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Potential ecological risk index of bottom sediments from small water reservoirs

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ABSTRACT

The aim of this study was to determine the degree of contamination of bottom sediments from two water reservoirs, Rejów and Wojciechów, with heavy metals based on geochemical criteria. These reservoirs differ in terms of their lifetime, capacity, and the size and land use of the catchment area. The sediment samples were analyzed for group of heavy metals (HM) including cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), zinc (Zn), nickel (Ni), manganese (Mn) and iron (Fe). Additionally, the pH, particle size distribution of the sediments was examined and the content of organic matter expressed as losses on ignition (LOI), total content of nitrogen and phosphorus, T_N and T_P, respectively were determined. The degree of contamination of the sediments with selected HM was assessed using the enrichment factor, geoaccumulation index (I_{geo}) and potential ecological risk index. Analysis showed that the sediments from two reservoirs were characterized by high variability in both the content of HM and their contamination index, which may be related to the source of the elements, as well as with the development of the catchment areas.

Keywords: Bottom sediments; Heavy metal; Risk assessment; Enrichment factor; Potential ecological risk index; Geoaccumulation index

1. Introduction

Population distribution and growth, use of different chemical compounds and land use are affecting the water environment. To assess surface water quality status there are used many water quality indicators (WQI) methods which are also designed for a different purpose, location and even an expert assessment. Studies on environmental aspects of water reservoirs use usually major inorganic chemical parameters such as total phosphorous, nitrates, chlorides, alkalinity, total dissolved solids or total hardness are taken into consideration together with physical parameters (pH, electrical conductivity, dissolved oxygen, turbidity), as well as organic matter indicators (biological oxygen demand, chemical oxygen demand) [1–4].

Bottom sediments play a major role in the determining pollution pattern of aquatic systems, having an impact on mobility of pollutants and interactions between water and sediment. For this reason, it is very important to investigate the environmental risk derived from the presence of trace elements in the sediments and the toxicological implications that these can have for the human health [5,6]. The group of heavy metals (HM) is among the most common pollutants in this environment. Heavy metals are naturally occurring elements that are found throughout the earth's crust, most environmental contamination and human exposure result from anthropogenic activities such as industrial production and use and also domestic and agricultural use of metals and metal-containing compounds. Environmental contamination can also occur through atmospheric deposition, soil erosion of metal ions

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and leaching of HM, sediment re-suspension and metal penetration from water resources to soil and ground water [7,8]. Although it is acknowledged that HM have many adverse health effects and last for a long period of time, HM exposure continues and is increasing in many parts of the world. Heavy metals are significant environmental pollutants and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons. The most commonly found HM in water-sediment phase include cadmium, chromium, copper, lead, nickel, and zinc, all of which cause risks for human health and the environment [9].

The aim of this study was (1) to examine content of selected HM in sediments, (2) determine the degree of contamination of them and finally (3) to assess ecological risk using geochemical indicators.

2. Materials and methods

2.1. Study area

In this article, the subjects of research are two small water reservoirs located in south-eastern Poland, in Świętokrzyskie Voivodeship – its capital and largest city is Kielce (Fig. 1). They include catchments with diversified land use (Table 1). The area of the Kamionka river catchment up to the dam of the Rejów reservoir (RR) is much larger (103.00 km^2) than the Pierzchnianka rivers in the cross-section of the Wojciechów reservoir (WR) – 49.80 km^2. However, it should be emphasized that above the RR there is the Suchedniów reservoir (SR) (it has a catchment area of 83.00 km^2), which retains part of the sediment transported by the river. The RR is located at km 1+170, and the SR at km 7+754 of the Kamionka river.

Forests and meadows predominate in the RR catchment (45% and 32% of the area, respectively), and built-up areas are concentrated mainly along the S7 expressway. In the case of WR, agricultural land and meadows dominate (in total 69% of the total catchment area), mostly located in the Pierzchnica commune. It is a typically agricultural area where cereals and vegetables are grown due to the fertile land – the largest acreage is the cultivation of wheat, barley and rye. Nearly 78% of households running agricultural activity use fertilizers, mostly nitrogen [10]. The farms also raise poultry, cattle and pigs.

In the RR catchment, built-up areas constitute only 5% of its area (Table 1), of which the city of Suchedniów is the largest below the SR, from where rainwater and snowmelt are discharged into the Kamionka river bed through the existing rainwater drainage system. There is a former site of Transport Equipment Factory (FUT in Polish), where research has shown soil contamination with hydrocarbons, HM (chromium, cobalt, nickel, copper, lead) and detergents [11]. Currently, there are a heating plant and a plant manufacturing chemical products and plastics. Rainwater from the area of the former FUT is treated in sedimentation and filtration tanks. Above the RR, there are also municipal sewage treatment plants (in Suchedniów and Łączna), where there were system failures, the last one in May 2021, which resulted in the discharge of untreated municipal sewage to the Kamionka River. In the immediate vicinity of the RR, on average 500 m from the right riverbank, there are MESKO metal industry plants, defined as a plant with a high risk of damages [12]. The production process uses, among others: sodium cyanide, sodium hydroxide, acids: hydrochloric, sulfuric, nitric; sodium sulphate, sodium hypochlorite, potassium cyanide, ammonia, petroleum substances [11].

