies suggested that the complexation of metals with the organic matter in the bottom sediments decreases their toxicity for *A. fischeri* (Baran et al., 2019).

According to the hazard classification proposed by Persoone et al. (2003), sediments from the Rybnik, Chechło, Ożanna, Rzeszów, and Brzóza Królewska reservoirs were assigned to toxicity class III, suggesting that they may represent an acute hazard to aquatic environments. Sediments collected from the Rożnów, Besko, Narożniki, and Głuchów reservoirs were assigned to class II, i.e., low toxicity, low hazard, and sediments from Zesławice reservoir were assigned class I, meaning "non-toxic sediments, no acute hazard". Sediments from the Chechło reservoir were characterised by a high pseudo-total content of Cd, Zn, and Pb, and the Rybnik reservoir by a high pseudo-total content of Cu. Moreover, bottom sediments from the Chechlo, Ożanna, and Brzóza Królewska reservoirs were acidic, which could have resulted in greater mobility and thus bioavailability of the contaminants. Bottom sediments of the Ożanna, Brzóza Królewska, and Brzóza Stadnicka reservoirs also had relatively high contents of Cd, Zn, and

Ni in the exchangeable fraction (F1). The share of Cd, Zn, and Ni in F1 was 47%, 31%, 24% (Ożanna), 32%, 36%, 24% (Brzóza Stadnicka), 25%, 22%, 14% (Brzóza Królewska), respectively. Moreover, bottom sediment from Chechło and BK reservoir have the highest TOC content of all. Organic matter is the most important sediment sorption factor and thus influences the bioavailability and toxicity of metals and other pollutants (PAHs, dioxins) not investigated in this study but potentially affecting the toxicity of sediments.

3.4. Multivariate statistic and assessment of contaminant sources

The first PC analysis for parameters of sediments showed important relationships between the content of trace elements in bottom sediments, sediment properties and ecotoxicity (Figure 4a). PC analysis identified four main factors explaining 72.2% of the total variance of the data set (Table 7SI). PC1 explained 31.8% of the total variance, and the main components of the first factor were pseudo-total Zn, Pb, and Cd contents, their contents in individual fractions (except for F4), and sediment toxicity to *H. incongruens* (positive loads > 0.50). The second factor (PC2) accounted for 16.9% of the total variance and was dominated by the pH value, the contents of clay, silt, Fe, Mn, Ni (pseudo-total content and F2, F3, F4) and Cr (pseudo-total content, F2, F4) (positive load), and the sand content and *A. fischeri* response (negative load). The third factor (PC3) explained 15.5% of the total variance and was related to the pseudo-total Cu content (total content, fractions) and the content of Ni in F1 and Cr in F3. The fourth factor (PC4) explained another 7.9% of the total variance and was related to the contents of F4 Zn, F4 Pb, F4 Cd as well as F2 Ni and F1 Cr.

Analysis of the main factors revealed significantly positive correlations between the studied metals and additionally distinguished three groups of trace elements. PC1 represents a group of elements: Zn, Cd, and Pb. PC1 also confirmed the effect of the content of the above elements on the ecotoxicity of sediments to *H. incongruens*. Additionally, the lack of significant correlations between sediment properties and Cd, Pb, and Zn contents may suggest their anthropogenic sources or may be due to variability in environmental pollution with these elements among sites. PC2 represents a group of elements including Ni and Cr, which are characterised by low mobility, and their content in bottom sediments is determined mainly by natural factors, as evidenced by positive correlations within PC2 between the content of silt and clay fractions and the content of Mn and Fe in bottom sediments. PC3 is related to the content and mobility of Cu; that element was a significant environmental problem in sediments of the Rybnik reservoir. Overall, it could be observed that the obtained principal components represent both natural (PC2, PC4) and anthropogenic (PC1, PC3) factors determining the content of metals in sediments and their ecotoxicity.

Numerous factors, such as pH, granulometric composition, organic matter, and total contents, determine the chemical fractions of trace elements and their ecotoxicity in bottom sediments (Boguta et al., 2022). Our previous studies revealed that organic matter dominates trace element sorption in the bottom sediments from the Rybnik reservoir, while clay and carbonate dominate in the Rożnów reservoir. Both the neutral to alkaline sediment pH and the low element contents in fractions F1 and F2 (Szara-Bąk et al., 2021) suggest that the mobility of trace elements in the Rożnów reservoir sediments is low. In sediments of the Rzeszów reservoir, clay and TOC contents are likely to be important factors that control metal concentrations (Tarnawski and Baran, 2018). In the current study, a significant positive correlation was also found between the pseudo-total content of metals (Ni, Zn, Pb, Cu, Cd (F1-F3), Cr (F1, F4)) and their concentration in the analysed fractions (SI Table 6).

The second PC analysis, applied for the indices calculated in this study, confirmed the identification of three groups of trace elements as reported above (Figure 4b, Table 8SI): PC1 represents Zn, Pb, and Cd; PC2 and PC4 represent Ni and Cr; and PC3 represents Cu. All geochemical and ecological single-element indices were correlated with each other, and clearly assigned elements to individual PCs. Additionally, the PC analysis confirmed a similar pattern among the three geochemical indices, i.e. I_{geo}, PI, EF, for the analysed metals (Pb, Cd, Zn, Cu). These indices are calculated based on the geochemical background and have been quite widely used for many years in assessing the level of bottom sediment contamination. The disadvantage of I_{geo} and PI is that they do not distinguish among sources (natural, anthropogenic) of trace elements (Kowalska et al., 2018). However, the PCA highlighted differences between I_{geo}, PI (PC2) and EF (PC4) for Ni and Cr. The enrichment factor (EF) is a commonly used index that determines how much metals in samples have increased because of human activity with respect to the natural content (Bern et al., 2019). Apart from the geochemical background of the element, the reference value for the element which is characterised by a low variability of occurrence is needed for its calculation (Kowalska et al., 2018; Bern et al. 2019). Although based on the geochemical background, similarly to I_{geo} and PI, it is a standardised index that allows for the differentiation between natural and anthropogenic sources of trace elements, which turned out to be useful in the context of the current study.

