Plastics-derived and heavy metals contaminants in the granulometric fractions of bottom sediments of anthropogenic water reservoir – comprehensive analysis

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A B S T R A C T

The aim of this study was to evaluate the condition of the Rybnik Reservoir (South Poland, Central Europe) – anthropogenic water body, heavily impacted by human activities, based on the chemical composition of bottom sediments, that is, additives to plastics (selected phthalates and phenol derivatives) and heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) content. The study was also aimed to assess the potential ecological risk, and determination of the relationship between the sediments particle size fraction and the concentration of tested pollutants. In this case, the authors proposed a method of separating sediments into sedimentation fractions, taking into account the natural behavior of their particles in the aquatic environment. The analyzed plastics-derived and metals showed a spatial and fractional variability. Among plastic additives, bis(2-ethylhexyl) phthalate and dibutyl phthalate dominated. The highest ecological risk for fauna and flora of Rybnik Reservoir posed Cd, Cu, Zn and Ni, while the most dangerous was Cd and Zn, whose share in mobile forms was the highest. The results of statistical analyses, indicated that regardless of sampling points location, phthalates and metals were strongly bound with the smallest particles of sediments (0.1–50 μm). Strong correlations between the selected pollutants, indicate their anthropogenic sources of origin.

Keywords: Bottom sediments; Granulometric composition; Sediments particle size; Sedimentation fractions; Phthalates; Phenol derivatives; Heavy metals; Sequential extraction; Potential ecological risk

1. Introduction

Bottom sediments are one of the main and integral elements of aquatic ecosystems. Unfortunately, the organic (including those derived from plastics) and inorganic (heavy metals) pollutants contained in sediments have a negative impact on the condition of the aquatic environment [1,2].

The problem of environmental pollution with plastics and heavy metals is global and affects almost every element of the environment. Due to the high rate of economic development and population growth, there is an increased accumulation of the above-mentioned pollutants. This process is additionally intensified by the properties of these pollutants, mainly by their high resistance to degradation [3–6].

The plastics industry is developing dramatically. In 1950, 1.5 million tons of plastics were produced in the world, while in 2019 as much as 368 million tons [7]. It is predicted, that at the present rate of growth, plastics production is estimated to double within the next 20 years [8]. With the dynamic development of the plastics industry, the consumption of additives for these plastics, including plasticizers, also increases. The main role of plasticizers is to improve the properties of polymers, including their flexibility, stability and resistance [9]. The most commonly used plasticizers are phthalates (PAEs), such as dimethyl phthalate

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(DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), bis(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DOP). It is estimated that the production of phthalates in the world amounts to 92% of all plasticizers [10]. Plasticizers also include other non-phthalate additives, such as bis(2-ethylhexyl) adipate (DEHA) or phenol derivatives, including 4-n-nonylphenol (4nNP), 4-tert-octylphenol (4tOP), bisphenol A (BPA) [11]. All mentioned plasticizers belong to the group of the endocrine disrupting compounds (EDC), substances that disrupt the functioning of the endocrine system [12]. In animals, bisphenol A and alkylphenols (e.g. 4nNP, 4tOP), lead to feminization or hermaphroditism, while in humans they can cause cancer of the sex organs [11,13]. While some phthalates are suspected of mimicking estrogen [14].

Due to the wide use of the above-mentioned plasticizers in the production of plastics, they occur in almost all elements of the environment. They get to the aquatic environment mainly with sewage or are leach out of the plastic to water [15]. In addition, phthalates may be released directly from plastics into the atmosphere, where they remain as gaseous particles or adsorb to particles suspended in the atmosphere and, through deposition, may re-contaminate other ecosystems [16].

Heavy metals in water bodies come from natural or anthropogenic sources. Among the natural ones, we can distinguish mainly rock weathering and soil erosion. However, still the main source of these elements in surface waters is human activity, that is, mining, mineral processing industry, sewage (municipal and industrial), surface runoff from fields (fertilizers) and roads, atmospheric deposition, etc. [17–20]. These elements are accumulated in bottom sediments. Therefore, the chemical composition of these sediments largely depends on human activity, which affects the geochemical situation in the catchment area [4,21]. Heavy metals, due to their toxicity and stability in the environment and the ease of getting into the food chain, pose a serious threat to organisms living in aquatic ecosystems and, indirectly, also to human health [19,20,22,23]. Therefore, it seems necessary to constantly monitoring bottom sediments in terms of the total content of metals and chemical forms of their occurrence, which will enable the assessment of the ability of these elements to migrate from sediments to the environment, as well as provide information on their mobility and bioavailability. One of the methods allowing to determine with what components of sediments particular metals are associated is the sequential extraction process. A commonly used method is the three-step sequential extraction (BCR) procedure proposed by European Community Bureau of Reference [24,25].

Bearing in mind that the assessment of the chemical quality of bottom sediments determines the cleanliness of water reservoirs and is the basis for the development of a management system strategy for this component of the environment, it seems that research on the content of organic and inorganic pollutants is a priority. However, it should be mentioned that in order to fully assess the ecological condition of water reservoirs, it becomes necessary to use appropriate criteria and indices (tools) to estimate the potential ecological risk posed by pollutants present in sediments.

Scientific literature provides papers on tools used in ecological risk analysis [1,4,19,20,26].

Treating bottom sediment as an integral part of the aquatic ecosystem, the authors proposed its separation into sedimentation fractions, differing in the falling rate of particles in the aquatic environment. The division of the sediment mass into groups differing in terms of the particle falling rate gave an overview of the differences in the chemical composition of these sediments. Moreover, proper preparation of bottom sediments can provide information which of the separated fractions most precisely reflects their chemical composition.

The conducted research was aimed at: (a) a comprehensive assessment of the condition of the Rybnik Reservoir (South Poland, Central Europe), based on the chemical composition of bottom sediments, that is, additives to plastics and heavy metals content, (b) analysis of potential ecological risk; (c) determination of the relationship between the bottom sediments particle size fraction and the concentration of tested pollutants and (d) checking the differences in the content of tested pollutants in sedimentation fractions of bottom sediments.

2. Materials and methods

2.1. Study area and sampling

The Rybnik Water Reservoir (50°08′29.7″N, 18°29′52.4″E) is located in the south-western part of the Silesia Voivodeship, Poland (Central Europe). It was situated in the northern part of the city of Rybnik, in the middle section of the Ruda Valley, which is the right-hand tributary of the Odra River. This reservoir was created by damming the river waters with a dam located in the 22.5 km of the river course. It was put into operation in 1971 and is part of the Rybnik Power Plant, which is situated on its shores. The reservoir is characterized by a variable depth ranging from 2 to 12 m. On the western side of the Rybnik Reservoir there is a provincial road connecting the city of Rybnik with Rudy City. The catchment area of the reservoir is 316.78 km², of which agricultural land accounts for 41.7%, forest areas account for 33.6% (northern part), urbanized areas account for 22.6% (southern part), while surface waters cover only 2.1%. The reservoir is intended for cooling condensers of the Rybnik Coal-Fired Power Plant. There is a recreation and relaxation area on the shores of the reservoir [27,28].

The test samples were bottom sediments of the Rybnik Reservoir, collected at three sampling points, which were marked along the central axis of the reservoir, that is, *S*1, *S*2 and *S*3, corresponding to 3, 5 and 9 m depth of the reservoir. The thickness of the collected sediments layer was 5 cm. Samples were collected in 2021. The coordinates and the location of the sampling points are presented in Fig. 1.