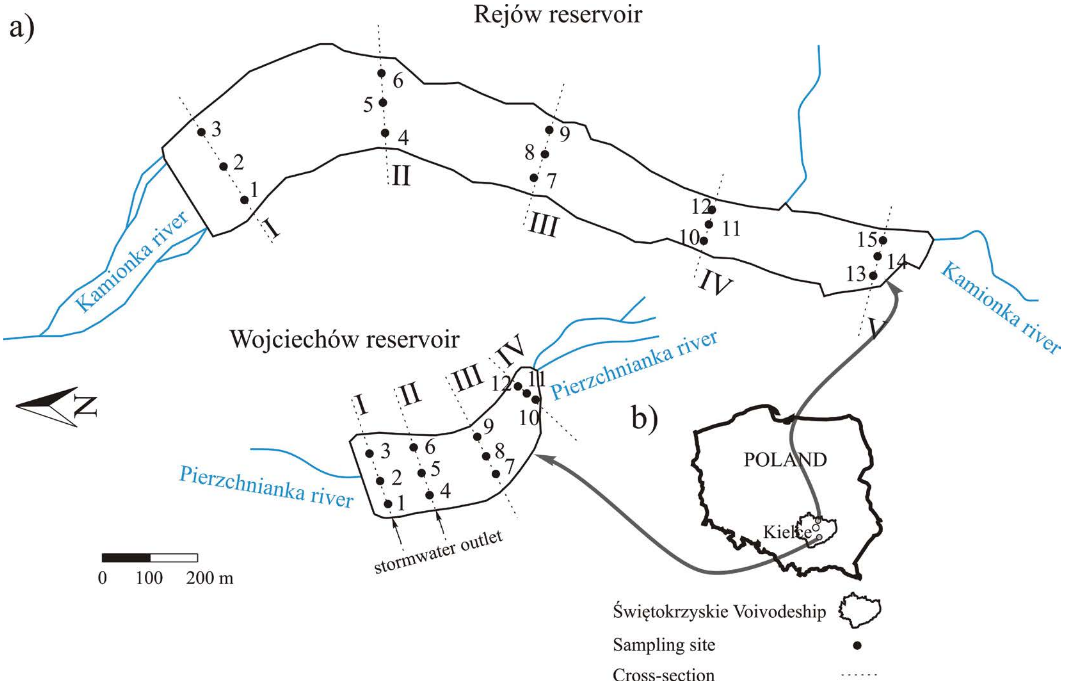

Fig. 1. Studied reservoirs.

Table 1
Basic characteristics of studied reservoirs and catchments [13]

Parameter	Rejów reservoir	Wojciechów reservoir
Characteristics of catchments		
Area – CA (km^2)	103.0	49.8
Forests – F (%)	45.0	21.0
Meadows/wastelands – M (%)	32.0	27.0
Agricultural areas – AA (%)	18.0	42.0
Build-up areas – U (%)	5.0	10.0
Sewage treatment plants (amount)	2.0	2.0
Micro enterprises (0–9 employees)	1316	322
Small enterprises (10–49 employees)	37	15
Medium enterprises (50–249 employees)	8	2
Length of national roads (km)	12.0	0.0
Average slope of the catchment area – J (%)	1.64	0.97
Denivelation – D (m)	166.3	68.6
$H_{\min}$ (m n.p.m.)	245.0	252.6
$H_{\max}$ (m n.p.m.)	411.3	321.2
Characteristics of reservoirs		
Construction year	Beginning of the 19th century – last reconstruction	1973 2002 – reconstruction
Capacity – V (tys. m^3)	1,165.00	104.55
Water surface area – RA (ha)	30.00	7.20
Avg. depth – MD (m)	3.88	1.45
Max. depth – MaxD (m)	6.70	2.50
Max. width – MaxW (m)	245	173
Length – L (m)	1,800	470

*Values refer to the communities through which the river Kamionka and Pierzchnianka flows

The catchment area of the WR consists of 10% of urbanized areas. The largest city, from which rainwater is discharged into the Pierzchnianka River, is Pierzchnica. There are also two municipal sewage treatment plants (in Pierzchnica and Skrzelczyce) discharging the treated sewage directly or indirectly to the Pierzchnianka River. One of the greatest natural resources of the Pierzchnica commune are minerals – mainly carbonate resources represented by limestones, dolomites and clays. At present, three beds of raw materials are in continuous exploitation, while in three others, exploitation has been discontinued. The mining and processing facilities in Wierzbica and Drugnia Rządowa are among the largest employers within the catchment area of the reservoir (Table 1).

