Geochemistry indices and biotests as useful tools in the assessment of the degree of sediment contamination by metals

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Abstract: Ecological and geochemical indicators have been widely accepted as tools with the potential for rapid risk assessment of metal contamination of bottom sediments. In this study we propose a selection of such indicators to characterize the potential ecological risks stemming from metal contamination of the bottom sediments of the Chechło reservoir (S Poland). The Chechło reservoir is located in an area formerly occupied by zinc and lead ore mining and processing industry. High amounts of metals, especially zinc (39.37–4772.00 mg/kg d.m.), cadmium (0.37–21.13 mg/kg d.m.) and lead (4.50–434.49 mg/kg d.m.) have been found in the bottom sediments. Both geochemical (CD – contamination degree) and ecological indices (mean PECQ) were indicative of bottom sediment contamination and their potential toxicity to living organisms. Most of the bottom sediment samples (71%) examined were toxic for *Heterocypris incongruens*, while only 9% of the samples were toxic to *Sinapis alba*. However, no significant correlations between the metal content and the response of the test organisms were observed. Correlation and principal component analyses (PCA) showed that silt and clay fractions were the key factors influencing the metal content in the sediments. Our study makes a contribution to building evidence of the need to integrate several indices for the assessment of environmental risks related to the presence of metals in bottom sediments rather than relying on a single one.

Keywords: metals, bottom sediments, zinc and lead ore mining area, ecotoxicity, risk assessment

INTRODUCTION

Bottom sediments constitute an important element of aquatic ecosystems, providing a habitat for organisms, but they also absorb various pollutants, making them a natural geosorbent when pollutants introduced to the water accumulate (Förstner & Salomons 2010, Shirneshan et al. 2013, Koniarz et. al. 2014, 2015, Baran et. al. 2016, Kulbat & Sokołowska 2019, Tytła & Kostecki 2019, Vignati et al. 2019, Zhou, et al. 2020). Furthermore, the supply of harmful substances is particularly intensive in areas of strong industrial human pressure. Metals constitute a large proportion of bottom sediment pollutants due to their persistence, toxicity, tendency to concentrate in organisms and incorporation into food chains (Baran et al. 2016). Currently, the ecological risk assessment of heavy metals in bottom sediments is attracting considerable attention in the subject literature (Kulbat & Sokołowska 2019, Tytła & Kostecki 2019, Heise et al. 2020, Castro et al. 2021, Nawrot et al. 2021, Baran et al. 2023). Some researchers advocate assessing the potential risk based on chemical analyses, i.e. assessing the total content of metals in sediments and their mobility (Apitz 2011, Baran et al. 2019). Geochemical indicators are frequently used in assessing the risk related to the presence of metals in bottom sediments, while also considering the degree of contamination of sediments by metals and identifying their sources (Kulbat & Sokołowska 2019, Tytła & Kostecki 2019). Biological aspects have been taken into account in other indicators, such as the sediment quality standards (SQG) (MacDonald et al. 2000, Apitz 2011), which allows for the assessment of the potential risk from the presence of metals to living organisms inhabiting the bottom sediment environment (Baran et al. 2016, Szara et al. 2020). However, ecological risk assessment based exclusively on chemical indicators may not always be indicative of the real risk related to the presence of heavy metals in bottom sediments. Biotests can be a useful tool in the assessment of the ecological risk related to the presence of heavy metals in bottom sediments (Baran et al. 2016, Heise et al. 2020). The use of biotests has many advantages over chemical methods, the most important being that biotesting, as a method for assessing the quality of bottom sediments, allows the investigation of the effects caused by all contaminants present in the sediment, taking into account bioavailability and interactions between substances in the sediment (Apitz 2011, Heise et al. 2020), which in turn may save time and cost of analyses. However, due to the difference in test sensitivity, it is essential to use a battery of biotests (Baran et al. 2023). Currently, a battery of biotests is used as a monitoring tool to assess ecotoxicity in sediments, with the battery including organisms from all trophic levels: algae or plants as producers, invertebrates or vertebrates as consumers, and bacteria as decomposers (Heise et al. 2020, Baran et al. 2023).

In order to properly understand the risks associated with metal contamination of bottom sediments, the selection of indicators is crucial. This study aimed to investigate whether the use of geochemical, ecological and ecotoxicological indicators would allow a comprehensive assessment of the potential ecological risk associated with the metal content, as well as to identify their origin in contaminated bottom sediments of the Chechło reservoir. The geochemical and ecological indicators used are based on total metal contents in sediments, and some of them allowed for a quantitative assessment of the cumulative risk from metals. The utilized bioassays allowed the evaluation of the extent to which metals in sediments negatively affect this environment. A comprehensive assessment of metal content in sediments allowed estimates to made of the needs for reservoirs, and for public health protection measures to be considered.

STUDY AREA

The Chechło reservoir is located in the catchment of the Chechło River, in southern Poland, 40 km to the west of Krakow (Fig. 1). It was built in the years 1944–1945 as a result of the construction of an earth dam (from local materials) with a trapezoidal cross-section (Zawisza et al. 2014, Koniarz et al. 2022). The dam is located about 16 km from the mouth of the Chechło River to the Vistula River and approx. 2 km south of Trzebinia. The reservoir has a maximum capacity of $10.74 \cdot 10^8$ m^3 and 0.544 km^2 of the reservoir backwater area. The water damming height is 6.5 m (276.03 m above sea level). The Chechło reservoir is located in an area formerly occupied by zinc and lead ore mining and processing industry. Underground mining of lead ores was documented in the area as far back as the early 15th century (Zawisza et al. 2014). The rapid development of industrial plants in Upper Silesia in the second half of the 20th century contributed to the emission of large amounts of dust being soil contamination in the catchment (Pasieczna et al. 2008). The long history of metal ore mining and processing, together with transport, manufacturing and use of construction materials connected with it, led to significant degradation of the natural environment of the Trzebinia commune where the analyzed reservoir is located.