The sediments were collected with the usage of Birge-Ekman sampler, and placed in labeled clean glass jars to avoid contact with plastics at early stage of the study. All samples were stored at 4°C and divided into fractions no later than 72 h after collection. After dividing into sedimentation fractions and granulometric analysis, all samples were dried at room temperature, then milled in a mortar

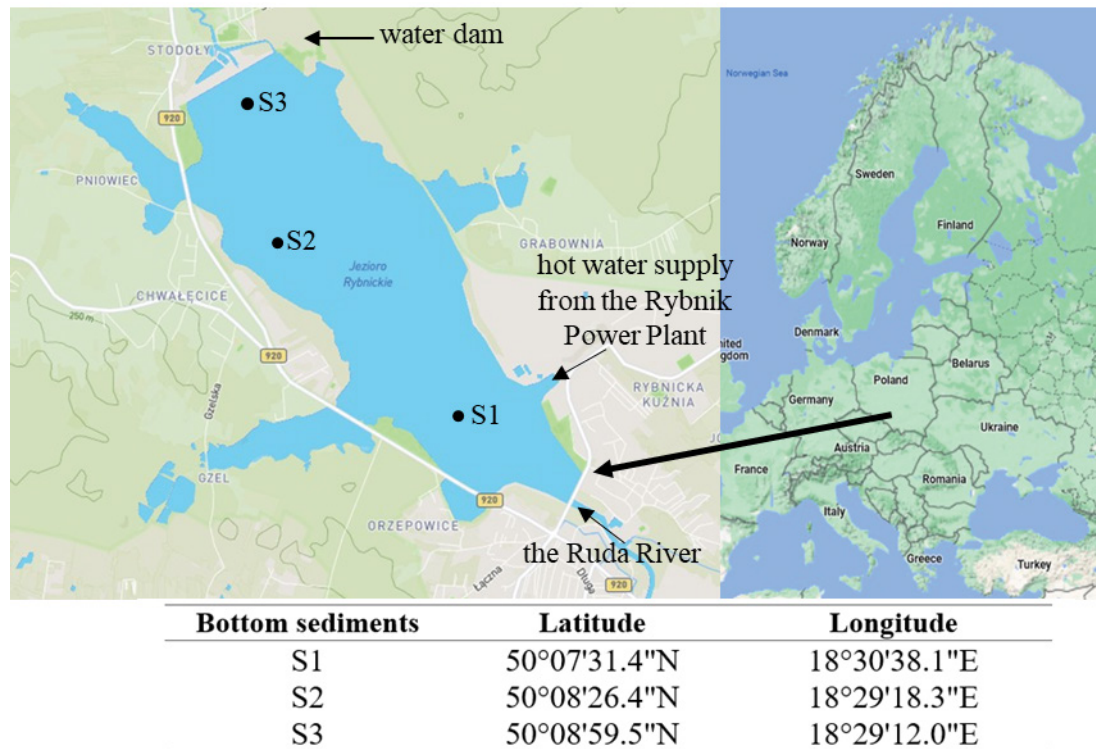| Bottom sediments	Latitude	Longitude
S1	50°07'31.4"N	18°30'38.1"E
S2	50°08'26.4"N	18°29'18.3"E
S3	50°08'59.5"N	18°29'12.0"E

Fig. 1. Location of the study area and sampling points [29,30].

grinder and sieved through a sieve with a mesh 0.2 mm, to homogenize the samples. Afterward, the quantitative analysis of the content of plastic additives and heavy metals were conducted.

2.2. Laboratory analysis – sedimentation division of sediments

In this study, the authors proposed a method of separating bottom sediments into sedimentation fractions, taking into account the natural behavior of their particles in the aquatic environment. This direction of research takes into account the complicated system of interdependencies that take place inside water reservoirs during the formation of bottom sediments, including sedimentation processes.

The separation of bottom sediments was made based on the differences in the rate of falling of their particles in the water environment, thus maintaining their actual size and shape. The first stage of the research was to determine the particle fall times. For this purpose, about 200 g of wet sediments were weighed into a glass beaker with a volume of 3 L and 500 mL of water taken from the Rybnik Reservoir were added. Everything was mixed and poured into the Spilner funnel. Observing the natural process of sedimentation, the time intervals of 2, 5, 15 and 30 min were determined, obtaining 4 fractions of sediments (Fraction 1, Fraction 2, Fraction 3, Fraction 4) (Fig. 2). Then, each of the collected sediments were divided into fast and slowly falling fractions, taking into account the above assumptions.

The chosen direction is a new look at bottom sediments as an integral part of the aquatic ecosystem. It is possible that for bottom sediments from a different water reservoir, the falling times of particles will be different than those proposed, therefore each case should be treated individually.

2.3. Chemical analyzes in sediments fractions

2.3.1. Principal physicochemical analysis

In the sediment samples the following parameters were measured: pH, redox potential, dry matter (DM), dry organic matter (DOM), dry mineral mass (DMM) content. Moreover, the granulometric composition of the sediments was also determined. The values of pH and redox potential were measured by the potentiometric method according to the manufacturer's instructions for the CX-401 (Elmetron), while the content of DM, DOM, DMM was determined using the weight method according to PN-EN 15935:2013-02 [31]. The granulometric composition of the sediments was determined by the laser diffraction technique in accordance with ISO 13320: 2020 [32].

2.3.2. Plastic-derived contaminants – organic analysis

In order to determine the concentration of phthalates in bottom sediments, the methodology proposed by Lee et al. [33] with some modifications was used. Therefore, 2 g of dried sediment was extracted with dichloromethane in ultrasound (3 × 30 min). The supernatant was decanted, filtered, and concentrated to 2 mL. Then, the extract purification procedure was started. For this purpose, columns with SiO_2-Florisil 1 g (1:1, v/v) packed, which were
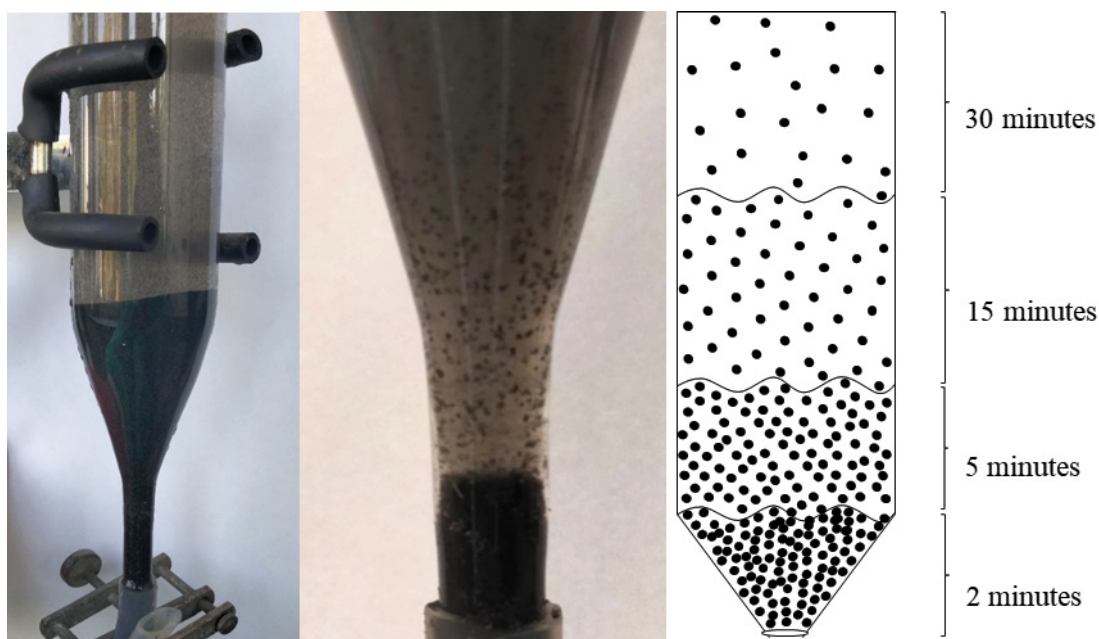
Fig. 2. Sedimentation distribution of bottom sediments in the water environment.

pre-conditioned with 5 mL of hexane, were prepared. The concentrated extract was passed through the column bed and the analytes were eluted with 10 mL of hexane: acetone (4:1, v/v) solvent mixture. The sample was evaporated to dryness, then dissolved in 1 mL of acetone and analyzed.