2.2. Sampling

Samples of bottom sediments from the RR (15 samples) and the WR (12 samples) were collected on June 2020 using the Becker-type sampler. The kit allows collecting sediment samples at the quasi-undisturbed state, that is, with their structure and layer thickness preserved, into transparent cylinders. The physico-chemical investigations were conducted on top layer of sediment deposits, 10 cm in thickness, which was placed, immediately after collection, into sterile polyethylene containers. Containers with samples were tightly sealed and transported to the laboratory for physico-chemical analyses. In the laboratory, bottom sediment samples were naturally dried to obtain air-dry condition. Dried sediments were sieved (2 mm mesh) to remove the gravel fraction and plant debris, and finally crushed. Sediment samples prepared in this way were stored in prewashed glass containers at room temperature. The sediment sampling sites, shown in Fig. 1, were positioned using differential GPS receiver.

2.3. Analytical procedures

2.3.1. Physicochemical analysis

The pH and temperature were measured promptly after samples homogenization in accordance with the PN-EN 12176:2004 method using SevenMulti™ meter (Mettler Toledo) [14]. Organic content, measured as a loss of ignition (LOI), was determined in accordance with the PN-78/C-04541 method [15], which involved drying the sediment at 105°C to a constant weight, and then heating it at 550°C for 2 h. Total phosphorus (T_P) content was determined by ammonium molybdate spectrophotometric method in accordance with EN ISO 6878:2004 [16]. Total nitrogen content was determined by distillation in accordance with the Polish

Standard PN-ISO11261:2002 after prior mineralization of the samples [17].

2.3.2. Determination of heavy metals

For HM determination, the sediment samples were oven-dried at 80°C on glass dishes until constant weight, homogenized with a mortar and pestle and each of the weighed samples (approximately 0.5 g) was transferred into Teflon vessels, and then digested with HNO_3 in the microwave oven (Multiwave 3000, Anton Paar). The digestates were left to cool at room temperature and then filtered through a 0.45 μm nitrocellulose membrane filter. The filtered digestates were diluted with distilled and deionised water to 100 mL in a volumetric flask. The total concentrations of lead, chromium, cadmium, copper, nickel, zinc, iron, manganese, mercury and cobalt were determined using inductively coupled plasma-atomic emission spectrometry ICP-AES (Perkin Elmer Optima 8000) with certified multi element standards. Analytical blanks and standard reference material were run in the same way as the samples, and HM concentrations were determined using standard solutions prepared in the same acid matrix. Sediment reference material was used to ensure the validation of the data, and also the accuracy and precision of the analytical method. The recoveries were 96%–103% for all metals regarding their certified/non-certified values, which in general is considered satisfactory. Total HM concentrations were expressed in mg/kg dry sediments (PN-EN ISO 11885:2009) [18].

2.4. Geoaccumulation index (I_{geo})

Geoaccumulation index (I_{geo}) was developed by Műller [19] and had widely been used in trace elements studies of sediments [20–22]. To quantify the degree of HM pollution I_{geo} was calculated using Eq. (1):

$$I_{\text{geo}} = \log_2\left(\frac{C_n}{1.5B_n}\right) \tag{1}$$

where C_n is the measured concentration of the metal n in the bottom sediments (mg/kg) and B_n is the geochemical background value of given metal in the shale (mg/kg) [23] and the 1.5 factor was introduced for the purpose of assessing the natural fluctuations in the content of a given substance in the environment with minimum anthropogenic influence. I_{geo} classes are given in Table 2.

2.5. Enrichment factor

Normalized enrichment factor is applied to differentiate metal source originating from anthropogenic and natural means. This involves normalization of the sediment with respect to reference elements such as Al, Fe, Mn, Ti, Sc, Li and Cs. Normalized enrichment factor (EF) of metals in bottom sediments of each site was calculated using Eq. (2).

$$\text{EF} = \left(\frac{C_n}{C_{\text{Fe}}}\right)_{\text{sample}} \Big/ \left(\frac{C_n}{C_{\text{Fe}}}\right)_{\text{background}} \tag{2}$$

where $(C_n/C_{\text{Fe}})_{\text{sample}}$ is the ratio of concentration of the element of concern (mg/kg) to that of Fe in the sediment sample (mg/kg) and $(C_n/C_{\text{Fe}})_{\text{background}}$ is the same ratio in an unpolluted reference material [24]. According to Chen et al. [21] the EF values were categorized into seven classes where EF < 1 indicates no enrichment, EF < 3 is minor enrichment, EF = 3–5 is moderate enrichment, EF = 5–10 is moderately severe enrichment, EF = 10–25 is severe enrichment, EF = 25–50 is very severe enrichment, and EF > 50 is extremely severe enrichment (Table 2). Enrichment factor values between 0.5 and 1.5 indicate the metal is entirely from natural processes, whereas values greater than 1.5 suggest that the sources are more likely to by anthropogenic [25].