METHODS AND MATERIAL

Sample collection

Field studies were carried out in the Chechło reservoir and on the Chechło River floodpain in 2014. A total of 56 surface samples of sediment were collected in four zones: upper part (7 samples), middle part (16 samples), lower part (15 samples), backwater (18 samples) (Fig. 1).

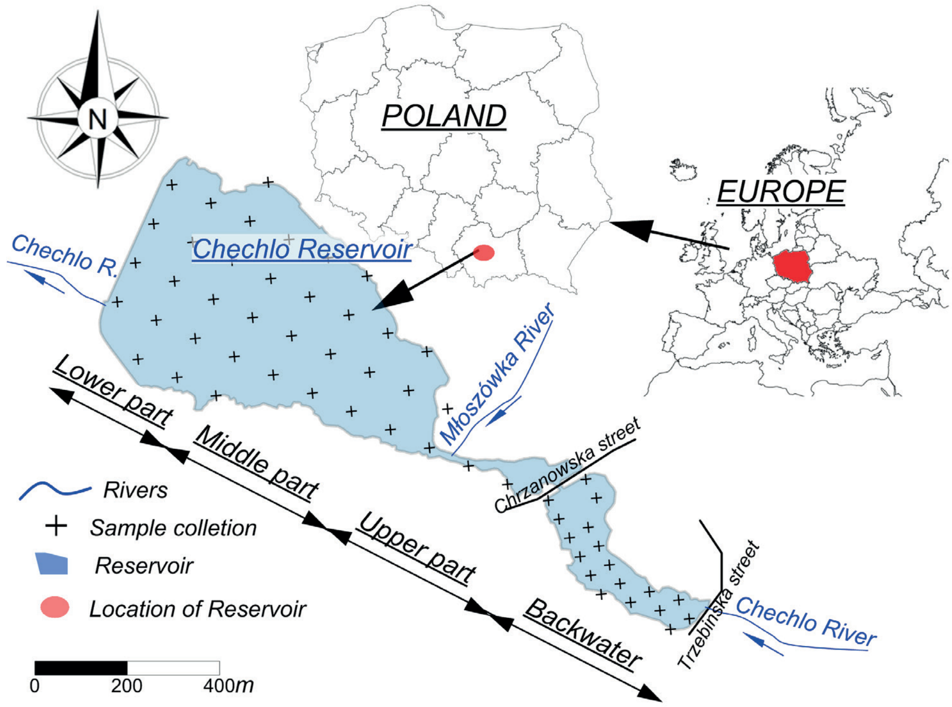

Fig. 1. *Location of sample stations*

The samples were taken with an Ekman sampler from five points around the designated sampling location, and then mixed. The sediment samples were taken from a depth of 0–15 cm. The collected samples were transported and stored in foil bags at approx. 4°C.

Physical and chemical analysis

After being delivered to the laboratory, the collected samples were air-dried and sieved through Ø2 mm sieve. In the air-dried samples of the bottom sediments, the following parameters were determined: particle size distribution using the PKN-CEN ISO/TS 17892-4 method, pH in 1 mol/dm^3 KCl by potentiometry, total organic carbon on the CNS Elementar Vario MAX cube analyzer. Total metal concentration (Zn, Cd, Pb, Cu, Ni, Cr, Fe, Mn) in the sediments was assessed after hot digestion in a mixture of HNO_3 and $HClO_3$ (3:2 v/v) acids (suprapure, MERCK). Metal concentrations were analyzed using the ICP-OES method (Inductively Coupled Plasma Atomic Emission Spectroscopy) on an Optima 7300 DV (PerkinElmer) (Koniarz et al. 2014, 2022, Baran et al. 2016). The total content of Hg in the bottom sediments was determined using the Atomic Absorption Spectrophotometer (AAS) for mercury determination (Advanced Mercury Analyser, AMA 254). The accuracy of the performed analyses was tested using reference material CRM 16-05 (fresh water sediment, trace elements, LGC Standards). The results showed that the percentage of recovery ranged from 73% Fe to 106% Ni.

Assessment of ecological risk potential

The bottom sediment quality was assessed using two criteria, i.e. geochemical and ecotoxicological. The first criterion allowed for the degree of bottom sediment contamination to be assessed in comparison with the local geochemical background. The second criterion allowed for the evaluation of the effect of contaminated sediments on aquatic organisms.

Geochemical indicators

The classification of the pollution of the sediments with metals was based on Bojakowska's geochemical quality classes of bottom sediments (Bojakowska 2001), as well as the calculated contamination factor (CF) and contamination degree (CD) of metals in the sediment samples (Baran et al. 2016, 2019, Al-Mur et al. 2017). The CF was calculated as a ratio between the content of a heavy metal in a bottom sediment and its geochemical background (73 mg Zn, 7 mg Cu, 6 mg Ni and Cr, 15 mg Pb, 0.5 mg Cd, 0.05 mg Hg per kg d.m.) (Bojakowska 2001). The level of heavy metal contamination was assessed using four categories: CF < 1 low contamination; 1 ≤ CF < 3 moderate contamination; 3 ≤ CF < 6 high contamination; CF ≥ 6 very high contamination (Tytła & Kostecki 2019). The total degree of contamination (CD) was calculated based on the sum of all contamination factors (CF) and four categories were used in the assessment: CD < 8 low contamination; 8 ≤ CD < 16 moderate contamination; 16 ≤ CD < 32 considerable contamination, and CD ≥ 32 very high contamination (Tavakoly Sany et al. 2012).