The results from PC analysis overall suggest that sediment contamination with Cd, Pb, Zn, Cu are generally of anthropogenic origin and high contents of these elements in sediments may pose a risk to organisms, whereas sediment contamination with Ni and Cr (PC2, PC4) may be of both natural and anthropogenic origin, but their contents are unlikely to pose an ecological risk. Moreover, a significant positive correlation ($p < 0.05$) between the concentrations of Cd, Zn, Pb and Cu in the PMF ($\sum$F1+F3) and corresponding EF values ($r = 0.89$ for Zn, $r = 0.69$ for Pb, $r = 0.91$ for Cd, $r = 0.92$ for Cu) may confirm that anthropogenic inputs significantly increased trace element concentrations in the reservoir sediments. Since bioavailability and toxicity depend on the forms of trace metals in sediments, metals with high EF values and large labile fractions are generally more mobile and toxic to aquatic organisms (Gao et al. 2018). Moreover, Cd, and Cu with the highest EF values and significant enrichment in F1 (only Cd), along with Cd, Cu, Zn, and Pb, exhibiting the highest concentrations in the PMF (∑F1+F3), might pose a substantial hazard to the test organisms. Zn, Cd and Pb (PC1), along with Cu (PC3), constituted the highest contamination and potential ecological and health risks for bottom sediments of the Chechło (Cd, Zn, Pb), Rybnik (Cu and Zn, Cd), and Rzeszów (Cd) reservoirs.

Undoubtedly, high contents of Zn, Cd, and Pb in bottom sediments of the Chechło reservoir are influenced by the reservoir location and the related anthropogenic sources of metal emission. Earlier research has shown the elevated contents of Cd, Zn and Pb in bottom sediments of this reservoir to be related to the historical exploitation of Zn and Pb ores in the reservoir catchment. The Chechło reservoir is situated in the north-western part of Małopolska, in the Chrzanów poviat, Trzebinia commune, in close proximity to the Olkusz region and the Upper Silesian Industrial Region (Koniarz et al., 2022). In this region, the high metal concentrations in the soil surface is due to metal-bearing minerals whose accumulation depends on natural and anthropogenic factors. The most important factors include geological structure and erosion of shallow ore-bearing Triassic formations, historical mining and processing of zinc and lead ores, which are responsible for surface deposition of zinc-, lead-, and cadmium-rich waste, the emission of metal-rich dust by the smelter, as well as high emission of industrial dust from the Upper Silesian Industrial Region (Koniarz et al., 2022). Similarly, one can expect the relatively high contents of Cd and Zn in bottom sediments of the Rybnik reservoir to be associated with mine exploitation, dust deposition, and sewage discharge in this area. Both reservoirs are located in Silesia, a highly urbanised region in Poland with a high concentratin of industries, including coal and non-ferrous metal mining, power generation, and metallurgy (Baran et al., 2019). Concerning the Rzeszów reservoir, the high Cd content in its sediments is presumably related to the location of the reservoir, i.e. almost in the city centre (about 6 km), as well as close to industrial and transport activities, along with local agriculture (Tarnawski and Baran et al., 2018).

A quite significant Cr contamination combined with a low risk to organisms was observed in bottom sediments of the Rożnów reservoir. The contamination is related to the activity of tanneries in the area near the reservoir and the inflow of Cr-containing effluents (Szara-Bąk et al., 2021).

The study of de Castro-Catala et al. (2016) showed that a high Ni concentration might be a good indicator of recent anthropogenic pollution. Nickel has been widely used in industry and can be found in elevated concentrations in freshwater zones surrounding developed urban areas (de Castro-Catala et al., 2016; Tarnawski and Baran 2018). In contrast, however, Szarek-Gwiazda (2014) found that the high Ni content (15.6-83.1 mg/kg dm) in bottom sediments of sub-mountain reservoirs located in the Carpathian Flysch was mainly explained by a high natural background content in the area.

PC3 was related to the contamination with Cu, which was estimated to be of significant environmental concern only in sediments of the Rybnik reservoir. Our previous study showed that the main source of Cu in sediments of this reservoir is its leaching from the cooling system of the Rybnik power plant and the inflow of municipal wastewater (Baran et al., 2019). Other authors also pointed out that wastewater from power plants that use Cu alloys in heat exchangers of the cooling system can be an important source of Cu in bottom sediments of reservoirs (Loska and Wiechuła, 2003; Bojakowska and Krasuska, 2014).

The second PCA also revealed similarities among the multi-element indices. A significantly positive correlation was found among the geochemical parameters, i.e. PLI and PI_N, ecological parameters, i.e. ∑TU, ∑TRI, RI, PECq, and those related to the health risk assessment, i.e. HI total and CR total. PC1 explained 56.4% of the total variance, the main components of this first factor being single-element indices for Cd, Pb, and Zn along with all multi-element indices (positive loads > 0.50). This essentially suggests that Cd, Zn, and Pb have the greatest impact on the level of sediment contamination and pose the greatest potential ecological and health risks to organisms.

The third PCA confirmed the previously observed difference among the reservoirs in the profile of variables analysed as part of the bottom sediment quality assessment indices (Figure 4c). Most of the points were separated within the plane by the first two principal factors and were concentrated in a small area near the coordinate centre. These points represent bottom sediments from the Narożniki, Brzóza Królewska, Brzóza Stadnicka, Ożanna, Besko, Zesławice, and Głóchów reservoirs (G1, G2). In general, these sediments were contaminated with metals to a low degree, and showed low to medium ecological risk. Points representing bottom sediments from the Chechło, Rybnik, Rzeszów, and Rożnów reservoirs differed from this group. These sediments generally showed contamination or elevated concentrations of metals (Cr – Rożnów, Ni – Rzeszów) and significant ecological risk associated with Cd, Zn, Pb (Chechło), Cu (Rybnik), or Cd (Rzeszów). In addition, these reservoirs, as indicated above, are subject to intensive anthropopressure related to industry (Chechło, Rybnik), transport, and sewage inflow (Rzeszów, Rybnik, Rożnów).

Summarizing the different PCAs, the integration of indices highlighted that the highest contamination level and the greatest potential ecological risks were related to the presence of metals in sediments of the Chechło and Rybnik reservoirs. The risk associated with the sediments of the Rzeszów reservoir was slightly lower, whereas low to medium risk was linked with the sediments of the Rożnów, Besko, Narożniki, Zesławice, Ożanna, Brzóza Królewska, Głuchów, and Brzóza Stadnicka reservoirs. According to the applied indices, Zn, Pb, and especially Cd were responsible for the contamination of the sediments and could pose high ecological and health risks (Cd and Pb). Additionally, Cd, Zn, and Pb taken altogether have the greatest impact on the level of sediment contamination and could pose considerable adverse effects on organisism. Geochemical indices revealed local contamination of bottom sediments with Cr and Ni, although at a level that does not pose a threat to aquatic ecosystems based on ecological indices. In the case of Cu, sediments from only one reservoir (Rybnik) showed a high contamination level associated with a high potential ecological risk.