2.6. Potential ecological risk index estimation

Potential ecological risk index (PERI) was established by Håkanson [26] in 1980 and can be calculated as follows:

$$\text{PERI} = \sum_{i}^{m} E_r^i = \sum_{i}^{m} T_r^i \cdot C_f^i = \sum_{i}^{m} T_r^i \cdot \frac{C^i}{C_n^i} \tag{3}$$

where E_r^i is the potential ecological risk of the trace elements, T_r^i is the toxic-response factor of the trace elements, C_f^i is the contamination factor of the trace elements, C^i represents measured values of the trace elements (Hg, Cd, As, Pb, Cu, Cr and Zn) in the sediments (mg/kg), and C_n^i is the background value of the trace elements in the study area (mg/kg).

The T_r^i depends on the sedimentological toxic factor (STF – includes a toxicity variable that reflects the different toxic effect of the metal on the aquatic system, for individual elements is equal: Zn = 1, Cu, Pb, Ni = 5, Cr = 2, Cd = 30)

Table 2
Enrichment factor and I_{geo} classes in relation to sediment quality

Enrichment factor	Sediment quality	I_{geo}	I_{geo} classes	Sediment quality
<1	No enrichment	≤0	0	Unpolluted
<3	Minor enrichment	0–1	1	Unpolluted to moderately polluted
3–5	Moderate enrichment	1–2	2	Moderately polluted
5–10	Moderately severe enrichment	2–3	3	Moderately to highly polluted
10–25	Severe enrichment	3–4	4	Highly polluted
25–50	Very severe enrichment	4–5	5	Highly to very highly polluted
>50	Extremely severe enrichment	5–6	6	Very highly polluted

and bioproduction index (BPI) and was calculated for each trace elements as follows: Zn = $1\cdot(5/\mathrm{BPI})^{0,5}$, Cr = $2\cdot(5/\mathrm{BPI})^{0,5}$, Cu, Pb, Ni = $5\cdot(5/\mathrm{BPI})^{0,5}$, Cd = $30\cdot(5/\mathrm{BPI})^{0,5}$ [25]. BPI is related to the trophic status of the system, which affect the bioavailability of metals. The original model proposed for PERI utilized total nitrogen content and organic matter for sediment bioproduction determination [27]. In the study the value of BPI was equal to 38 for RR and 32 for WR and was calculated as the nitrogen content on the regression line for the organic matter content value of 10% [28]. The classification according to PERI results in Table 3.

For I_{geo} and C^i_f calculation, the background value (C^i_n) was obtained for national standards: Fe = 2,694, Cr = 6, Zn = 73, Ni = 6, Mn = 330, Cu = 7, Pb = 15, Cd = 0.5, Hg = 0.05 (mg/kg) [29].

Classic PERI method considers eight pollutants, including polychlorinated biphenyls (PCBs), Hg, Cd, As, Pb, Cu, Cr and Zn. However, in this study, we did not consider PCBs – due to the lack of analyzes, and in the case of Hg and As the measured values were below detection limit.

3. Results and discussion

3.1. Particle size distribution, total HM content

The pH value of soil and sediments was usually divided into five grades, that is, slightly acidic (pH < 5.0), mildly acidic (5.0–6.5), neutral (6.5–7.5), mildly alkaline (7.5–8.5) and the strongly alkaline (pH > 8.5) [30]. The average of pH values in RR sediment samples were within the range 6.75–6.89 and WR sediments 7.14–7.26.

The total content of HM in the bottom sediments of the studied reservoirs was as follows: 4.9–25.1 mg Cr, 50–105.1 mg Zn, 5.6–13.7 mg Ni, 3.4–6.7 mg Cu, 51.2–87.6 mg Pb and 98.8–18.4 mg Cd – RR and 0.1–30.2 mg Cr, 18.3–485.6 mg Zn, 4.4–28.3 mg Ni, 0.1–17.3 mg Cu and 21.2–58.6 mg Pb – WR (per kilogram dry weight). No Cd was found in the WR bottom sediment samples. The average content of trace elements in the sediments of the RR and WR reservoirs can be arranged as follows, respectively: Zn > Pb > Cr > Cd > Ni > Cu and Zn > Pb > Ni > Cr > Cu > Cd. The highest concentration of Cr (25.1 mg/kg), Ni (13.4 mg/kg), Cu (6.7 mg/kg), Pb (87.6 mg/kg) and Cd (18.4 mg/kg) was observed in sediment samples collected near the RR dam (section 1), while Zn (105.1 mg/kg) in section 3 located in its central part.