Ecotoxicological indicators

In the ecotoxicological criterion, sediment quality guidelines (SQGs) of the numerical indices, i.e. Threshold effect concentration (TEC) and probable effect concentration (PEC), were used to assess the potential hazard connected with the content of metals in the sediments to organisms (Apitz 2011, Baran et al. 2016). The TEC values (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, Hg 0.18 mg/kg) represent the content of metals below which harmful effects on benthic organisms are not expected. The PEC values (Zn 459 mg/kg, Cu 149 mg/kg, Pb 128 mg/kg, Cd 4.98 mg/kg, Ni 48.6 mg/kg, Cr 111 mg/kg, Hg 1.10 mg/kg) were used for the identification of the content of metals which is expected to be harmful to organisms once exceeded (MacDonald et al. 2000). The mean PECQ was used for the assessment of the potential harmful effect associated with metals when they occur in a complex mixture in the sediments (Apitz 2011, Tarnawski & Baran 2018). For each sample, the mean PECQ was calculated as the mean of the ratio of metals content to its corresponding PEC (probable effect concentration). The mean PECQ < 0.1 corresponded to no-adverse effect; mean PECQ between 0.1 to 0.5 corresponded to a slightly adverse effect (low probability to toxic effect), mean PECQ between 0.5 to 1 corresponded to a moderate effect, and mean PECQ > 1.0 corresponded to a heavy effect (a high probability of a toxic effect) (Tavakoly Sany et al. 2014, Tarnawski & Baran 2018). Perrodin et al. (2006) used two ranges of the mean PECQs for ranking samples in terms of incidence of toxicity: < 0.5, indicating a low potential toxicity to the benthic fauna, and >0.5 representing a high potential risk to the benthic fauna.

Ecotoxicity analysis

The ecotoxicity of the bottom sediments was studied using biotests based on two trophic levels: producers and consumers. In the battery of biotests used, the plant, *Sinapis alba* (Phytotoxkit), was the producer cell, and a crustacean, *Heterocypris incongruens* (Ostracodtoxkit), was the consumer. The Phytotoxkit and Ostracodtoxkit test procedures were described in detail in our earlier studies (Baran et al. 2016, Szara et al. 2020). Phytotoxkit is a plant test based on the evaluation of germination and early growth of *Sinapis alba* (Phytotoxkit 2004, ISO 11269-1, 2012). The test was performed in three repetitions according to standard procedures (Phytotoxkit 2004). 90 cm^3 of the samples of sediment was placed and covered with a paper filter on the bottom part of the test plate. Ten seeds of the plant were sown in one line at the same distance from one another. Plates were incubated in the dark for 72 hours at 25°C in an upright position. After incubation, photographs were taken to measure root lengths. Then, we calculated germination inhibition (GI) and root length inhibition (RLI) relative to the reference sediment (Phytotoxkit 2004):

$$\text{GI or RLI} = [(A - B)/A] \cdot 100\%,$$

where A is the mean number of germinated seeds or root length in the control, and B is the mean number of germinated seeds or root length in the test sediment.

The Ostracodtoxkit direct contact test was used to determine the toxicity of bottom sediment samples to consumers (Ostracodtoxkit F 2001, ISO 14371, 2012). This is a 6-day test which determines mortality and growth inhibition of the *Heterocypris incongruens* crustacean. Previously hatched organisms were transferred to the test wells together with the tested sediment. After 6 days of incubation, we counted the number of living organisms and measured their length in both the sediment and a reference sediment sample. According to the standard procedure provided by the manufacturer, the reference sediment was used as reference (control) sediment in the test (Ostracodtoxkit F 2001). The obtained results allowed for the calculation of the mortality and length inhibition (LI) of the test organisms (Ostracodtoxkit F 2001):

$$LI\% = 100 - [(B/A) \cdot 100],$$

where A is the mean growth of ostracode in the reference sediment, and B is the mean growth of ostracode in the test sediment.

We assessed the toxicity of the bottom sediments estimating the percent toxic effect (PE) for the biotests used. We assigned samples to appropriate toxicity: PE ≤ 20% no significant toxic effect, no toxic sample; 20% < PE ≤ 50% significant toxic effect, low toxic sample, 50% < PE < 100% significant toxic effect, toxic sample; PE = 100% high acute hazard, very toxic sample (Persoone et al. 2003).

Statistical and graphical analysis

The properties of the sediments were characterized using three basic statistical parameters: position (central tendency) represented by the median and arithmetic mean; spread (dispersion): minimum, maximum, standard deviation (SD), coefficient of variation (CV), and asymmetry represented by the skewness coefficient. The Pearson correlation coefficient and principal component analysis (PCA) were used to assess the relationship between the analyzed properties of the bottom sediments. The results were verified statistically using the Statistica 13 software package. The maps were created in Surfer 16 using the geostatistical gridding method (kriging). Kriging was custom-fit to a data set by specifying the appropriate variogram model.

RESULTS AND DISCUSSION

Basic properties of bottom sediments

The mean fraction content in the collected bottom sediment samples decreased as follows: sand > silt > clay. Of the 56 samples, more than half contained between 50–100% sand and exhibited negative skewness (–0.18). These were samples from the backwater, the upper part of the reservoir and the northern bank of the reservoir. The bottom sediment samples varied from very acid to neutral, with pH values ranging from 4.26 to 6.77. Neutral and slightly acidic pH was found in the upper part of the reservoir and at the dam (lower part). The TOC content in the bottom sediments ranged from 0.07 to 19.26%. The highest TOC content was found in the upper zone of the reservoir. The variability of the above parameters suggests low variation for pH (CV = 10%), and high variation for sand (CV = 69%), silt (CV = 80%), clay (CV = 77%) and TOC (CV = 75%) (Tab. 1).