3.5. Critical comments on the indices used

The geochemical and ecological indices used in this study are based on pseudo-total metal contents in bottom sediments, and some of them allow for a quantitative assessment of the cumulative risk from metals acting collectively. Risk assessment based on these indices seems to be the convenient, and standardized approach, and is quite often used; however, these indices have several disadvantages. Problems arise, among other things, from the fact that the selection of parameters for these indices is arbitrary and thus debatable. For geological indices, the choice of a correct geochemical background is critical, as it will determine the appraisal of the observed contamination (Birch, 2017; Kowalska et al., 2018; Nawrot et al., 2021). In the case of ecological indices, which are mostly based on SQGs, problems are related to a variable degree of bioavailability of metals in sediments, which depends on various properties of sediments and chemical mixtures between environments (Kwok et al., 2014; Zhang et al., 2016; Nawrot et al., 2021). For example, DelValls et al. (2004) reviewed SQGs from many European countries and found that they differ by up to two orders of magnitude for some substances (e.g. As, Cu). Moreover, the existing SQGs cover a limited number of substances, and therefore substances of emerging concern cannot be reliably assessed with this tool (Heise et al., 2020). Another problem of the above-cited indices is that they often have been calibrated to limited study areas, while some authors might assume them to be valid within different regions (Kowalska et al., 2018; Heise et al. 2020).

In contrast to indices, bioassays involve a case specific investigation of adverse, measurable effects on mortality (Ostracodtoxkit), growth (Phytotoxkit, Ostracodtoxkit), and disturbance of physiological processes (Microtox) of living organisms exposed to sediment samples. The three bioassays used examined the responses of organisms representing different trophic levels and adopting various routes of exposure. The use of bioassays can be an effective approach in risk assessment although for each case, it requires extensive research to recognise how metals or other pollutants in bottom sediments correlate with the response of the test organism. The diversity of the test organism responses, the antagonistic and synergistic relationships between elements and other substances and the matrix, and whether a metal is essential or not, all affect the actual effects of the metals on the test organisms (Naracci et al., 2009; Wieczerzak et al., 2016; Goksøyr et al., 2021).

The present study uses another important chemical tool, namely fractionation of metals, which allows to infer about the environmental behaviour of metals (Liang et al., 2017). However, this method provides information regarding potential bioavailability only, which will then often need to be validated by other risk assessment tools, as our findings suggested. The procedure, moreover, is labor intensive (Nawrot et al., 2021).

To sum up, the analysis of generic risk associated with metals in bottom sediments is a complicated process, so it should comprise various methods. In this study, the first step in the risk assessment was the evaluation of the pseudo-total metal content in bottom sediments using geochemical and ecological indices. Their application allowed for an assessment of pollution degree of bottom sediments and potential hazards connected with pseudo-total contents of metals in the sediments to organisms. The second step in the generic risk analysis was the identification of the forms in which metals occurred in bottom sediments. In the risk analysis, the knowledge about the content of readily soluble or exchangeable metal forms is particularly useful, due to assessment their possible mobilisation from the bottom sediments. The third step in risk analysis was the assessment of sediment toxicity using three bioassays. These show the responses of different organisms to the different stresses associated with the bottom sediments, which may include elevated metal contents.

Each method proposed for assessing the quality of bottom sediments has its own advantages and disadvantages. Hence, a combination of these methods should be recommended for a more robust and comprehensive risk assessment of metals in sediments.

4. Conclusions

To appropriately understand the risk associated with metal contamination of bottom sediments, the choice of assessment indexes is key, and both the properties of bottom sediment and the purpose of indices calculation should be considered. Geochemical indices require the use of the geochemical background, and in turn most ecological indices are based on SQG. Both the geochemical background and appropriate interpretation of SQG play an important role of the assessment process.

In this study, among the individual geochemical indices, EF turned out to be the most useful, whereas TRI ($\sum$TRI) has been found to be the most important ecological index. EF values allowed for assessment of enrichment whether anthropogenic or natural, and TRI allowed to assess the potential toxic risk for both acute and chronic effects. All multi-element indices were in agreement, indicating that Cd, Zn, and Pb taken altogether have the greatest impact on the level of sediment contamination and pose the greatest potential ecological and health risks to organisms. Complementarily to these indices, the study of the fractionation of metals, along with sediment ecotoxicity analyses, agreed with the conclusions obtained from the generic risk assessment based on numerical indicators.

Bottom sediments, in order to be properly managed, require a comprehensive evaluation. Our study contributed to build further evidence on the importance of integrating multiple indices for the generic assessment of environmental risks related to the presence of metals in bottom sediments. Future research should focus on pursuing the development of methods and tools for more comprehensive assessments of sediment quality.

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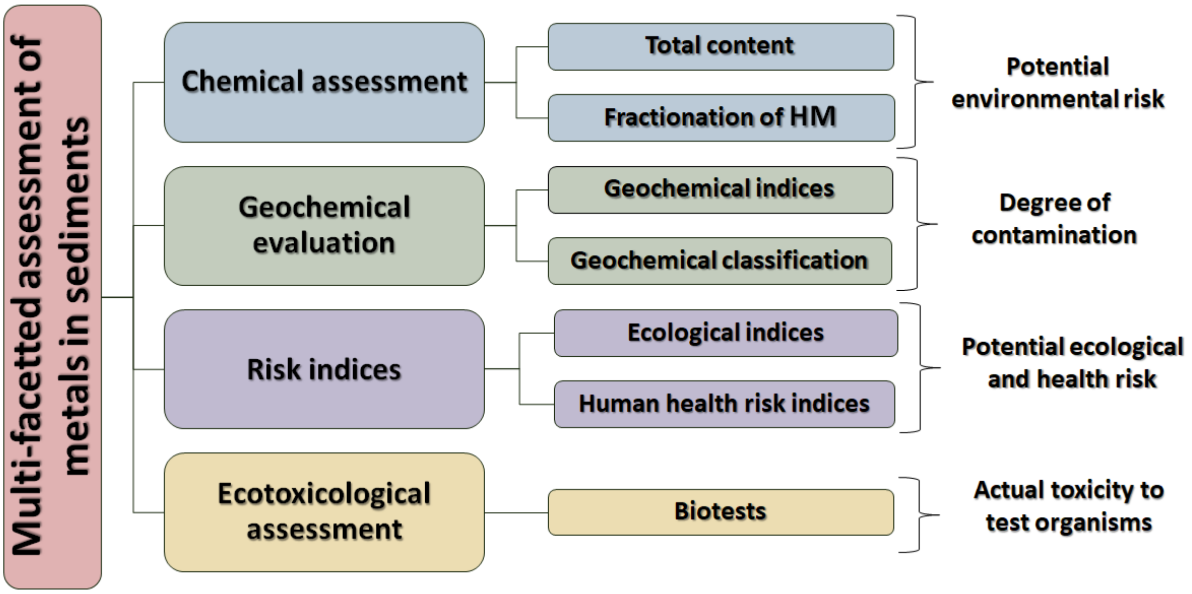
1071 **Graphical abstract**