These sediments were also characterized by the highest content of dust and clay fractions and organic matter (OM) (8.2%–11.6%). The lowest content of tested metals was found in sediments from the inlet part of the reservoir, in which mainly sandy material with a negligible content of organic matter (<0.5%) was deposited. Numerous studies confirm the above dependence – the content of individual metals increases with the increase in the content of colloidal fractions in the sediments [31,32]. In the case of WR, the highest concentration of tested metals (Cr 30.2 mg/kg, Zn 485.6 mg/kg, Ni 28.3 mg/kg Cu 17.3 mg/kg and Pb 58.6 mg/kg) was observed in sediment samples collected in the vicinity of the left bank of the reservoir running along the asphalt road (sections 1 and 2), from which rainwater is discharged directly into it, without any treatment. The average HM content here is from 1.2 (Pb) to 19.3 (Cr) times greater than the average for the remaining sediment samples. The particle size distribution of the investigated sediments was slightly different than in the case of RR. Sediments with a significant content of sand fraction, apart from the upper part of the WR, also occurred along its western shore (Sa > 38%). Along with rainwater, significant amounts of suspended solids flow into the reservoir, which change the natural composition of the sediments. The particle size distribution has a relation with the adsorption of metals. The results show that other than for a few exceptions, the majority of the metal concentrations in solids particles decrease with the increase in particle size. This highlights the importance of fine particles in the adsorption of metals [31]. Comparing the content of the tested s HM in the sediments of reservoirs with the value of the geochemical background for alluvia and water sediments of Poland [32], we note that in over 90% of the tested samples with RR, the concentration of Cr, Ni, Pb and Cd was higher than the limit value. On the other hand, in the case of WR, the exceedance of the geochemical background limits for Cr, Zn and Cu was observed only in sediment samples collected near the places where rainwater was discharged into the reservoir. In the case of Ni and Pb, the geochemical background was exceeded in 33% and 83% of the tested samples, respectively. Compared to the analyzed trace elements, the level of Cd contamination of RR sediments was highlighted. The average value of this metal in the sediments is over thirty-three times higher than the background value. This situation should be considered dangerous to the environment due to the strong toxic properties of this element. The mean Pb content in RR sediments was over five times higher than the background value, while Cr and Ni from 2.0 to 3.3 – times higher. In the WR, the only Winsor mean (as a measure more resistant to outliers than the usual arithmetic mean), the content of Ni and Pb was from 7.3 to 1.8 times higher than the background. The OM content in the sediments varied from 0.2% to 11.6% in the RR and from 7.9 to 23.2% in the WR. The greater content of OM in WR sediments results from its morphology – it is a reservoir much shallower than the RR, heavily overgrown with vegetation. Organic matter is largely autochthonous. The obtained OM values, however, are consistent with those given by [33] for small dam reservoirs. Considering the percentage distribution of OM in the sediments of the RR, it can be noticed that there is a division into sediments in which the share of OM is from a few to a dozen or so percent – these are fine-grained sediments collected from the central and near the dam part of the reservoir. Whereas, sandy sediments deposited directly at the inlet have a OM share of less than 1%. This is justified by the greater moving force of the water stream, were the organic parts are transferred

Table 3
Potential ecological risk index

PERI	Classification
PERI < 150	Low
150 ≤ PERI < 300	Moderate
300 ≤ PERI < 600	Considerable
PERI ≥ 600	Very high

into the reservoir [34]. In the case of WR there is no relationship like in RR. The sediments from the heavily overgrown inlet and middle part of the reservoir were characterized by the highest content of OM.

High content of Cr, Pb and Cd in the sediment RR and increased contents of Cr, Zn, and Pb in sediment WR indicate anthropogenic origin of these elements. As mentioned earlier, rainwater is an anthropogenic source of HM in WR. However, in the case of RR HM anthropogenic sources are agricultural activities (intensive farming requires large amounts of mineral fertilizers which contain HMs, including Cd [35–37] and industrial activity). In the 19th and 20th centuries, the foundry, mechanical, transport, ceramics and armaments industries developed in the RR catchment. The small average content of Zn and Cu in RR and Cr, Zn and Cu in WR below or slightly above the geochemical background value (Table 4) points to the geogenic origin of these metals.