Table 1
Properties of bottom sediments

Parameter		Mean	SD	Median	Minimum	Maximum	Skewness	CV%[1]
Sand	%	54	37	61	2	100	−0.18	69
Silt	%	38	31	37	0	87	0.09	80
Clay	%	10	8	8	1	23	0.29	77
pH	–	–	0.56	5.50	4.26	6.77	0.05	10
TOC	%	5.82	4.53	5.09	0.07	19.26	0.87	75
Fe	g/kg d.m.	10.56	6.67	10.97	0.80	19.96	−0.05	63
Mn	mg/kg d.m.	266.71	207.88	206.97	14.00	852.65	0.55	78
Zn	mg/kg d.m.	1768.00	1693.00	1012.00	39.37	4772.00	0.60	96
Cu	mg/kg d.m.	38.35	34.38	23.40	1.06	113.51	0.72	90
Ni	mg/kg d.m.	20.51	19.01	15.07	1.36	79.92	1.29	93
Cr	mg/kg d.m.	17.55	13.01	15.71	1.18	37.78	0.24	74
Pb	mg/kg d.m.	151.39	116.42	129.06	4.50	434.49	0.50	76
Cd	mg/kg d.m.	5.42	4.34	4.39	0.37	21.13	1.17	77
Hg	mg/kg d.m.	0.15	0.14	0.13	0.003	0.55	0.77	80
Biotests		**Percent toxic effect (PE%)**						
S. alba GI[2]		7	6	5	0	25	0.58	80
S. alba RLI[3]		14	23	16	−32	76	0.35	79
H. incongruens M[4]		49	49	35	0	100	0.06	99
H. incongruens LI[5]		68	36	81	−8	100	−0.54	53

[1]CV% – variation coefficient, [2]germination inhibition, [3]root length inhibition, [4]mortality, [5]length inhibition.

Metal content in bottom sediments

Metal content in the sediments was as follows (Tab. 1):

- Fe: between 0.80 and 19.96 g/kg d.m.;
- Mn: between 14.00 and 852.65 mg/kg d.m.;
- Zn: between 39.37 and 4772.00 mg/kg d.m.;
- Cu: between 1.06 and 113.51 mg/kg d.m.;
- Ni: between 1.36 and 79.92 mg/kg d.m.;
- Cr: between 1.18 and 37.78 mg/kg d.m.;
- Pb: between 4.50 and 434.49 mg/kg d.m.;
- Cd: between 0.37 and 21.13 mg/kg d.m.;
- Hg: between 0.003 and 0.55 mg/kg d.m.

The average content of elements in the sediments was arranged in the descending order: Fe > Zn > Mn > Pb > Cu > Ni > Cr > Cd > Hg. Metal content in the bottom sediments of the Chechło reservoir varied greatly, which is illustrated by maps of their spatial distribution and coefficients of variability (Tab. 1, Fig. 2). For most of the analyzed metals, their content in the bottom sediments showed high variability (CV%), ranging from 63% (Fe) to 96% (Zn). The coefficient of variation (CV%) values for metals were in the following order: Zn > Ni > Cu > Hg > Mn > Cd > Pb > Cr > Fe. For the majority of the elements, the highest content was observed in the lower part (near dam) and middle parts of the reservoir and locally in the backwater. The lowest content of these elements was recorded near the right bank of the reservoir, partly near the left bank, in the upper part of the reservoir and in the backwater (Fig. 2).

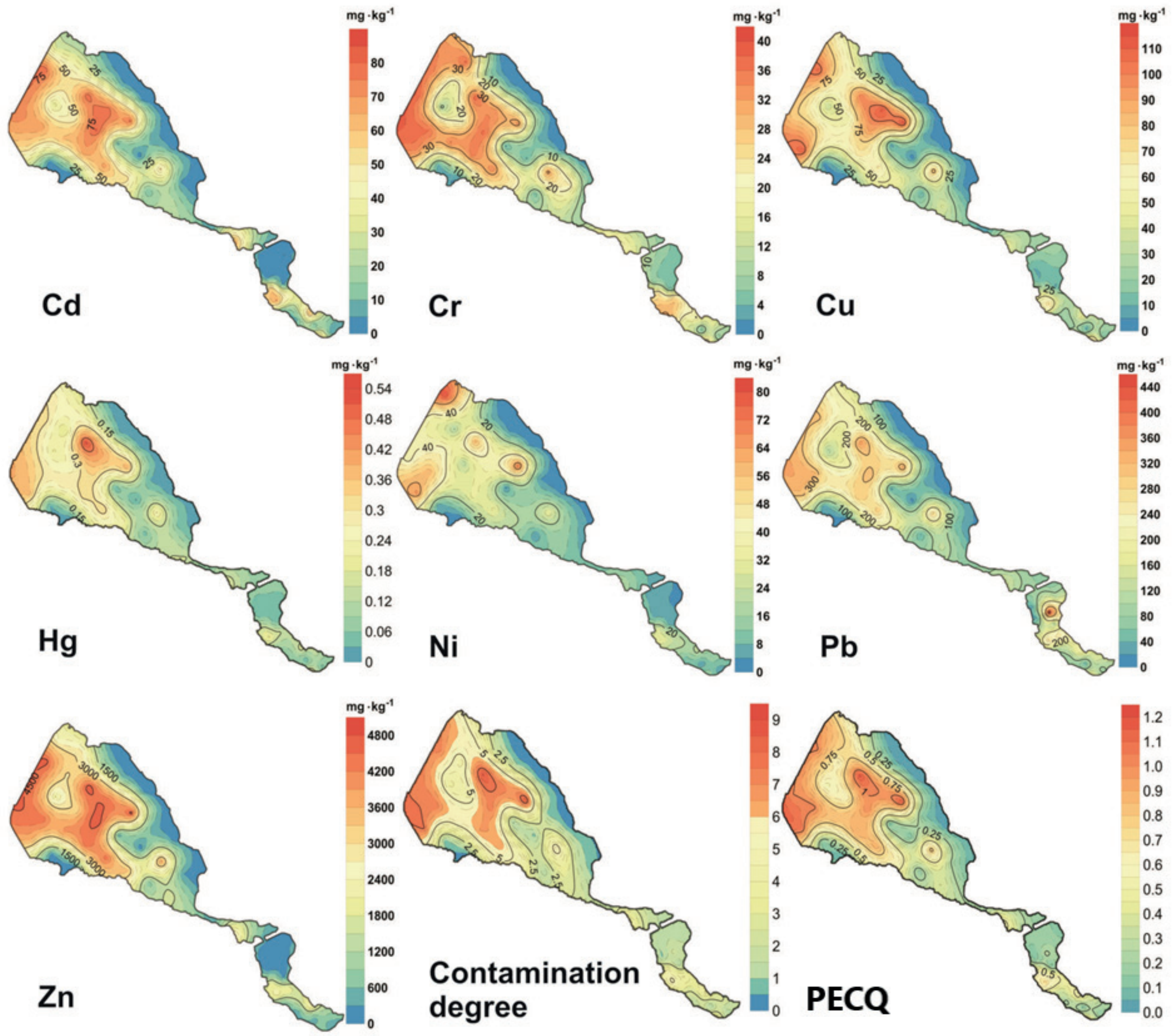

Fig. 2. Spatial distribution of metals content in bottom sediments and multi-element indices