The concentration of phthalates was analyzed using the GC-MS. A TG-5MS column (30 m × 0.25 mm × 0.25 µm) was used to separate the target substances. The carrier gas was Helium with a constant flow of 1 mL/min. The ion source temperature and the MS transfer line temperature were 250°C and 280°C, respectively. The GC oven temperature was programmed as follows: increase the temperature to 80°C and hold for 1 min, next up to 11 min increase the temperature to 180°C (rate 10°C/min), then increase the temperature to 290°C (rate 8°C/min) and hold for 10 min. The total time for one analysis was 35 min. PAEs were analyzed in the selected ion monitoring mode.

In order to determine the concentration of phenol derivatives in the sediments, the methodology proposed by Lubecki and Kowalewska [34] was used. 2 g of sediment was sonicated (3 × 10 min) with a solvent mixture of n-hexane: acetone (1:1, v/v) 3 × 20 mL. The supernatant was decanted, filtered, evaporated to dryness, and then dissolved in 0.5 mL of n-hexane. The extracts were purified successively on columns packed with silica gel (0.8 g) and with florisil (1.0 g). The silica gel column was conditioned with 3.5 mL of hexane, the extract was passed through the bed. Then the residue in the vial was dissolved in 3.5 mL of a mixture of hexane: dichloromethane (1:1, v/v) and the bed was rinsed with this solution. The phenol derivatives containing fractions were eluted with 6 mL of a mixture of dichloromethane: ethyl acetate (9:1, v/v). The extract was then further purified with florisil column (1.0 g). The purification steps were the same with the analytes eluted with less solvent (5 mL). The samples were concentrated to a volume of 1 mL.

The concentration of phenol derivatives using the GC-MS and the TG-5MS column, were also analyzed. The carrier gas was Helium with a constant flow of 1 mL/min. The ion source temperature and the MS transfer line temperature were 250°C and 280°C, respectively. The GC oven temperature was programmed as follows: temperature increase to 100°C during the first 10 min of the analysis, later increase to 200°C (rate 10°C/min), from 18 min of analysis, increase to 280°C (rate 10°C/min), then increase the temperature to 320°C (rate 20°C/min) and hold for 10 min. The total time for one analysis was 35 min. Phenol derivatives were analyzed in the selected ion monitoring mode.

Standards, including the mix of phthalates, BPA, 4nNP, 4tOP from Sigma-Aldrich (United States) were used. Solvents for chromatographic analysis, including dichloromethane, acetone, hexane were obtained from POCH Company (Poland). The quality assurance and quality control systems were used. The quality control of research was based on the analysis of blind samples and recovery with the working standard parallel for each series of samples. The obtained recovery values ranged from 52%–126% for phthalates and 71%–115% for phenol derivatives.

2.3.3. Heavy metals analysis

The total heavy metal concentrations in the sediment samples and obtained extracts were determined using inductively coupled plasma optical spectrometry (Avio 200 ICP-OES, PerkinElmer Inc., Waltham, MA, USA). The limit of detections (LODs) were 0.004, 0.006, 0.005, 0.007, 0.009 and 0.008 mg/L for Cd (cadmium), Cr (chrome), Cu (copper), Ni (nickel), Pb (lead) and Zn (zinc), respectively. All measurements were performed in duplicate. Before measuring the total concentration of heavy metals, 0.5 g of each sediment sample was subjected to digestion in a microwave system (Multiwave 3000, Anton Paar GmbH, Graz, Austria),

by a mixture of HNO_3 (5 mL), HCl (15 mL) and HF (1 mL). To control the digestion process, blank reagent sample with the same amount of acids but without the sediments was used. The obtained solutions were filtered through the quantitative filters paper (diameter: 150 mm; grade: 390) and diluted with 5% HNO_3 to volume of 50 mL.

2.3.4. Sequential extraction of heavy metals

To identify the chemical forms of heavy metals ($F1$–$F3$) in sediments samples, we used the BCR three-step sequential extraction procedure proposed by the Community Bureau of Reference (now the Standards, Measurements and Testing Programme). Moreover, the residual heavy metal concentrations were also determined ($F4$), which is optional. The recovery rate (R; %) in the extraction procedure was calculated by comparing the sum of the four fractions with the total concentrations of metals in the sediment samples. All standards were prepared on the day of analysis. The obtained extracts were stored at 4°C until laboratory examination. A scheme of the BCR sequential extraction is shown in Table 1 [24,25].

2.4. Potential ecological risk analysis

To assess the potential ecological risk posed by heavy metals and selected organic pollutants in bottom sediments of the Rybnik Reservoir, the chosen criteria/indices were used (Table 2).

2.5. Statistical analysis

In order to investigate the relationship between the analyzed variables, correlation matrices were prepared. The

Table 1
The BCR sequential extraction procedure

Step/Form	Chemical forms	BCR procedure
Step I/$F1$	Acid soluble/exchangeable; bound to carbonates (mobile)	To 0.5 g of sample add 20 mL of CH_3COOH (0.11 mol/L) and then shake for 16 h.
Step II/$F2$	Reducible; bound to Mn and Fe oxides (mobile)	To residue from Step I add 20 mL of $HN_2OH \cdot HCl$ (0.1 mol/L) and then shake for 16 h.
Step III/$F3$	Oxidizable; bound to organic matter and sulfides (immobile)	To residue from Step II add 5 mL of H_2O_2 (8.8 mol/L) and incubate at 85°C for 1 h (repeat twice). Afterwards, add 25 mL of CH_3COONH_4 (1 mol/L) and then shake for 16 h.
Step IV/$F4$	Residual (immobile)	To residue from Step III add 5 mL of HNO_3 and 15 mL of HCl and mineralize the mixture.

Table 2
Criteria and indices (tools) for the assessment of potential ecological risk of heavy metals and selected organic pollutants in bottom sediments

Criteria/Indices	Equation	Scale	Category
Geochemical quality classification (GQC) [21,35]	-	class I - non-contaminated class II - moderately contaminated class III - contaminated, class IV - highly contaminated	Total metal content
Ecotoxicological criteria Probable Effect Concentration (PEC) *i* Threshold Effect Concentration (TEC) [26,36].	$C_P < $ TEC TEC $< C_P < $ PEC $C_P > $ PEC C_P - measured concentration of pollutant in the sediment sample	non-polluted neither polluted nor non-polluted polluted	Total metal content or bis (2-ethylhexyl) phthalate content
Potential Ecological Risk Factor (ER) [37]	T- toxic response factor of metal; CF - Contamination Factor	ER < 40 - low risk 40 < ER ≤ 80 - moderate risk 80 < ER ≤ 160 - considerable risk 160 < ER ≤ 320 - high risk ER > 320 - very high risk	Total metal content
Risk Assessment Code (RAC) [38]	$F1$ – mobile form	RAC ≤ 1% - no risk 1% < RAC ≤ 10% - low risk 10% < RAC ≤ 30% - medium risk 30% < RAC ≤ 50% - high risk RAC > 50% - very high risk	Chemical form of metal

strength of correlation was analyzed using Pearson's coefficients and Spearman's rank. In the case of Pearson's correlation, the correlation coefficient has a value between −1 and 1. The greater the absolute value is, the stronger the linear relationship between the analyzed variables. While in the case of Spearman's correlation, the value of the correlation coefficient is also in the range [−1, 1], but in this case it indicates any monotonic dependence, also non-linear. The calculations were made in the Statistica 12 (StatSoft).

3. Results and discussion

3.1. Principal physicochemical analysis of bottom sediments

The Rybnik Reservoir is a sink for many pollutants flowing in with the Ruda River waters. Presumably for this reason, the bottom sediments of the reservoir show a wide variety of certain pollutants, which accumulate.