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Figures

Figure 1. Location of investigated reservoirs and their schematics indicating sampling stations (inlet (green), middle (red), and outlet (blue)

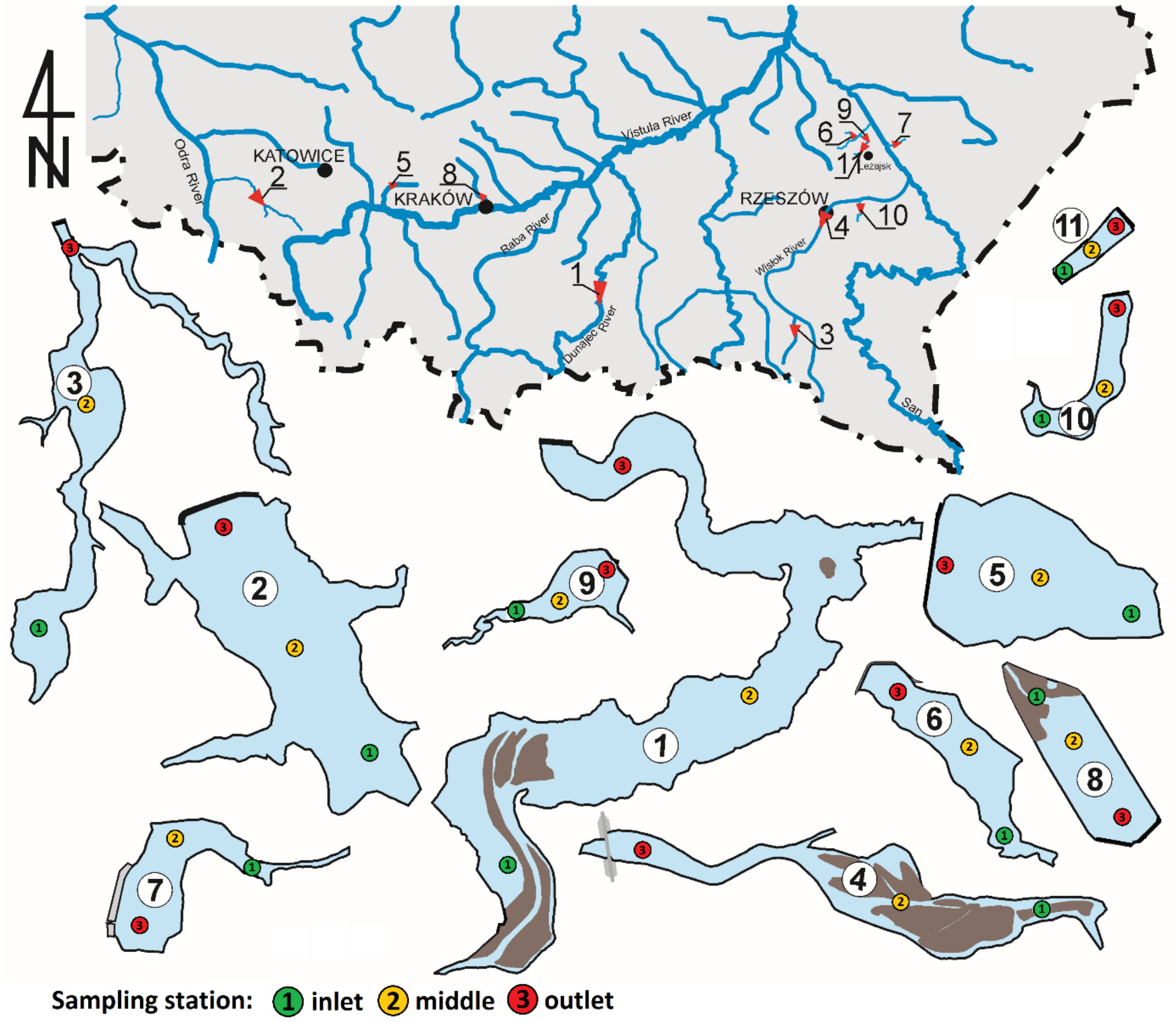


Figure 2. The hazard quotient (HQ), hazard index (HI) and carcinogenic risk (CR) with analysed metals in bottom sediments

*Ro – Rożnów, Ry – Rybnik, B – Besko, Rz – Rzeszów, Ch – Chechło, N – Narożniki, Z – Zesławice, O – Ożanna, BK – Brzóza Królewska, G – Głuchów, BS – Brzóza Stadnicka