It is worth mentioning that these areas were characterized by a high content of sand fractions. The highest Zn content was found in samples collected from the dam area and the middle part of the reservoir. In the remaining reservoir areas, zinc content did not exceed 2200 mg/kg (2 times less than in the areas mentioned above). The highest nickel content was found in sediments from the dammed part of the reservoir. In our previous studies, we also measured very high content of metals, especially cadmium, zinc and lead in the bottom sediments of the Chechło reservoir, which was connected with the history of zinc and lead ore mining in this area (Zawisza et al. 2014).

Assessment of sediment contamination and ecological risk

Based on geochemical criteria (Bojakowska 2001), the sediments were highly contaminated. The values for most elements: Cd (68% of samples), Cr (68% of samples), Zn (52% of samples), Pb (32% of samples) and Ni (9% of samples) were classified as class IV. The lowest values of contamination factor (CF) were found in the backwater for mercury, whereas its highest values were for cadmium found in the lower part (Tab. 2). The highest values of total metal contamination degree (CD) in the bottom sediments of the Chechło reservoir were also observed in the lower part. The CD for zones decreased in the following sequence: lower > middle > backwater > upper part (Fig. 2, Tab. 2). Approximately 9% of the samples had low contamination (CD < 8), about 11% of samples had moderate contamination (8 ≤ CD < 16), 16% of samples had considerable contamination (16 ≤ CD < 32), and over 64% samples had very high contamination (CD ≥ 32). The application of TEC and PEC allowed for the assessment of the potential danger connected with the occurrence of particular metals in sediments, while mean PECQ allowed for the potential assessment of their total impact on living organisms. In the case of all metals in the sediments, 100% (Cr), 68% (Ni), 62% (Hg), 54% (Cu), 18% (Pb), 9% (Zn) and 2% (Cd) of the samples were below the TEC guidelines for these metals. TEC values were exceeded in the case of Cu (46% of samples), Hg (37% of samples), Pb (30% of samples), Zn (28% of samples), Cd (26% of samples), Ni (23% of samples), and Cr (14% of samples). In the case of all metals in the sediments, 71% (Cd), 62% (Zn), 52% (Pb), 9% (Ni) of the samples were above the PEC guidelines for these metals. The mean PECQs of trace elements ranged from 1.08 to 2.93 (Tab. 2, Fig. 2). The highest mean values of mean PECQs were found in the lower part (dam section). In the ranges proposed by Ingersoll et al. (2001), mean PECQ values in all zones were greater than 1, which indicates a high probability of them having toxic effects on organisms. For Cd and Zn, PECQ values were higher than 1 in each zone. The PECQ for individual metal decreased in the following sequence: Cd > Zn > Pb > Ni > Cu > Cr > Hg. Please note that both calculated indices, i.e. CD and mean PECQ, exhibited similar spatial distribution in the bottom sediments (Fig. 2).

Table 2
Contamination degree and hazard quotients calculated for heavy metals in the sediment

Zone	Zn	Cu	Pb	Cd	Ni	Cr	Hg	Multi-element indices
	CF							CD
Upper part	14.51	2.94	5.66	39.91	1.91	2.33	1.95	69.22
Middle part	26.15	5.22	8.53	61.20	2.94	2.50	2.86	109.40
Lower part	44.03	9.23	15.33	99.68	6.44	4.46	5.60	184.78
Backwater	11.42	3.93	9.42	41.48	2.19	2.48	1.85	72.77
All samples	24.22	5.48	10.09	61.23	3.42	2.92	3.08	110.44
Zone	**PECQ**							**mean PECQ**
Upper part	2.31	0.14	0.66	4.01	0.24	0.13	0.09	1.08
Middle part	4.16	0.25	1.00	6.14	0.36	0.13	0.14	1.74
Lower part	7.00	0.43	1.80	10.01	0.80	0.24	0.26	2.93
Backwater	1.82	0.18	1.10	4.16	0.27	0.13	0.09	1.11
All samples	3.85	0.26	1.18	6.15	0.42	0.16	0.15	1.74

The differences between these indicators are worth emphasizing. CD is a geochemical index indicating the degree of sediment contamination, while the PECQ mean is based on ecotoxicological data and indicates the potential risk to organisms associated with the presence of metals in bottom sediments. The similarity in the spatial distribution of these two parameters may therefore be indicative of sediment contamination by metals and their potential toxicity to living organisms.