The results of the conducted analyzes indicate the stability of the pH values in the investigated sediments in the period under consideration (Table 3). Taking into account the values of the redox potential (Eh), it can be assumed that the conditions in the reservoir are slightly reducing. It was observed that the sediments at the $S1$ point were characterized by the lowest value of this parameter (−372 mV), while those at the $S3$ point were the highest (−205 mV). It was found that in the sediments of Fraction 4 (the slowest falling) the redox potential values were the highest.

The conducted research has shown that the sediments located near the dam, that is, at the $S3$ point, are the richest in organic matter. The existence of the dam on the Rybnik Reservoir favors the accumulation of mineral and organic materials in its basin, which is carried by the Ruda River (the main inflow to the reservoir). The content of organic matter in the bottom sediments, after division into fractions, was variable. In each sediment sample, the highest share fell on the Fraction 1 – the fastest falling fraction and the lowest on the Fraction 4 – the slowest falling fraction. Large differences were observed especially at the $S3$ sampling point, where the share of DOM in the Fraction 1 and Fraction 4 amounted to 55.48% and 5.18%, respectively. The obtained results indicate the differentiation of the basic parameters of bottom sediments, both in terms of the spatial and in the separated sedimentation fractions.

The division of sediments into sedimentation fractions revealed differences in the weight share of individual groups of particles with different precipitation. In each of sediments, the dominant fraction was the fastest falling one, that is, Fraction 1, the share of which was respectively: S1 – 64.9%, S2 – 39.8%, S3 – 36.3%. While, the smallest share fell on the slowest falling fraction, that is, Fraction 4: S1 – 0.2%, S2 – 9.1%, S3 – 9.7%.

In terms of particle size distribution, bottom sediments from the Rybnik Reservoir consisted mainly of particles with a size of 0.1–50 μm (Fig. 3), while the granular structure of the sediments changed in the longitudinal profile of the reservoir. At the $S1$ sampling point, the share of these particles ranged from 36% (Fraction 1) to 58% (Fraction 2, Fraction 4). The sediments from the $S2$ sampling point were characterized by a higher proportion of small particles (0.1–50 μm) than the $S1$ sediments – on average 71% (the highest share of 74% in Fraction 3 and Fraction 4).

Table 3
Range of physicochemical properties of bottom sediments of the Rybnik Reservoir

Sampling point	pH (−)	Redox (mV)	DM (%)	DOM (%)	DMM (%)
S1 ($n = 5$)	7.38 – 7.71	−372 – −130	5.01 – 5.97	3.51 – 4.17	1.50 – 1.81
S2 ($n = 5$)	7.29 – 7.48	−368 – −191	10.09 – 22.57	7.79 – 19.85	2.30 – 3.22
S3 ($n = 5$)	7.36 – 7.65	−205 – −195	5.18 – 57.66	4.07 – 55.48	1.11 – 4.08

Table 4
Concentrations of phthalates and phenol derivatives in bottom sediment of the Rybnik Reservoir (μg/kgDM)

Samples		DMP	DEP	DBP	BBP	DEHA	DEHP	DOP	∑PAEs	4tOP	4nNP	BPA	∑Phenols
S1	Fraction 1	<LOD	445.29	489.31	58.65	<LOD	526.33	<LOD	1,519.58	72.17	121.99	<LOD	194.16
	Fraction 2	<LOD	<LOD	607.02	106.09	<LOD	809.56	409.25	1,931.92	<LOD	84.01	<LOD	84.01
	Fraction 3	<LOD	<LOD	576.77	178.45	<LOD	1,040.20	164.50	1,959.92	66.12	88.37	<LOD	154.49
	Fraction 4	<LOD	<LOD	964.16	<LOD	<LOD	1,045.93	<LOD	2,010.09	<LOD	<LOD	<LOD	<LOD
S2	Fraction 1	<LOD	<LOD	655.99	117.47	<LOD	631.74	125.47	1,530.67	74.05	134.32	<LOD	208.36
	Fraction 2	<LOD	<LOD	652.82	147.02	<LOD	803.06	<LOD	1,602.91	73.84	120.56	<LOD	194.40
	Fraction 3	<LOD	<LOD	431.48	157.95	<LOD	962.80	119.09	1,671.33	83.23	126.68	<LOD	209.92
	Fraction 4	<LOD	<LOD	1,023.50	392.72	241.08	930.65	423.62	3,011.56	<LOD	<LOD	<LOD	<LOD
S3	Fraction 1	<LOD	242.19	2,232.36	411.46	238.94	1,257.03	417.54	4,799.52	74.45	126.15	<LOD	200.61
	Fraction 2	<LOD	244.74	2,253.15	287.29	<LOD	1,383.22	307.69	4,476.08	75.82	148.03	<LOD	223.85
	Fraction 3	<LOD	<LOD	1,703.16	292.65	225.04	1,281.46	320.48	3,822.80	131.44	164.60	<LOD	296.04
	Fraction 4	<LOD	<LOD	859.67	225.00	303.58	891.04	685.29	2,964.58	<LOD	<LOD	<LOD	<LOD

<LOD – concentration below limit of detection

At the *S*3 sampling point, no particles with a size from 100 to 650 μm were observed. The sediments from this sampling point consisted on average in 89% of particles with a size of 0.1–50 μm (the highest share in Fraction 1 – 92%).

3.2. Plastic-derived contaminants

In the case of selected additives for plastics, that is, phthalates, their presence in bottom sediments of the Rybnik Reservoir was found at each sampling point (in the period under consideration). Their presence had previously been frequently studied in marine sediments [11,34,39–43], less frequently in bottom sediments of lakes and anthropogenic reservoirs [26,33,44].

In the case of the Rybnik Reservoir, the sum of phthalate concentrations increased along the central axis of the reservoir from 1,855.38 μg/kgDM (mean value for the *S*1) up to 4,015.75 μg/kgDM (mean value for the *S*3) (Table 4, Fig 4a). The average concentrations of the analyzed phthalates, except DEP, showed a relationship between the depth of sampling and the content of these substances, namely these concentrations increased with increasing depth of the reservoir (Fig. 5a). As already mentioned, the highest concentrations of organic matter were found
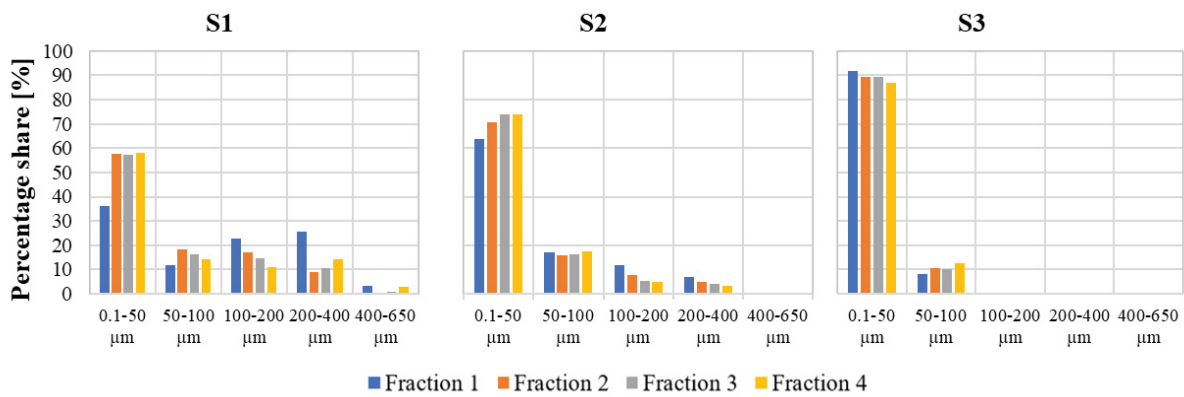