The occurrence of linear relationships between individual HMs provides information on their mobility and sources of origin. Positive value of the correlation coefficient between HMs indicates to the same source of their origin and similar behavior during transport [38]. The occurrence of a strong statistical correlation between Fe and the content of another element may be the basis for the differentiation of sediments into: sediments with its natural content and enriched sediments as a result of human activity. The lack of correlation between Fe and another elements may indicate their anthropogenic origin. The analyzes show that there is a significant and statistically strong relationship between the pairs of metals Ni and Cr in RR and Cr and Cu, Cr and Pb, Pb and Zn in WR, which may indicate a common source of origin for these elements and a similar mechanism of their transport (Table 5).

3.2. Geoaccumulation index with enrichment factor

Geoaccumulation index I_{geo} was used to assess the quality of bottom sediments. The obtained values of the index for the tested reservoirs are shown in Fig. 2. The analysis of the data contained in Fig. 2 shows that the value of this indicator varies considerably depending on the given HM. This index in all analyzed samples from RR reached the value < 0 for Cu and with the exception of one sample from

Table 4
HM concentration in bottom sediments

Parameters	Cr	Zn	Ni	Mn	Cu	Pb	Cd	Cl	Si	Sa	OM
	mg/kg							%			
Rejów reservoir											
Minimum	4.9	50.1	5.6	300.0	3.4	51.2	9.8	0.00	10.0	1.0	0.2
Maximum	25.1	105.1	13.7	633.2	6.7	87.6	18.4	5.00	85.0	98.0	11.6
Mean	19.1	91.1	10.3	519.1	5.5	72.8	15.8	1.5	62.5	38.4	6.9
Median	19.2	92.6	10.5	522.0	5.4	73.4	16.2	1.9	69.4	33.6	7.6
CV %	28	18	21	16	15	14	17	76	48	64	62
Wojciechów reservoir											
Minimum	0.1	18.3	4.4	79.8	0.1	21.2	–	0.00	5.5	1.0	7.9
Maximum	30.2	485.6	28.3	3,892.4	17.3	58.6	–	2.50	95.5	97.0	23.2
Mean	9.05	171.1	13.2	1,162.0	6.4	35.3	–	0.8	58.2	39.2	16.5
Median	0.1	60.7	9.4	421.4	1.4	27.9	–	1.0	58.5	30.5	17.6
CV %	150	117	73	130	122	43	–	59	42	74	57

Table 5
Value of Pearson correlation coefficient between selected indicators

Correlation	Fe	Cr	Zn	Ni	Cu	Pb	Cd	PERI
Fe		0.74*	0.70*	0.64*	0.33	0.65*	0.36	0.58*
Cr	0.39		0.65*	0.92*	–0.04	0.55	0.55*	0.72*
Zn	0.50	0.81		0.64*	0.32	0.67*	0.37	0.58*
Ni	0.93*	0.58	0.47		–0.22	0.59*	0.52	0.70*
Cu	0.36	0.99*	–0.73	0.59		0.48	0.20	0.26
Pb	0.31	0.89*	0.89*	0.40	0.86		0.58*	0.78*
Cd	–	–	–	–	–	–		0.94*
PERI	1.0*	0.39	0.50	0.93*	0.37	0.32	–	

* – correlation significant at the 0.05 level; 0.2 – Rejów reservoir; 0.2 – Wojciechów reservoir; number of samples: $n = 15$ RR; $n = 12$ WR.