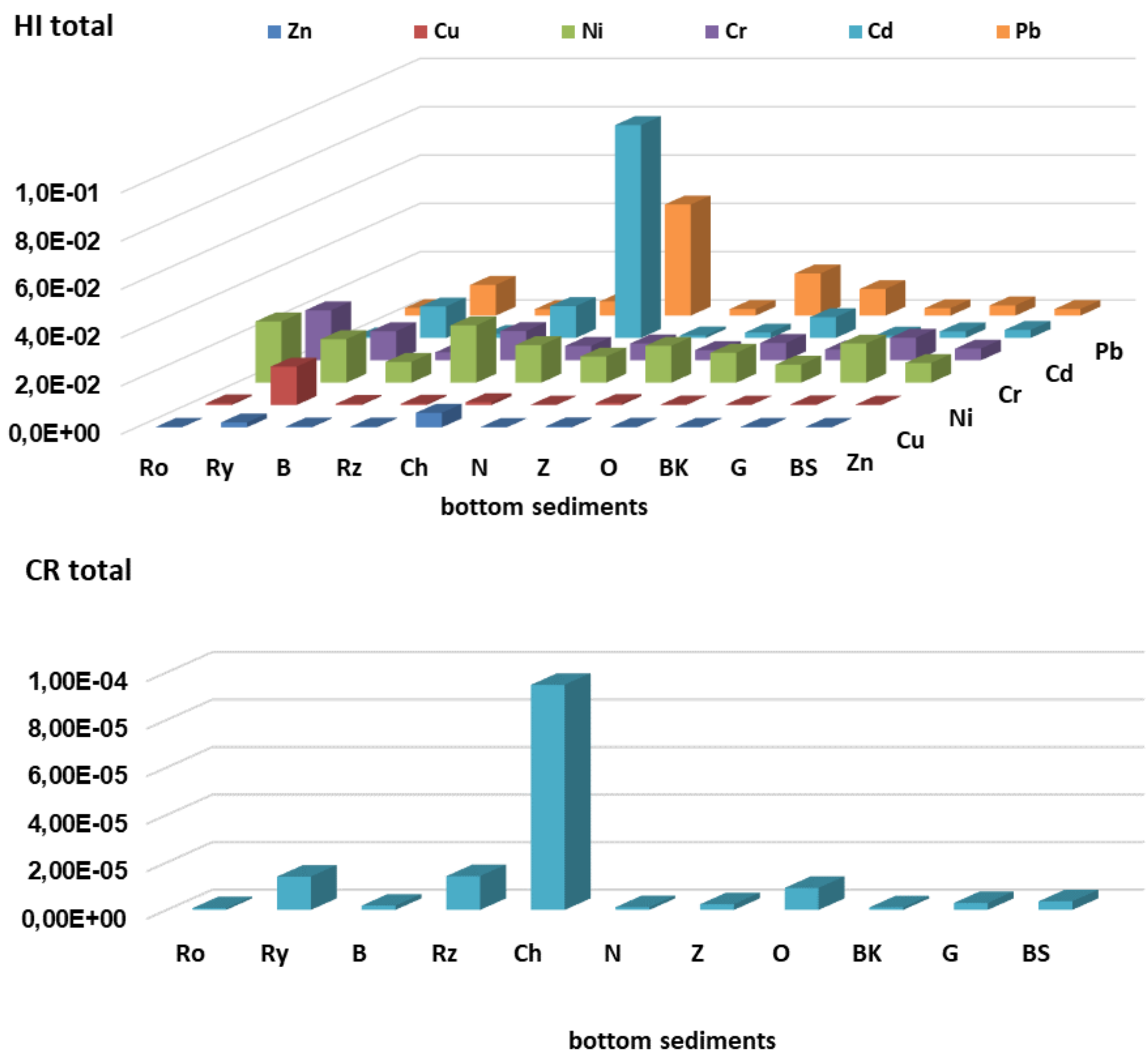


Figure 3. Fractionation of metals in bottom sediments.

*Ro – Rożnów, Ry – Rybnik, B – Besko, Rz – Rzeszów, Ch – Chechło, N – Narożniki, Z – Zesławice, O – Ożanna, BK – Brzóza Królewska, G – Głuchów, BS – Brzóza Stadnicka; **Fraction: F1 – exchangeable, F2 – reducible, F3 – oxidizable, F4 – residual

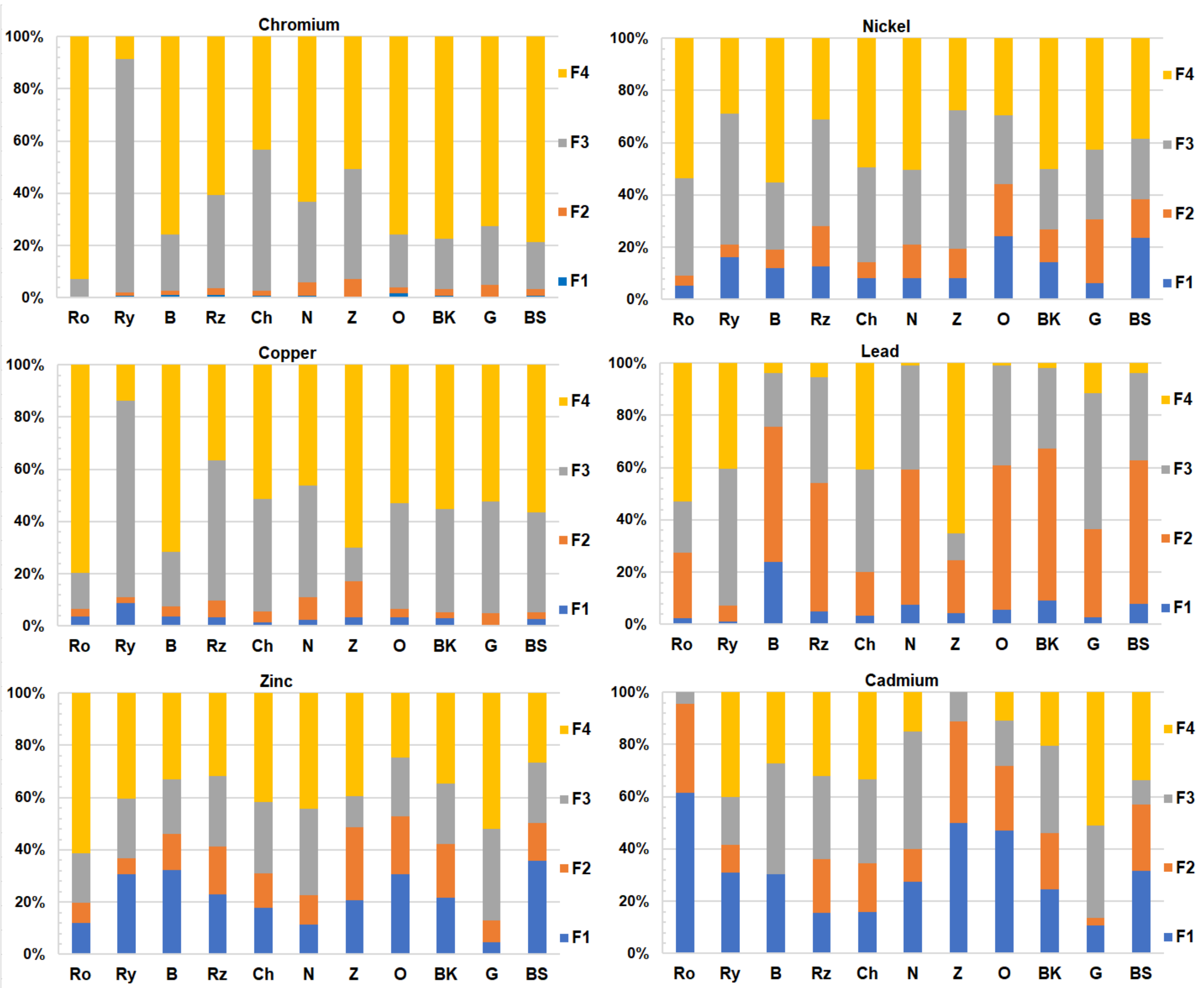
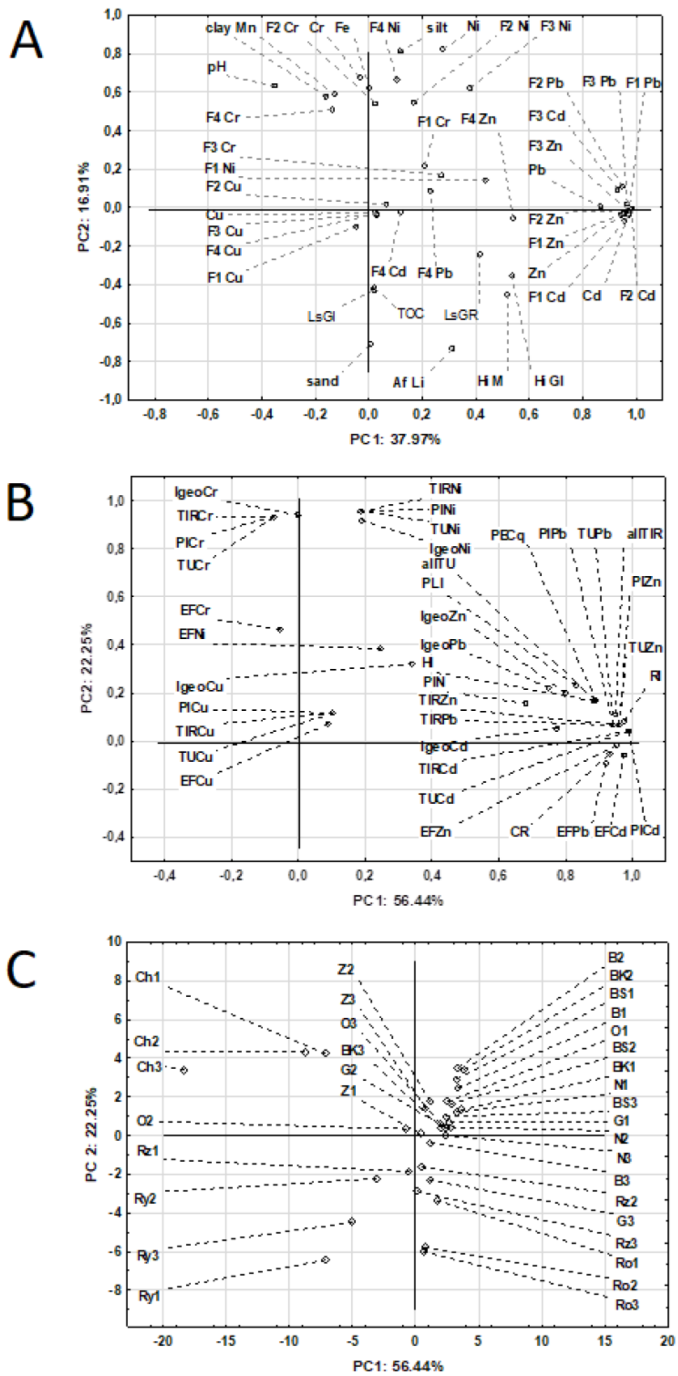