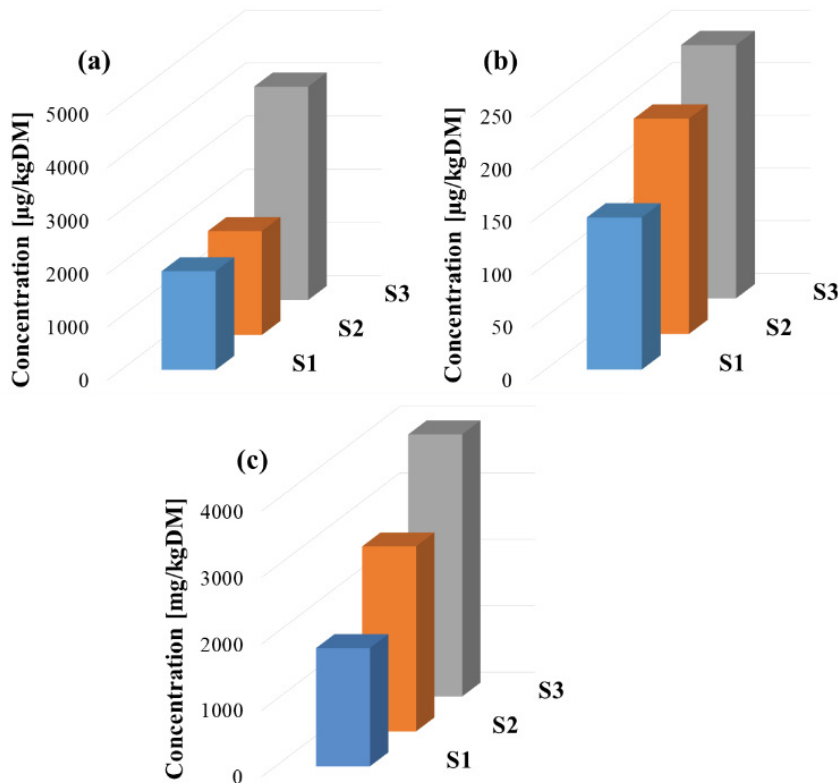Fig. 3. Granulometric composition of bottom sediments of the Rybnik Reservoir.

Fig. 4. Mean total concentration of: (a) phthalates, (b) phenol derivatives, and (c) heavy metals in bottom sediment of the Rybnik Reservoir.
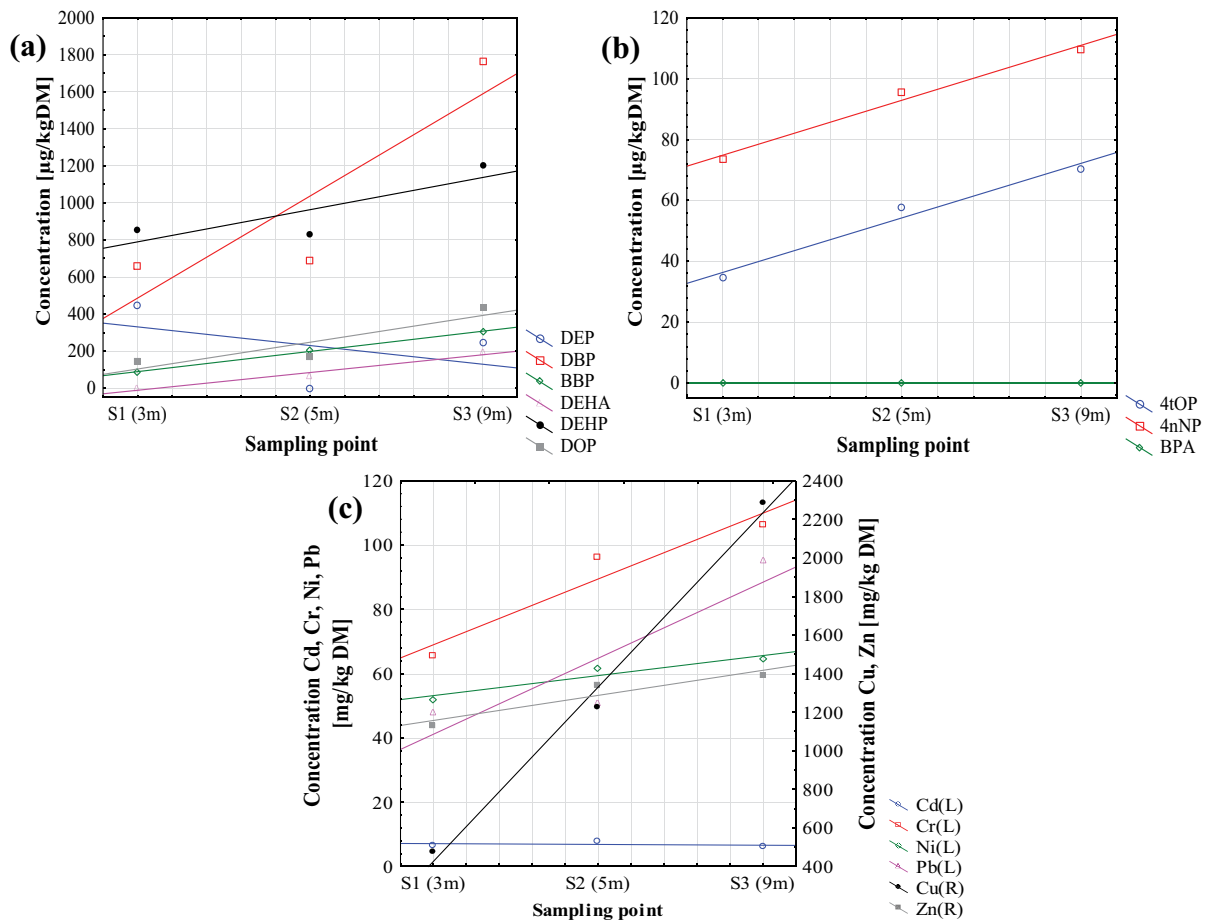
Fig. 5. Position variability for organic and non-organic substances: (a) phthalates, (b) phenol derivatives, and (c) heavy metals in the bottom sediments of the Rybnik Reservoir and the depth of sampling points ($S1$ – 3 m; $S2$ – 5 m; $S3$ – 9 m).

at the $S3$ (near the dam). Organic matter acts as a specific sorbent for hydrophobic organic pollutants in the sediment [39], which was confirmed in this study.

Apart from the spatial variability of the tested phthalates, also the fractional variability of these compounds was found. At the $S1$, the lowest concentration of the phthalates sum was found in Faction 1. The values of the sum of phthalate concentrations in the subsequent fractions were comparable. In the sediments collected at the sampling point $S2$, the sum of phthalate concentrations in the first three fractions was comparable (mean 1,601.63 μg/kgDM) and slightly lower than the sum recorded in the sediments from the $S1$. While, in Fraction 4 the sum was twice as high and amounted to 3,011.56 μg/kgDM. In turn, in the sediments from the sampling point $S3$, the concentrations of phthalates were the highest, and their values decreased from Fraction 1 to Fraction 4. As a large variation in the concentrations of the analyzed phthalates in the fractions of the sediments was found, it cannot be clearly indicated whether any sedimentation fraction is responsible for the accumulation of these pollutants in an increased amount than the remaining ones.

Dimethyl phthalate, which is highly soluble in water (4,000 mg/L at 25°C) [45], was not noted in any of the

sediment samples. Bis(2-ethylhexyl) phthalate and dibutyl phthalate were the dominant phthalates in the sediments studied (Fig. 6). DEHP and DBP are the most abundant PAEs found in the environment [44,46]. With large population and industrialization (including the development of the plastics industry), and continuous inflow to the reservoir of water with quality, in the case of many parameters, described as below good, as well as poor air quality, especially during the heating season, may be contributed to the high concentration of PAEs, including DEHP and DBP. Increased getting into the reservoir, with low solubility of these compounds in water, promotes their absorption and deposition in bottom sediments.

In the case of the second group of tested additives for plastic, that is, phenol derivatives, the levels of contamination were lower compared to the results of other researchers from the country, but at the same time in Poland, these compounds are mainly tested in the Gdansk Bay area (Baltic Sea) [11,34,39,40].