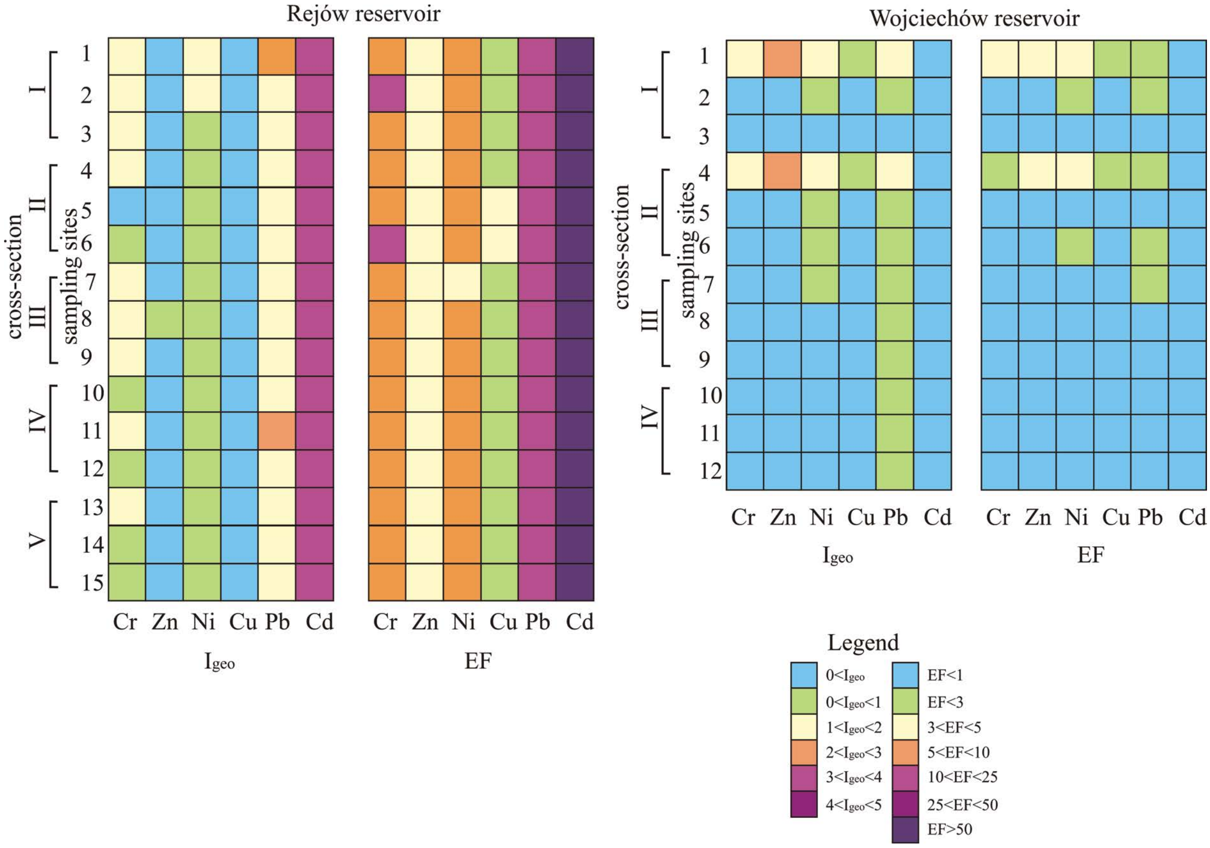

Fig. 2. Ecological risk assessment with I_{geo} and enrichment factor.

cross-section III (sampling sire 8) for Zn, which indicates no contamination of the sediments with these elements.

Considering the case of Ni, the value of the I_{geo} index for over 86% of the tested sediment samples was <1, and for the remaining 14% it slightly exceeded the value of 1, which proves a moderate contamination of the sediments with this metal. Due to Cr contamination, RR sediments can be classified as class 0–2 (6.6% – class 0 samples, 33.3% – class 1 samples and the remaining 60.1% – class 2). Pb and Cd are of the greatest importance in the chemical degradation of RR sediments. In the case of lead, all analyzed samples should be classified as class 2 – moderately contaminated and in the case of Cd, up to class 5 – highly to very highly polluted. WR sediments are much less polluted. The value of the I_{geo} index ranging from 1 to 2 (moderately polluted sediments) was found only in sediment samples collected near the places where rainwater was introduced into the reservoir. In other cases, the value of the geoaccumulation index was lower than one or slightly higher than this value which indicates no or moderated contamination of the sediments with these trace elements.

The values of the enrichment factor for selected HM of the analyzed sediments indicate both – natural and anthropogenic sources of their origin (Fig. 2). The analysis of the data presented in Fig. 2 shows that the RR sediments are characterized by extremely severe cadmium enrichment (EF > 50). EF values between 10–25 indicate a severe enrichment of the sediments of the Pb in this reservoir. In the case of Cr and Ni, a moderately severe enrichment of the sediments with these elements was observed.

Completely different results were observed in the case of the WR sediment contamination analysis. The calculated EF values in most of the analyzed samples for Cr, Zn, Cu and Cd were less than one – which indicates that the sediments were not enriched with these elements and that they were of natural origin.

The greatest enrichment of Cr, Zn and Ni sediments was observed in the samples taken in the lower part of the reservoir, near the left bank (sampling sites 1 and 4) where, as mentioned earlier, rainwater is discharged from a nearby road. For Cr, Zn and Ni (sampling site 1) and Zn and Ni (sampling site 4) moderate enrichment was found (3 < EF < 5). For Pb, in 42% of the tested samples minor enrichment was observed, while in the remaining samples (58%) no enrichment was observed. In the Cu case, only two samples (16%) of sediments were characterized by minor enrichment and these were sediments taken from locations 1 and 4.