Figure 4. Principal component analysis (PCA) for: physical, chemical and ecotoxicological properties of bottom sediments (A), all indexes (B), factor loadings obtained as a result of metal indicators in sediments collected from the eleven reservoirs (C).

* loadings >0.5 are shown in bold; n=33



Tables

Table 1. Characteristics of water reservoirs

Reservoir / River (abbreviation)	Years of operation	Catchment		Total capacity		Surface area of flooding [ha]	Max/Mean depth [m]
		area [km^2]	dominant anthropogenic pressure	[ML]	typ of reservoir		
Rożnów / Dunajec (1Ro)	80	4 874	agricultural	165 000	Large	1 776	32 / 9.5
Rybnik / Ruda and Nacyna (2Ry)	50	316	industrial	24 000		555	11.0 / 5.5
Besko / Wisłok (3B)	44	207	industrial	14 200		126	29 / 12.0
Rzeszów / Wisłok (4Rz)	49	2 061	industrial	1 800		68.2	4.0 / 1.6
Chechło / Chechło (5Ch)	62	42.5	industrial	600	Small	54.4	3.8 / 1.5
Narożniki / Dęba (6N)	21	25.0	agricultural	283		28.0	3.5 / 1.0
Zesławice / Dłubnia (7Z)	56	218	industrial	228		9.5	3.6 / 2.4
Ożanna / Złota (8O)	44	136	agricultural	252		18.0	3.5 / 1.4
Brzóza Królewska / Tarlaka (9BK)	37	30.4	agricultural	49	Very small	6.1	3.2 / 0.8
Głuchów / Graniczna (10G)	27	10.1	agricultural	23		1.5	2.0 / 1.0
Brzóza Stadnicka / Tarlaka (11BS)	27	7.6	agricultural	11		1.2	1.2 / 0.8

1102 Table 2SI. Calculation of geochemical and ecological indices

Formula	Explanation	Reference
Geoaccumulation index (I_{geo}) – individual $$I_{geo} = log_2 \cdot \left[\frac{C}{1.5 \cdot B}\right]$$	C – content of single M* in bottom sediment 1.5 – constant allowing the analysis of fluctuations of M content as result of natural processes B – M's content in reference background (Bojakowska and Sokołowska 1998)	Müller 1969 Kulbat and Sokołowska 2019
Single Pollution Index (PI) – individual $$PI = \frac{C}{B}$$	C – content of single M in bottom sediment B – M's content in reference background (Bojakowska and Sokołowska 1998)	Wieczorek and Baran 2022
Enrichment factor (EF) – individual $$EF = \frac{\left(\frac{C}{C_{ref}}\right)}{\left(\frac{B}{B_{ref}}\right)}$$	C – content of single M in bottom sediment C_{ref} – content of Fe in bottom sediment B – M's content in reference background (Bojakowska and Sokołowska 1998) B_{ref} – content of Fe in reference background	Gao et al. 2018 Castro et al. 2021
Pollution load index (PLI) – complex $$PLI = \sqrt[n]{PI_1 \cdot PI_2 \cdot \cdots PI_n}$$	n – the number of analysed M PI – calculated values of index for single M	Kulbat and Sokołowska 2019
Improved Nemerow pollution index (PI_N) – complex $$PI_N = \sqrt{\frac{\left(\frac{1}{n}\sum_{i=1}^{n} PI\right)^2 + (PI_{max})^2}{n}}$$	n – the number of analysed M PI – calculated values of index for single M PI_{max} – calculated maximum value of index for all M	Wieczorek and Baran 2022
Potential ecological risk (RI) – complex $$RI = \sum_{i=1}^{n} E_r^i$$	n – the number of analysed M E_r – single index of the ecological risk factor calculated based on the equation: $$E_r^i = T_r^i \cdot PI$$ PI – calculated values of index for single M T_r^i – the toxicity response coefficient of single TE (Håkanson 1980)	Aleksander-Kwaterczak et al. 2021
Sediment quality guideline (SQG): C < TEC sample is predicted to be non-toxic C > PEC sample is predicted to be toxic	C – content of single M in bottom sediment TEC – Threshold Effect Concentration PEC – Probable Effect Concentration	MacDonald et al. 2000
Risk assessment code (RAC)	Content % of single elements in mobile fraction (F1 – BCR)	Zhang et al. 2017
Toxic unit TU. ∑TU $$\sum TU = TU = \sum_{i=1}^{n} \frac{C}{PEC}$$	C – content of single M in bottom sediment PEC – Probable Effect Concentration (MacDonald et al. 2000)	Gao et al. 2018
Toxic risk index TRI $$\sum TRI = TRI = \sqrt{\frac{\left(\frac{C}{TEC}\right)^2 + \left(\frac{C}{PEC}\right)^2}{2}}$$	C – content of single M in bottom sediment TEC − Threshold Effect Concentration (MacDonald et al. 2000) PEC – Probable Effect Concentration (MacDonald et al. 2000)	Gao et al. 2018
PECQ $$PECQ = \sum_{i=1}^{n} \frac{C}{PEC} / n$$	C – content of single M in bottom sediment PEC – Probable Effect Concentration (MacDonald et al. 2000) n − the number of analysed M	Tarnawski and Baran 2018
Non-carcinogenic risk HQ: ingestion: $$HQ\ ing = \frac{CS \cdot EF \cdot ED \cdot IR_O \cdot CF_1}{BW \cdot AT\ \cdot RfDing}$$ dermal:	CS – concentration of M in sediment (mg/kg) EF – exposure frequency (days/year) ED – exposure duration (years) IR_O – ingestion rate for sediments (mg/day) CF_1 – conversion factor (10-6 kg/mg) BW – body weight (kg)	Wcisło et al. 2016 Li et al. 2020 Gruszecka-Kosowska et al. 2020