In the bottom sediments of the Rybnik Reservoir, no BPA was found at any sampling point. The total concentration of 4nNP and 4tOP increased from the sampling point $S1$ (mean 144.22 μg/kgDM) to the $S3$, located near the dam (mean 240.17 μg/kgDM) (Table 4, Fig 4b). The increase in
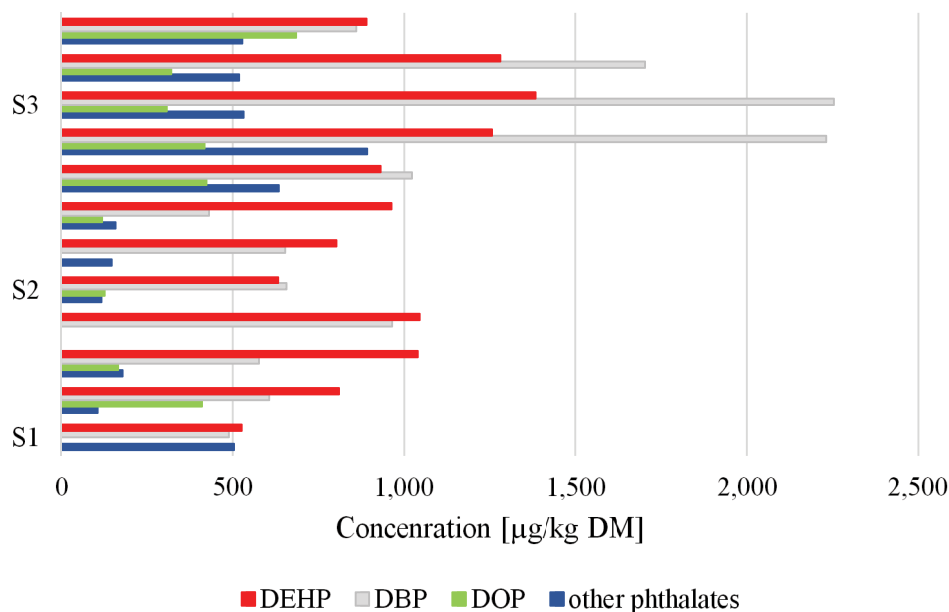
Fig. 6. Occurrence of phthalates in bottom sediments of the Rybnik Reservoir.

the concentration of the tested phenol derivatives with the increase in the depth of the reservoir (Fig. 5b). This tendency is analogous to that in the case of the tested phthalates, and may also be related to increase in the content of organic matter at individual sampling points.

In the case of phenol derivatives, the fractional variability was also found, while compared to phthalates, the concentrations of phenol derivatives were at a more comparable level. In the sediments at *S*1, the sum of phenols ranged from 84.01 μg/kgDM in Fraction 2 to 194.16 μg/kgDM in Fraction 1. In the sediments from sampling point *S*2, the sum of phenols ranged from 194.40 μg/kgDM in Fraction 2 to 209.92 μg/kgDM in Fraction 3. In turn, in the *S*3 sediment, the sum of phenols was from 200.61 μg/kgDM in Fraction 1 to 296.04 μg/kgDM in Fraction 3. At each sampling point, in Fraction 4, the analyzed phenols were below the limit of detection. As in the case of phthalates, the alkylphenols did not show a tendency to accumulate in the selected sedimentation fraction of the sediments.

3.3. Results of total heavy metals analysis

The results of long-term monitoring of the waters of Rybnik Reservoir in the field of, that is, heavy metals (carried out by the Institute of Environmental Engineering in Zabrze, Polish Academy of Sciences), indicate that the source of metals, such as Cr or Cu, may be discharges of water from the Rybnik Power Plant. In turn, pollution with Ni, Pb or Zn is caused by the waters of Ruda River. Fig. 4c and Table 5 present the total content of the analyzed heavy metals in the bottom sediments at individual sampling points (*S*1–*S*3) and in the granulometric fractions separated according to the lab-testing methodology (Fraction 1 – Fraction 4).

The conducted research showed spatial variability of heavy metal concentrations in the analyzed bottom sediments. Despite relatively stable conditions in the reservoir,

the total concentrations of metals at individual sampling points were subject to fluctuations. In total, the highest concentrations of the elements under consideration were recorded at the sampling point *S*3 (reservoir depth 9 m), and the lowest at the *S*1 (reservoir depth 3 m) (Fig. 5c). A similar relationship was noted for the separated sediment fractions (Table 5). The above observations indicate the existence of a relationship between the depth of sampling sediments and the content of individual elements, namely the concentration of metals increases with increasing depth of the reservoir (except for Cd), the concentration of which is at a similar level at all sampling points. Moreover, conducted research has also shown that sediments located near the dam (*S*3) are the richest in organic matter. Therefore, this parameter might be an important factor, which controls heavy metal distribution. The above finding confirmed also other scientists [47].

The research showed that heavy metals in sediments of Rybnik Reservoir formed the following series: Zn > Cu > Cr > Ni > Pb > Cd (*S*1 and *S*2) and Cu > Zn > Cr > Ni > Pb > Cd (*S*3). With regard to individual fractions of sediments, at a given sampling point, at the *S*1, there were some differences in the above-mentioned series for Cr and Ni (Fraction 1 and Fraction 3); at the *S*2 for Cu and Zn, as well as Ni and Pb (Fraction 3 and Fraction 4), and at the *S*3 for Ni and Pb (Fraction 1 to Fraction 4). However, this was not a significant difference.

In order to compare the concentration values of the analyzed heavy metals obtained in the bottom sediments before and after their separation into fractions (Fraction 1 – Fraction 4), the contents of these elements in individual fractions were summed (Table 5). As the contents of individual metals in the separated fractions were similar, the relative error value was calculated for each fraction. This was to investigate which fraction should be used for the determination of metals in the analyzed bottom sediments. Based on the obtained results, it can be assumed

Table 5
Concentrations of heavy metals in bottom sediments of the Rybnik Reservoir

| Sample		Cd	Cr	Cu	Ni	Pb	Zn	Σ	Relative error
					(mg/kgDM)				%
S1	Total	6.62	65.59	477.50	52.00	48.00	1,129.50	1,779.21	
	Fraction 1	6.30	36.98	261.88	39.59	28.95	975.77	1,349.47	−24.2
	Fraction 2	9.39	58.08	458.87	57.05	39.13	1,361.39	1,983.91	11.5
	Fraction 3	8.09	51.58	493.43	56.67	52.17	1,344.40	2,006.34	12.8
	Fraction 4	5.81	52.10	518.92	48.32	42.62	897.77	1,565.54	−12.0
S2	Total	7.81	96.20	1,225.50	61.70	51.05	1,342.00	2,784.26	
	Fraction 1	9.91	75.91	980.71	62.37	51.55	1,275.06	2,455.514	−12.0
	Fraction 2	11.41	104.81	1,396.18	69.16	69.11	1,461.49	3,112.161	11.8
	Fraction 3	11.79	123.48	1,691.84	71.87	75.71	1,531.99	3,506.696	25.9
	Fraction 4	12.00	127.96	1,693.37	77.64	84.04	1,579.54	3,574.543	28.4
S3	Total	6.12	106.50	2,284.00	64.45	95.25	1,389.50	3,945.82	
	Fraction 1	9.29	124.95	2,351.17	74.61	108.55	1,464.89	4,133.47	4.8
	Fraction 2	10.02	115.92	2,218.79	74.04	110.54	1,436.33	3,965.65	0.5
	Fraction 3	10.47	127.81	2,056.05	83.38	106.61	1,469.65	3,853.96	−2.3
	Fraction 4	11.15	128.71	2,004.49	81.67	110.14	1,511.77	3,847.94	−2.5
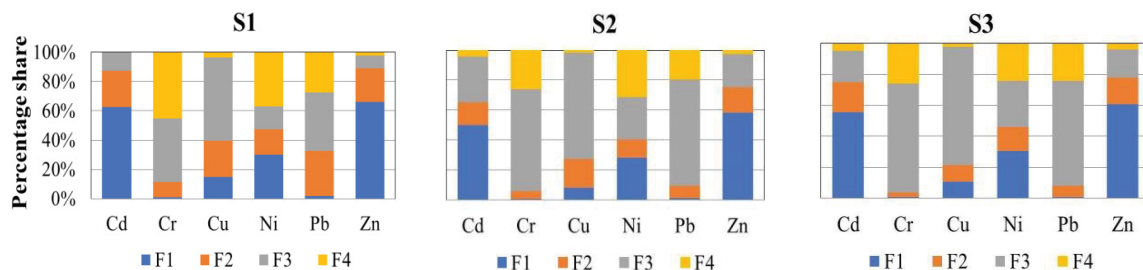
Fig. 7. The average percentage distribution of each heavy metal chemical fraction in bottom sediment samples.