3.3. Potential ecological risk index

The PERI index was also used to assess the risk of HMs toxicity in the bottom sediments of the studied reservoirs. According to this criterion, RR bottom sediments are characterized by a considerable potential for ecological risk related to the concentration of the studied HMs. In over 80% of the analyzed samples, the value of this index

Table 6
Results of statistical analysis for PERI

Parameter	PERI	PERI
	Rejów reservoir	Wojciechów reservoir
Minimum	229.3	7.3
Maximum	425.1	36.2
Mean	367.2	17.2
Median	391.3	9.4
CV %	16.7	76.4
SD	61.3	13.1

Percentage share in the PERI index

	Cr	Zn	Ni	Cu	Pb	Cd
RR mean PERI	0.75	0.19	1.06	0.46	3.60	93.95
WR mean PERI	8.33	8.21	30.42	12.39	40.64	0.01

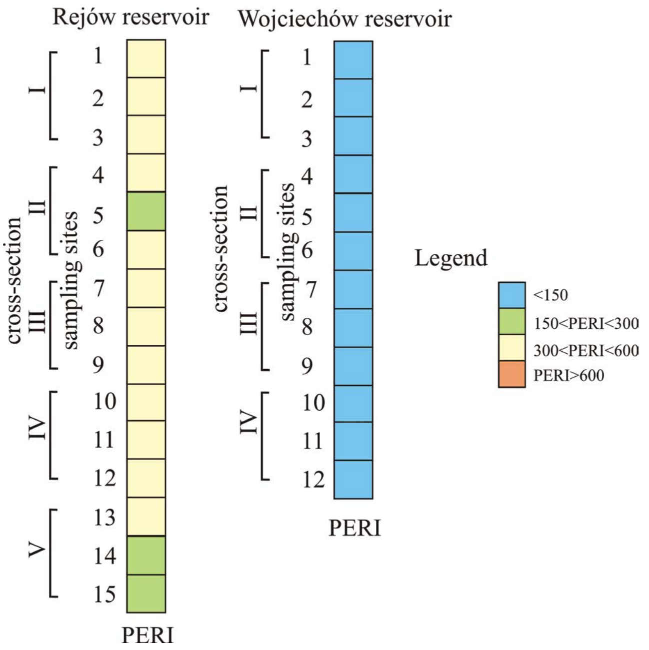

Fig. 3. Ecological risk assessment with potential ecological risk index.

ranged from 300 to 600 – which proves a considerable ecological risk. The mean PERI value for the analyzed samples was 367.2 and the coefficient of variation was 17% – which proves the low variability of the analyzed index (Table 6). The highest share in the PERI index had the concentration of Cd over 90% – which proves that Cd is responsible to the greatest degree of the ecological risk of sediments. Lower values of the PERI index was observed for the sediments from WR. The PERI index value for none of the tested samples exceeded the level of 150, which indicates a low potential for ecological risk (Fig. 3). The highest share in the PERI index had the concentration of Pb (over 40%) and Ni (over 30%). The average value of the PERI index was 17.2, while the value of the coefficient of variation was significantly higher than that calculated for the RR and was equal over 76%. The high value of the CV proves the strong diversification of the PERI values within the WR, which results from the presence of point sources of pollutions (on the right bank there are two outlets of the rainwater drainage system).

Significant differences in the PERI values between the studied reservoirs result from different management and land use of their catchments. In the catchment area of the RR there were and also are numerous industrial facilities of transport, ceramic industry (stoneware products) and mining and processing sandstone. In addition, in the RR catchment there are much larger population centers (Suchedniów, Total). The average number of inhabitants per km^2 is approximately 110. The WR catchment is typically agricultural, much less industrialized (the average number of inhabitants per km^2 is approximately 45). Pierzchnica is the only major population center within it.

4. Conclusion

Based on the results of the analyzes the following conclusions can be presented:

- The concentration of selected HM in sediment samples from the WR reservoir is very variable. This is especially noticeable in the case of Cr, Zn, Mn and Cu where the calculated value of the variation coefficient was sometimes much greater than 100%. For the sediments from the RR, the value of the coefficient of variation did not exceed 28%, which proves a slight variation in the content of tested metals in individual sediment samples.
- The values of the enrichment factor calculated for selected HM present in the RR sediments indicate the advantage of anthropogenic sources of the determined elements. The EF values indicate an extremely severe Cd enrichment and a severe Pb enrichment in all analyzed RR sediment samples. Different results were observed in the case of sediments from WR. For most analysis, the value of EF < 1 was obtained, therefore the analyzed elements were present in trace amounts in the sediments. Only in a few sampling points the value in the range 3 < EF < 5 can be obtained, which indicates a moderate enrichment of the Cr, Zn and Ni.
- The values of the potential ecological risk index (PERI) indicate that RR bottom sediments pose a significant ecological risk related to metal contamination (300 < PERI < 600), while the WR sediments do not pose such a risk (PERI < 150). The main factor influencing the toxicity of RR sediments is the Cd content, exceeding the value of 11.8 mg/kg in all analyzed samples.

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