Ecotoxicity of bottom sediments

Inhibition of germination and root growth of *Sinapis alba* ranged from 0 to 25% and from –32 to 76%, respectively (Tab. 1, Fig. 3). Phytotoxicity of the sediments was characterised by a high spatial variability, CV = 80% (inhibition of germination), and CV = 79% (inhibition of root growth) (Fig. 3). Responses of *Heterocypris incongruens* ranged from 0 to 100% (mortality) and –8 to 100% (growth inhibition) (Tab. 1, Fig. 3). The spatial variation in the distribution of mortality (CV = 99%) and growth inhibition of *H. incongruens* (CV = 53%) was also demonstrated (Tab. 1, Fig. 3). Generally, a higher toxicity of bottom sediments was observed for *H. incongruens* than *S. alba* (Tab. 1, Fig. 3). For *H. incongruens,* most of the bottom sediment samples (71%) were toxic, whereas only 9% of the samples were toxic for *S. alba*. Moreover, 34% (Phytotoxkit) and 30% (Ostracodtoxkit) of the samples were classified as slightly toxic. Most of the examined samples (57%) were classified as non-toxic for *S. alba* while only 9% of the sediments sample for *H. incongruens* were classified as non-toxic. It is worth noting that in nearly 28% of the sediment samples, the test plant root growth stimulation was observed. For both test organisms, the backwater was characterized by the lowest toxicity, whereas the areas in the middle of the reservoir and near the dam (*S. alba*) and on the whole surface of the reservoir (*H. incongruens*) exhibited the highest toxicity (Fig. 3). The study revealed a statistically significant positive correlation between the responses of the test organisms, which indicates similar reaction of both organisms to substances present in the bottom sediments of the Chechło reservoir.

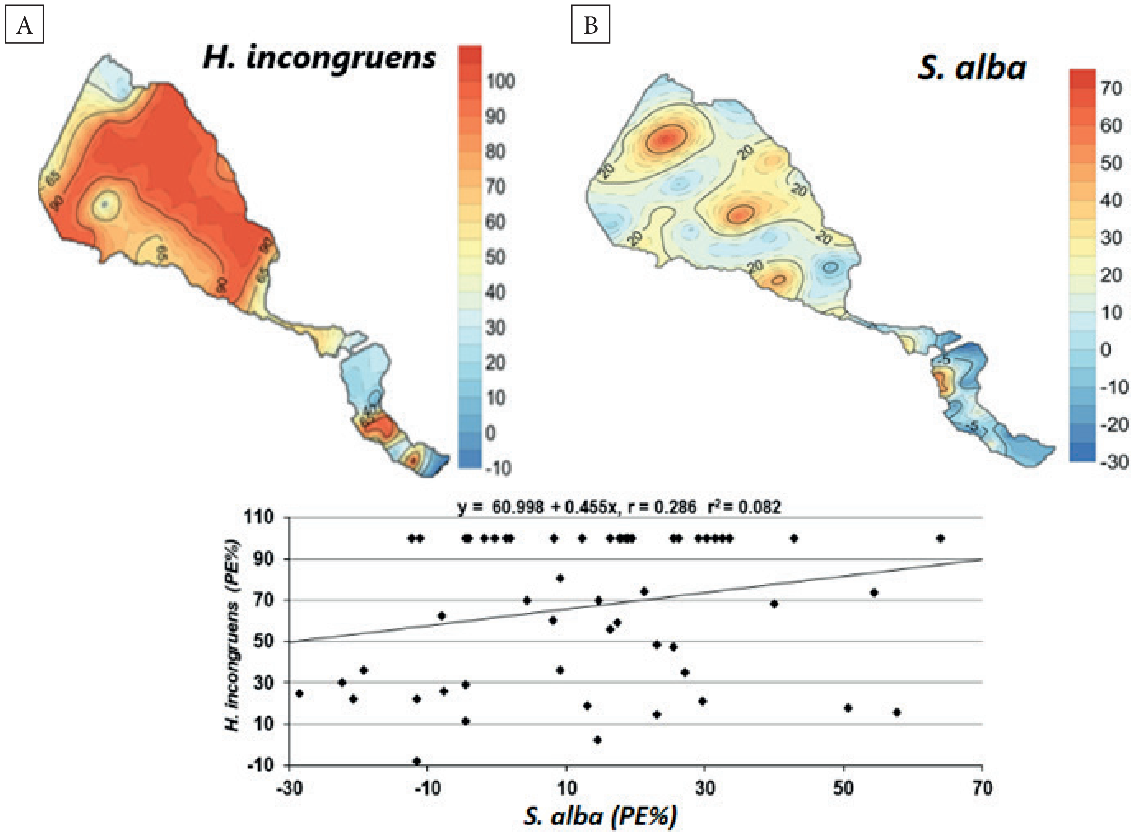

Fig. 3. Ecotoxicity of bottom sediment (PE%) for Heterocypris incongruens (growth inhibition) (A), and S. alba (roots growth inhibition) (B)

However, our analysis revealed that the correlation between organisms was low (r = 0.27, $p < 0.05$), and accounted for only 8% of the variability. In our study, the *H. incongruens* crustacean proved to be more sensitive than the *S. alba* plant. Many previous studies have shown that differences in the sensitivity between organisms depend on many factors, i.e. species, trophic group, type of contaminant, the form of occurrence of a given substance and its uptake mode (Apitz 2011, Heise et al. 2020, Szara et al. 2020).

H. incongruens was exposed to contaminants that were both soluble and adsorbed on sediment particles, and the oral route could be an important route of exposure for this crustacean (De Cooman et al. 2015, Baran et al. 2016). In the studies of Sevilla et al. (2014) it was also found that both aquatic and dietary exposure routes are important in evaluating metal toxicity to ostracods. The uptake of substances via the oral route is an ecologically significant behavior that directly affects the growth and reproduction of the organism (Nałęcz-Jawecki et al. 2011, De Cooman et al. 2015). It is worth mentioning that *H. incongruens* is sensitive to the acid substrate reaction (Ruiz et al. 2013). In fact, the most of the sediment samples were acidic, and pH values were below the tolerance range indicated for this ostracod species (pH 5.5–10) (Ruiz et al. 2013).

The root system was the main exposure route for *S. alba*. It is generally recognized that a reduction in root length is a plant's sensitive response to exposure to pollutants, as roots are in direct contact with pollutants and their properties play an important role in plant protective mechanisms (Szara et al. 2020). Many studies have also demonstrated a lower sensitivity of plants to toxic substances present in different samples compared to other organisms commonly used in biotests i.e. bacteria (*V. fischeri*), crustaceans (*D. magna, H. incongruens, T. platyurus*) (Oleszczuk et al. 2013, Baran et al. 2016, Szara et al. 2020).