that in the case of the conducted research, Fraction 2 seems to be the most appropriate for the analysis of heavy metals in the Rybnik Reservoir, as it is burdened with the lowest relative error for individual sediments. Therefore, the sediments in Fraction 2 were used for further stages of the research, that is, for chemical sequential extraction and for potential ecological risk assessment.

3.4. Results of the chemical sequential extraction

The results of sequential extraction process carried out in accordance with the BCR procedure shows that in total the bottom sediments of the Rybnik Reservoir are characterized by a higher share of heavy metals in immobile chemical forms ($F3$ and $F4$), in except for Cd and Zn (Fig. 7). The percentage share of Cd and Zn in mobile forms ($F1$ and $F2$) at individual sampling point was as follows: 62.4% (Cd, $F1$) and 24.9% (Cd, $F2$); 66.0% (Zn, $F1$) and 23.0% (Zn, $F2$) at $S1$;49.7% (Cd, $F1$) and 15.6% (Cd, $F2$); 58.3% (Zn, $F1$) and 17.0% (Zn, $F2$) at $S2$; 55.4% (Cd, $F1$) and 19.4% (Cd, $F2$); 60.6% (Zn, $F1$) and 17.2% (Zn, $F2$) at $S3$. High mobility of Cd and Zn in sediments of water reservoirs was also confirmed by other scientists [48,49].

Moreover, it was also observed that share of heavy metals in mobile forms decreases at successive sampling points, mainly in favor of immobile one, associated with organic matter and sulphides ($F3$).

The greatest difference between the percentage share of individual heavy metals in a given chemical form was noted at the sampling point $S1$. Presumably, this is due to the constant movement of water at this point, because the $S1$ is located near the place where the Ruda River is fed to the reservoir and the water discharge from the Rybnik Power Plant, which probably also influences the movement of bottom sediments and thus their mixing and changes in the conditions in the reservoir. In the bottom sediments, at the remaining sampling points, the percentage share of the analyzed heavy metals in individual chemical forms, in the separated fractions of bottom sediments were comparable.

3.5. Results of the potential ecological risk analysis

The results of the potential ecological risk analysis are shown in Table 6. In accordance to the classification based on the geochemical classification [21,35], the bottom sediments of the Rybnik Reservoir show moderate (Class II) to heavy contamination (Class IV) with the analyzed heavy metals.

Table 6
The results of the potential ecological risks analysis

Sampling point	Pollutant	GQC	PEC/TEC	ER	RAC, %
S1	Cd	IV	T	2,815.6 (VHR)	62.4 (VHR)
	Cr	II	NT	1.2	0.9
	Cu	IV	T	41.7	14.8
	Ni	IV	T	14.3	30.2 (HR)
	Pb	II	NT	13.0	1.7
	Zn	IV	T	19.4	66.0 (VHR)
	DEHP	–	NT	–	–
S2	Cd	IV	T	3,421.9 (VHR)	49.7 (HR)
	Cr	III	NT	2.1	0.4
	Cu	IV	T	126.9 (CR)	8.0
	Ni	IV	T	17.3	28.0
	Pb	II	NT	23.0	0.9
	Zn	IV	T	20.9	58.3 (VHR)
	DEHP	–	NT	–	–
S3	Cd	IV	T	3,007.5 (HR)	55.4 (VHR)
	Cr	III	T	2.3	0.4
	Cu	IV	T	201.7 (HR)	10.6
	Ni	IV	T	18.5	30.4 (HR)
	Pb	III	NT	36.8	0.7
	Zn	IV	T	20.5	60.6 (VHR)
	DEHP	–	NT	–	–

T – toxic; NT – not toxic; VHR – very high risk; HR – high risk; CR – considerable risk

The mean concentrations of potentially toxic elements in the bottom sediments were as follow: Cd, Cu, Zn> Ni> Cr> Pb.

For the analysis of the ecological risk, the ecotoxicological criteria based on probable effect concentration (PEC) and threshold effect concentration (TEC) indices [36] was used. The values of these indices inform about the content of a given element, above which its toxic effect on benthic organisms is noticeable. Based on the above classification, it was found that heavy metals present in the sediments of the Rybnik Reservoir may cause an adverse effects on aquatic organisms, the only exception being lead. It was also observed that the toxicity of individual metals increases at subsequent sampling points. The study conducted by other scientists, a few years earlier, confirmed our observations in relate to Cd, Cu, Cr, Ni and Zn [22]. Thus, it can be concluded, that the above-mentioned observations are in good agreement with results presented in this study. The toxicity aspect of heavy metals also includes another index, that is, the potential ecological risk factor (ER) [37]. Based on its values, it was found that the potentially highest ecological risk in the bottom sediments of the Rybnik Reservoir is caused by the presence of Cd and Cu. Similar observations in relation to Cd were also reported by other scientists from Poland and countries all over the world. For example, the researcher from Poland indicated moderate ecological risk (ER > 40) in the case of Cd in sediments of Straszny Lake (Northern Poland) [48] and very high risk (ER 420.0–3,180.0) in sediments of Bardowskiego Lagoon (Central Poland) [23], while others from Egypt and Mexico, a very high risk, that is, from 454.5 to 747.0 in sediments

of Burullus Lake [50], and from 600 to 16,800 in sediments of San – Juan – Taxco River system, respectively [20].

However, the above criteria and indices refer to the total content of heavy metals, hence the observed relationships between the sampling point (depth of sediments deposition), elements concentrations and their potential toxicity. Therefore, the ecological risk analysis was also performed based on the chemical forms of heavy metals. For this purpose, the risk assessment code (RAC) index [38] was used. The obtained results indicate that the potential threat may be posed by the presence of Cd and Zn and, to a limited extent by Ni. Similar observation made also other scientists, who indicated that in the sediments from Straszyn Lake (Northern Poland, Central Europe), according to RAC values; it was found to be a very high risk for Cd release from sediments; medium risk for Zn, Ni, Pb release, and low risk in case of Cu and Cr. The described reservoir was constructed in 1910, primarily to produce energy, as with the Rybnik Reservoir [48].

The conducted research revealed that bottom sediments of the Rybnik Reservoir are highly polluted by analyzed heavy metals that may pose a serious threat to organisms living in this water body. In addition, it was also found that metal that were present in lower concentrations than others may pose a higher or comparable level of ecological risk, which was particularly evident in the case of cadmium.

From 2013, the assessment of bottom sediment contamination in Poland was extended to include DEHP [26]. Ecotoxicological assessment of bottom sediments in terms of the content of other substances from the group of phthalic

acid esters and tested phenol derivatives has not been carried out. DEHP concentrations in sediments of the Rybnik Reservoir were within the II level of sediment contamination (i.e., >TEC ≤ MEC, where MEC is midpoint effects concentrations). The limit values for the III level of bottom sediments purity (>MEC ≤ PEC) were not exceeded, so the negative impact of DEHP on the benthic organisms of the tested reservoir should not occur.