$$HQd = \frac{CS \cdot EF \cdot ED \cdot SA \cdot AF \cdot ABS_d \cdot CF_1}{BW \cdot AT \cdot RfDd}$$ inhalation: $$HQ\ inh = \frac{CS \cdot EF \cdot ED \cdot IR_1 \cdot 1/PEF}{BW \cdot AT \cdot RfCinh}$$	AT – exposure averaging time (days) = ED 365days/year for noncarcinogenic substances = 70 years x 365 days/year for carcinogenic substances AD – dermally absorbed dose of a substances (mg/kg/day) SA – skin surface area in contact with dust (cm^2) ABS_d – dermal absorption factor. specific for the substance (unitless) PI – dose of a chemical absorbed through the respiratory route by inhaling particles (mg/kg/day) IR1 – inhalation rate value of daily lung ventilation (m^3/day) PEF – dust particle emission factor (m^3/kg) AF- coefficient of dust adhesion to the skin [mg/cm^2/day] RfD – reference dose for a given exposure route SF – slope factor for a given exposure route. ABS_d – dermal absorption factor. specific for the substance [unitless]	
Carcinogenic risk CR: ingestion: $$CR\ ing = \frac{CS \cdot EF \cdot ED \cdot IR_O \cdot Sfing \cdot CF_1}{BW \cdot AT}$$ dermal: $$CR\ d = \frac{CS \cdot EF \cdot ED \cdot SA \cdot AF \cdot ABS_d \cdot Sfing \cdot CF_1}{BW \cdot AT}$$ inhalation: $$CR\ inh = \frac{CS \cdot EF \cdot ED \cdot IR_1 \cdot Sfing \cdot 1/PEF}{BW \cdot AT}$$		

*M– metal

Table 3. Physical, chemical and ecotoxicological properties of bottom sediments (means of reservoir)

	[1]Ro	Ry	B	Rz	Ch	N	Z	O	BK	G	BS
Physico-chemical properties											
Sand %	14	80	6	8	56	59	8	64	66	18	70
Silt %	67	17	13	38	37	24	63	16	15	47	16
Clay %	19	3	81	54	7	17	29	20	19	35	15
pH	7.1	7.2	7.3	7.1	5.5	7.5	7.4	5.1	5.3	7.0	6.3
TOC %	1.49	5.56	1.75	2.50	5.85	1.42	5.56	3.08	24.7	0.88	2.55
Total content of metals (mg/kg d.m., Fe g/kg d.m.)											
Cr	60.8	35.3	9.7	35.5	17.5	20.4	12.4	21.1	13.2	27.5	14.2
Ni	35.8	25.4	12.2	33.5	21.9	15.2	21.5	17.5	10.5	22.8	11.5
Zn	67	605	113	107	1777	53	126	80	72	55	69
Pb	10.8	43.3	9.1	20.0	156.6	9.2	59.4	37.5	10.4	14.4	9.3
Cu	26.9	626	18.9	20.8	46.2	5.2	32.2	7.3	5.8	10.2	5.3
Cd	0.25	4.87	0.62	4.93	32.9	0.39	0.83	3.21	0.36	1.02	1.25
Mn	680	699	302	646	266	521	216	247	204	924	304
Fe	15.4	9.1	5.9	18.2	10.5	10.8	13.9	14.5	9.3	22.1	11.0
Ecotoxicological properties (*PE%)											
[2]LsGI	13	11	-10	12	14	0	6	36	61	14	4
LsRI	-5	8	11	57	47	-8	-12	43	39	4	24
HiM	10	24	10	2	67	37	0	38	5	0	55
HiGI	40	54	44	26	76	36	20	46	38	38	51
Af LI	38	62	13	12	76	21	16	91	83	20	68
Classes	II	III	II	III	III	II	I	III	III	II	III
Relevance %	67	46	17	22	79	67	100	72	75	67	67

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[2]LsGI – *Lepidium sativum*, germination inhibition; LsRI – *Lepidium sativum*, root growth inhibition; HiM – *Heterocypris incogurense*, mortality; HiGI – *Heterocypris incongurens*, growth inhibition; AfLI – *Allivibrio fischeri*, luminescence inhibition

*PE < 20% the sample is non-toxic; 20% ≤PE< 50%: the sample is low toxicity; 50% ≤PE< 100%: the sample is toxic; PE = 100%: the sample is very toxic