Correlation and PCA

The results of correlation analysis between metal content and the response of test organisms are presented in Table 3. No significant statistical relationship between metal content and ecotoxicity of bottom sediments was found. Other researchers also found no significant correlation between the content of hazardous substances in sediments and their toxicity to test organisms (Heise et al. 2020).

Table 3
Analysis of the correlation between the chemical and ecotoxicological parameters in bottom sediments

Parameter	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Hg
Cr	**0.85***	–	–	–	–	–	–	–	–
Cu	**0.91***	**0.87***	–	–	–	–	–	–	–
Fe	**0.89***	**0.96***	**0.87***	–	–	–	–	–	–
Mn	**0.73***	**0.82***	**0.75***	**0.88***	–	–	–	–	–
Ni	**0.74***	**0.82***	**0.86***	**0.80***	**0.69***	–	–	–	–
Pb	**0.81***	**0.82***	**0.85***	**0.80***	**0.67***	**0.74***	–	–	–
Zn	**0.96***	**0.88***	**0.94***	**0.90***	**0.77***	**0.80***	**0.84***	–	–
Hg	**0.91***	**0.88***	**0.95***	**0.88***	**0.75***	**0.87***	**0.85***	**0.96***	–
Sand	**−0.76***	**−0.82***	**−0.82***	**−0.76***	**−0.60***	**−0.71***	**−0.74***	**−0.82***	**−0.83***
Silt	**0.74***	**0.81***	**0.80***	**0.75***	**0.60***	**0.70***	**0.72***	**0.81***	**0.81***
Clay	**0.75***	**0.78***	**0.79***	**0.72***	**0.56***	**0.70***	**0.72***	**0.80***	**0.81***
TOC	0.25	0.20	0.15	0.24	0.26	0.08	0.16	0.14	0.12
pH	0.12	0.26	0.24	0.20	0.16	0.15	0.26	0.21	0.23
Sa RLI[1]	0.03	−0.16	−0.02	−0.12	−0.17	−0.05	−0.17	0.07	−0.01
Sa GI[2]	0.11	0.09	0.15	0.12	0.12	0.04	0.06	0.14	0.15
Hi M[3]	0.09	−0.04	0.11	−0.02	−0.11	0.11	−0.02	0.10	0.09
Hi LI[4]	0.12	0.00	0.19	−0.01	−0.06	0.19	0.15	0.20	0.21

*Correlation coefficients significant at the level of $p < 0.05$ are shown in bold, [1]*Sinapis alba* roots length inhibition, [2]*Sinapis alba* germination inhibition, [3]*Heterocypris incongruens* mortality, [4]*Heterocypris incongruens* length inhibition.

In the studies of Baran et al. (2019), high toxicity of polluted bottom sediments from Rybnik reservoir to *V. fischeri* was found. However, despite the high content of the mobile fraction and the potentially mobile fraction of metals, the correlation between the content of metals and the response of bacteria was insignificant (Baran et al. 2019). The authors suggested that these results may be an effect of the complexation of metals with dissolved organic carbon (DOC), which makes them less bioavailable for organisms. Moreover, sediment rich in TOC had a relatively low toxicity, which was probably due to the reduced bioavailability of metals (Jaiswal & Pandey 2018).

The lack of a significant correlation between metal content and ecotoxicity can be also explained by several factors. First, biotests indicate general toxicity resulting from the presence of various substances in the samples and their properties, but do not identify the specific cause of the toxic reactions observed (Wadhia & Thompson 2007, Baran et al. 2016, Heise et al. 2020). Second, the lack of significant relationships between metal content and response of test organisms suggests their relatively low mobility and bioavailability and that there might be other contaminants such as PAHs, pesticide residues, dioxins or other physicochemical factors present in the sediment of the Chechło reservoir that determine its toxicity. Additionally, antagonistic or synergistic relationships between different substances present in sediments may yield reactions that are difficult to identify (de Castro-Catala et al. 2016, Heise et al. 2020).

Table 4 presents the results of the PCA. Firstly, the PCA allowed us to assess the relationship between the metal content in the sediments and the physicochemical properties of the sediments. Secondly, it allowed us to identify their sources. The PCA allowed for separating three main components, explaining 74.85% of the total variance in the data set (Tab. 4). PC1 explained 55.91% of the total variance and exhibited strong positive correlation (>0.80) with the silt, clay and metal content in the sediments, and a negative correlation with the sand fraction content. The second PC2 factor accounted for 9.84% of the total variance and was related to the response of the test organisms. The third factor accounted for 9.09% of the total variance and was significantly positively correlated with pH and germination inhibition of *S. alba* (Tab. 4).

Table 4
PCA applied to the results of content of heavy metals in bottom sediments and physical-chemical, and ecotoxicological properties of sediments

Parameter	PC 1	PC 2	PC 3
Sand	**−0.87**	−0.14	−0.35
Silt	**0.85**	0.12	0.38
Clay	**0.85**	0.17	0.18
TOC	0.23	−0.30	−0.57
pH	0.23	−0.09	**0.65**
Cd	**0.93**	0.04	−0.07
Cu	**0.96**	0.09	0.04
Cr	**0.95**	−0.16	0.04
Fe	**0.95**	−0.17	−0.02
Ni	**0.87**	0.08	−0.03
Mn	**0.82**	−0.29	−0.06
Pb	**0.88**	−0.06	0.03
Zn	**0.96**	0.12	0.03
Hg	**0.96**	0.10	0.06
Sa RLI[1]	−0.07	**0.68**	0.14
Sa GI[2]	0.10	−0.04	**0.65**
Hi M[3]	0.07	**0.64**	−0.47
Hi LI[4]	0.14	**0.75**	−0.01
Total variance [%]	**55.91**	**9.85**	**9.10**
Cumulative [%]	**55.91**	**65.76**	**74.86**

Loadings >0.6 are shown in bold; $n = 56$, [1]*Sinapis alba* roots length inhibition, [2]*Sinapis alba* germination inhibition, [3]*Heterocypris incongruens* mortality, [4]*Heterocypris incongruens* length inhibition.