Table 4. Mean values of the geochemical indices

Elements	[1]Ro	Ry	B	Rz	Ch	N	Z	O	BK	G	BS
*Geoaccumulation index (I_{geo})											
Cr	2.74	1.91	-0.13	1.97	0.88	1.15	0.45	1.15	0.39	1.55	0.59
Ni	1.98	1.46	-0.04	1.89	1.14	0.73	1.18	0.92	0.02	1.26	0.29
Zn	-0.72	2.43	-0.81	-0.05	3.80	-1.12	0.17	-0.52	-1.13	-1.09	-0.77
Pb	-1.07	0.87	-1.41	-0.18	2.74	-1.39	1.38	-0.04	-1.40	-0.72	-1.35
Cu	1.32	5.88	0.81	0.98	2.04	-1.06	1.18	-0.58	-1.14	-0.21	-1.12
Cd	-1.62	2.67	-0.29	2.57	5.33	-0.95	0.10	1.85	-1.39	0.33	0.69
Single Pollution Index (PI)											
Cr	10.13	5.88	1.61	5.92	2.92	3.40	2.07	3.52	2.19	4.58	2.37
Ni	5.96	4.23	2.02	5.58	3.66	2.54	3.59	2.91	1.76	3.81	1.91
Zn	0.92	8.30	1.55	1.46	24.35	0.72	1.73	1.09	0.99	0.76	0.94
Pb	0.72	2.89	0.61	1.33	10.44	0.61	3.96	2.50	0.69	0.96	0.62
Cu	3.84	89.42	2.70	2.97	6.61	0.74	4.59	1.05	0.82	1.46	0.76
Cd	0.51	9.74	1.24	9.86	65.85	0.79	1.66	6.42	0.72	2.04	2.50
Enrichment factor (EF)											
Cr	7.85	7.72	3.38	4.08	3.27	4.03	1.78	2.90	4.14	2.64	2.65
Ni	4.62	5.55	3.67	3.84	3.99	3.00	3.08	2.45	3.18	2.18	2.15
Zn	0.71	10.89	2.42	1.00	26.02	0.85	1.50	0.90	1.20	0.44	1.02
Pb	0.56	3.79	1.50	0.92	11.79	0.69	3.41	1.80	1.01	0.56	0.68
Cu	2.97	117.35	7.66	2.05	7.50	0.88	4.00	0.86	1.44	0.78	0.80
Cd	0.39	12.79	3.47	6.70	72.44	0.95	1.44	5.15	1.05	1.12	3.21
Pollution load index (PLI)											
All elements	2.06	8.94	1.38	3.46	10.19	1.13	2.53	2.27	1.00	1.79	1.28
	3.96 (0.84-11.59)				4.03 (0.81-15.96)				1.37 (0.53-2.57)		
Improved Nemerow pollution index (PI_N)											
All elements	4.40	37.42	1.41	4.55	27.98	1.51	2.74	2.89	1.00	2.09	1.38
	11.94 (0.88-42.30)				8.78 (1.09-47.76)				1.49 (0.57-2.91)		

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*I_{geo} ≤0 Class 0 - practically uncontaminated, 0≤ I_{geo}<1 Class I - uncontaminated to moderately contaminated, 1≤ I_{geo}<2 Class II - moderately contaminated, 2≤ I_{geo}<3 Class III - moderately to heavily contaminated, 3≤ I_{geo}<4, Class IV - heavily contaminated, 5≤ Igeo Class VI - extremely contaminated; PI <1 unpolluted, low level of pollution, 1≤ PI <3 moderately polluted; 3 ≤PI strongly polluted; EF ≤1no enrichment, 1< EF ≤3minor enrichment, 3< EF ≤5moderate enrichment, 5< EF ≤10moderately severe enrichment, 10< EF ≤25severe enrichment, 25< EF ≤50very severe enrichment, EF >50extremely severe enrichment; PLI <1 unpolluted, PLI =1 baseline level of pollution, PLI >1 polluted; PI_N <0.7: Grade 1- safety domain, 0.7≤ PI_N <1.0, Grade 2 - precaution domain, 1.0≤ PI_N <2.0, Grade 3 - slightly polluted domain, 2.0≤ PI_N <3.0, Grade 4 - moderately polluted domain, PI_N >3.0, Grade 5 - seriously polluted domain

Table 5. Mean values of the ecological indexes

Elements	[1]Ro	Ry	B	Rz	Ch	N	Z	O	BK	G	BS
Toxic Unit (TU)											
Cr	0.55	0.32	0.09	0.32	0.16	0.19	0.11	0.19	0.12	0.25	0.13
Ni	0.73	0.52	0.27	0.68	0.45	0.31	0.44	0.36	0.21	0.47	0.23
Zn	0.15	1.32	0.25	0.23	3.86	0.11	0.27	0.17	0.16	0.12	0.15
Pb	0.08	0.33	0.07	0.15	1.20	0.07	0.46	0.29	0.08	0.11	0.07
Cu	0.24	5.69	0.17	0.19	0.42	0.05	0.29	0.07	0.05	0.09	0.05
Cd	0.05	0.97	0.12	0.99	6.59	0.08	0.17	0.64	0.07	0.20	0.25
Toxic risk index (TRI)											
Cr	1.07	0.62	0.17	0.63	0.31	0.36	0.22	0.37	0.23	0.48	0.25
Ni	0.73	0.52	0.25	0.68	0.45	0.31	0.44	0.36	0.21	0.47	0.23
Zn	0.41	3.69	0.69	0.65	10.82	0.32	0.77	0.48	0.44	0.34	0.42
Pb	0.22	0.88	0.19	0.41	3.19	0.19	1.21	0.76	0.21	0.29	0.19
Cu	0.47	11.05	0.33	0.37	0.82	0.09	0.57	0.13	0.10	0.18	0.09
Cd	0.19	3.55	0.45	3.59	23.97	0.29	0.60	2.34	0.26	0.74	0.91
∑TU											
All elements	1.81	9.15	0.97	2.57	12.68	0.81	1.74	1.72	0.70	1.24	0.88
	3.62 (0.84-11.59)				4.03 (0.81-15.96)				1.37 (0.53-2.57)		
∑Toxicity risk index (∑TRI)*											
All elements	3.09	20.31	2.08	6.32	39.56	1.56	3.81	4.45	1.46	2.51	2.10
	7.95 (1.16-24.65)				12.34 (1.12-64.41)				2.02 (0.70-3.34)		
PECQ											
All elements	0.30	1.53	0.16	0.43	2.11	0.13	0.29	0.29	0.12	0.21	0.15
	0.60 (0.09-1.83)				0.71 (0.10-3.44)				0.16 (0.07-0.29)		
RI											
All elements	89.1	795	68.5	358	2109	50.6	116	233	43.4	102	97
	327 (50.9-956)				627 (37.1-3362)				80.9 (20.7-125.7)		

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*∑TRI value: TRI <5, no toxic risk; TRI 5-10, low toxic risk; TRI 10-15, moderate toxic risk; TRI 15-20, considerable toxic risk; TRI >20, very high toxic risk, PECQ: non-adverse effect (PECQ <0.1), slightly adverse effect (0.1 < PECQ <0.5), moderate effect (0.5< PECQ<1.0), heavy effect (PECQ> 1.0); RI <150 low ecological risk; 150≤ RI <300 moderate ecological risk, 300≤ RI <600 considerate ecological risk, RI >600 very high ecological risk