It is widely recognized that relationships between metals in sediments may result from their geochemical relationships and may also provide information on their sources and distribution routes (Shaheen & Rinklebe 2014, Baran & Wieczorek 2015, Majumder et al. 2015). In our study, PC1 represented factors and sources determining the content of metals in the bottom sediments of the Chechło reservoir. A strong positive correlation was found in the analyzed metals (Tab. 4), which confirms their identical origin and routes of distribution as being partly natural and partly anthropogenic. Analysis of the correlation between iron content and the content of other elements may allow sediments with natural element content to be distinguished from those enriched as a result of human activities. The lack of a correlation between the content of iron and other metals may be indicative of their anthropogenic origin. Fe content in the bottom sediments of the Chechło reservoir was significantly positively correlated with the content of other elements, which may also attest to their natural origin. However, due to intensive human pressure in the area where the reservoir is located and high natural metal background levels related to the occurrence of zinc and lead ores, geochemical relationships between metals in the sediments of the reservoir may be disturbed. The proximity of the Chechło reservoir catchment area to the heavily mined Upper Silesian region (mining zinc and lead ores) and the presence of the metallurgical industry account for the high content of heavy metals in the soils of that region (Baran & Wieczorek 2015, Wieczorek et al. 2018), in particular Cd, Pb and Zn. The study of Bogdał et al. (2014) confirmed strong soil contamination with cadmium, together with a high content of lead and zinc in the vicinity of both the reservoir itself and its tributaries (Młoszówka and Chechło streams), which may influence the elevated content of these elements in the reservoir bottom sediments and their acid reaction. Ciszewski et al. (2018) lists the Chechło River as an example of a river heavily polluted due to the aforementioned activities of the Trzebionka mine (operating until 2009).

Additionally, the Chechło River was a receiver of wastewater from an oil refinery, metallurgical plants, a meat processing plant and a machine factory in Chrzanów (Ciszewski 1997). Based on the Chechło River sediment analysis (Ciszewski et al. 2018), it was established that the river system reacted relatively rapidly to the discontinuation of mining activities, with contamination levels dropping quickly in the riverbed where sediments were quickly supplied. At sites with continuous slow pollutant supply, no clear changes in metal content were recorded. Furthermore, PC1 indicated that silt and clay fractions have a significant effect on the total metal content in the sediment. The fine fraction, especially the clay fraction, has a large sorption surface in relation to trace elements. The study also showed a non-significant relationship between total metal content and TOC content in the sediments. Moreover, soils in the catchment area of the Chechło reservoir have slightly acidic to very acidic pH (Bogdał et al. 2014, Wieczorek et al. 2018). Some authors report that pH affects the mobility of metals: the lower the pH, the greater the solubility of individual metals and the greater their potential bioavailability (Baran et al. 2016). The study showed no significant effect of pH on the content and distribution of elements in bottom sediments. This is most probably because the Zn and Pb ores found in this area are not only a source of metals but also of calcium and magnesium carbonate, which has a beneficial effect on metal binding in stable carbonate minerals (Cabała et al. 2008, Wieczorek et al. 2018). Similarly to the correlation analysis, PC1 did not show any significant relationship between the metal content in sediments and their toxicity. In contrast, data associated with PC2 and PC3 is indicative of other factors present in the sediments of the Chechło reservoir affecting their toxicity to test organisms. In particular, PC3 is indicative of an association between sediment pH and toxicity to plants. Apart from clay and silt influencing the content and behavior of metals in bottom sediments, other natural factors include redox potential and geochemistry of iron and manganese (Gao et al. 2018, Zhou et al. 2020). Low redox potential affects sulfate reduction and the formation of insoluble sulfides, which in turn causes the immobilization and binding of some metals such as copper, zinc, lead, cadmium, nickel into sulfide immobile and unavailable to living organisms under reducing conditions. This may explain the lack of significant correlations between the occurrence of metals in sediments and the response of the test organisms.

To sum up, this study presented important information about (1) metal content in the bottom sediments of the Chechło reservoir, (2) methods for the assessment of metal contamination and identification of sediment properties with the effect of the behavior of metals in the investigated sediments. Moreover, the study of the ecotoxicity of bottom sediments played an important role in the assessment of the potential risk to organisms by metals in bottom sediments.

CONCLUSION

The work confirmed that a reliable assessment of the risk associated with the presence of metals in bottom sediments is a very complex process. It should be based not on a single parameter but on multidimensional analyzes determining the physicochemical, ecotoxicological, and geochemical properties of sediments. The analysis of the metal content, which allowed us to assess the degree of contamination of the sediments, revealed that the bottom sediments were characterized by a high content of metals, especially zinc, cadmium and lead. Taking into account the geochemical criteria, it was also found that the sediments were heavily polluted (over 64% of the samples showed a CD ≥ 32). In turn, high values of the mean PECQ in all zones (from 1.08 to 2.93) indicated a potential threat to living organisms related to the presence of metals in bottom sediments. Based on the performed biotests, the bottom sediments were more toxic to *H. incongruens* than to *S. alba*. In the case of *H. incongruens*, as much as 71% of bottom sediment samples turned out to be toxic, while in the case of *S. alba* only 9% of the samples. Interestingly, the correlation analysis did not confirm a significant relationship between the metal content in the sediments and their toxicity to the test organisms. Correlation and PCA analyzes showed that silt and clay fractions were the key factors influencing the metal content in the sediments. In conclusion, the risk assessment system presented in the paper, based on the selection of appropriate chemical and biological indicators, provided a lot of valuable information on the ecological hazard associated with metals in the bottom sediments of the Chechło reservoir. This approach enabled us to obtain a comprehensive assessment of bottom sediment quality. In addition, the results obtained may be helpful in making decisions regarding the management of the water reservoir, its protection needs and future utilization as local bathing center.

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