3.6. Results of statistical analysis

Pearson's linear correlation was used to analyze the relationship between the physicochemical properties of sediments and the concentrations of the tested heavy metals and plasticizers, all analyzed variables had a normal distribution (Table 7). In turn, in the case of the analysis of the relationship between the share of individual particle sizes of bottom sediments and the concentration of the tested pollutants, the Spearman correlation was used, the above-mentioned variables didn't have a normal distribution (Table 8).

Based on the statistical analysis carried out, a positive correlation between the total content of compounds for the studied groups of pollutants and the concentration of organic matter in bottom sediments was found, that is, $r = 0.670$ for the sum of phthalates; $r = 0.451$ for the sum of phenols and $r = 0.563$ for the sum of heavy metals. The content of organic matter increased in the direction of water flow from the sampling point $S1$ to $S3$. The same relationship was noted for the sum of phthalates, phenols and heavy metals.

Statistical analysis shows that there is a strong positive correlation between analyzed heavy metals ($r > 0.6$) and also some phthalates ($r > 0.6$). Moreover, strong correlations between different groups of pollutants were also found. The values of the correlation coefficient between the sum of the tested metals and selected phthalates, in particular DBP, BBP, DEHA, DEHP, DOP were high ($r > 0.6$), and similar to the sum of phthalates and selected metals, including Cr, Cu, Ni, Pb. Based on the high values of the Pearson's r coefficient, it can be assumed that the analyzed heavy metals and phthalates may have a common source of origin. However, in order to identify them, it would be necessary to carry out long-term studies of the reservoir.

Taking into account the location of the reservoir, namely the location in the area of the Upper Silesian Industrial Region – the largest industrial region in Poland; water discharges from the Rybnik Power Plant; its continuous supply with the waters of the Ruda River (the water quality for many parameters is defined as below good), as well as the proximity of the provincial road; its recreational function, which is associated with a large number of people (especially in the summer season); the air quality in the city of Rybnik and the associated dry and wet deposition; as well as the year of its creation, it can be assumed that heavy metals and phthalates present in bottom sediments accumulated in them over the years as a result of different types and intensity of anthropopressure.

In the case of phenol derivatives, a strong correlation was found between the concentrations of 4tOP and 4nNP ($r = 0.9$), but there was no correlation between these compounds and metals or phthalates. It follows that some of the analyzed alkylphenols may have a similar source of origin, however different from heavy metals or phthalates.

The results of the statistical analysis of the correlation matrix for the relationship between the concentrations of particular pollutants and the share of bottom sediment particles of different sizes are presented in Table 8. In the case of small particles 0.1–50 μm, in all cases (except for DEP) a positive correlation was found, where not statistically significant correlations were obtained for DOP ($r = 0.521$), 4tOP ($r = 0.545$), 4nNP ($r = 0.408$), sum of phenols ($r = 0.465$) and Cd ($r = 0.483$). In all other cases, the relationship was strong and statistically significant ($r > 0.6$). As for the larger particles, ranging from 50 μm to 650 μm, in each case inversely proportional relationships were found. The correlations between the proportion of 50–100 μm particles and the tested compounds (except for DEP), as well as all correlations between the proportion of particles, regardless of their size and the concentrations of phenol derivatives turned out to be not statistically significant. For the phthalates and heavy metals analyzed in the bottom sediments, in most cases these relationships were strong and statistically significant.

The existence of a relationship between the size of sediment particles or the content of organic matter and the concentration of heavy metals in bottom sediments was also confirmed by the study of He et al. [51] and Huang et al. [52]. In the case of bottom sediments, certain physicochemical properties that determine their sorption capacity are indicated. The most important are: the content of small fractions characterized by a large specific area, the content of organic matter or total organic carbon (TOC). High values of the mentioned parameters are usually associated with an increased content of hydrophobic organic pollutants [53].

The obtained correlations clearly confirm that the increased participation of the small particles (size 0.1–50 μm) and the increased content of organic matter in sediments are related to the increased content of the tested pollutants, namely selected heavy metals and plastic additives – phthalates.

4. Conclusion

The presence of plastics-derived contaminants and heavy metals in water reservoirs is a result of different types and intensity of anthropopressure. Moreover, their properties, that is, low solubility in water and resistance to degradation, promotes their sorption on suspended particles and accumulation in bottom sediments, where can be accumulate over the years. Treating sediment as an integral part of the aquatic ecosystem and separating them on sedimentation fractions can provide information on differences in their chemical composition.

The concentrations of the analyzed heavy metals in the bottom sediments of the Rybnik Reservoir were characterized by low fractional variability. The opposite tendency was noted in relation to the concentrations of additives to plastics, the value of the redox potential and the content of organic matter. However, the differences in the concentrations of the

Table 7
Pearson's correlation matrix for analyzed pollutants and sediments physicochemical properties

	pH	Redox	DM	DOM	DMM	DMP	DEP	DBP	BBP	DEHA	DEHP	DOP	∑PAEs	4tOP	4nNP	BPA	∑Phenols	Cd	Cr	Cu	Ni	Pb	Zn	∑Heavy metals
pH	1.000																							
Redox	-0.554	1.000																						
DM	-0.031	0.179	1.000																					
DOM	-0.029	0.186	0.999	1.000																				
DMM	-0.055	-0.066	0.429	0.381	1.000																			
DMP						1.000																		
DEP	0.366	-0.155	0.324	0.334	0.096		1.000																	
DBP	-0.132	0.643	0.739	0.731	0.431		0.318	1.000																
BBP	-0.307	0.446	0.604	0.600	0.296		0.055	0.687	1.000															
DEHA	-0.506	0.554	0.251	0.270	-0.232		-0.100	0.417	0.724	1.000														
DEHP	-0.129	0.746	0.482	0.468	0.383		-0.049	0.825	0.590	0.313	1.000													
DOP	-0.237	0.414	0.152	0.164	-0.230		-0.155	0.378	0.638	0.782	0.324	1.000												
∑PAEs	-0.184	0.679	0.673	0.670	0.299		0.258	0.958	0.814	0.611	0.822	0.592	1.000											
4tOP	0.299	-0.232	0.432	0.409	0.640		0.255	0.292	0.177	-0.123	0.264	-0.338	0.196	1.000										
4nNP	0.527	-0.437	0.489	0.462	0.684		0.350	0.281	0.087	-0.319	0.164	-0.312	0.154	0.900	1.000									
BPA																1.000								
∑Phenols	0.442	-0.360	0.477	0.451	0.682		0.318	0.293	0.128	-0.243	0.211	-0.331	0.176	0.966	0.982		1.000							
Cd	-0.420	-0.030	0.181	0.155	0.446		-0.445	0.079	0.570	0.407	0.144	0.464	0.207	0.105	0.082		0.094	1.000						
Cr	-0.584	0.413	0.461	0.445	0.443		-0.212	0.512	0.777	0.676	0.521	0.564	0.627	0.197	0.066		0.124	0.824	1.000					
Cu	-0.482	0.486	0.628	0.613	0.493		-0.019	0.714	0.810	0.648	0.652	0.559	0.791	0.292	0.186		0.236	0.673	0.955	1.000				
Ni	-0.507	0.424	0.388	0.371	0.394		-0.359	0.498	0.780	0.698	0.550	0.658	0.627	0.188	0.063		0.119	0.841	0.959	0.912	1.000			
Pb	-0.438	0.582	0.537	0.527	0.388		-0.041	0.737	0.812	0.706	0.715	0.650	0.837	0.243	0.110		0.170	0.604	0.911	0.972	0.912	1.000		
Zn	-0.248	0.085	0.315	0.296	0.373		-0.358	0.258	0.750	0.504	0.360	0.609	0.420	0.149	0.126		0.139	0.928	0.830	0.735	0.880	0.714	1.000	
∑Heavy metals	-0.458	0.423	0.579	0.563	0.485		-0.105	0.641	0.834	0.652	0.616	0.600	0.742	0.269	0.174		0.219	0.765	0.975	0.988	0.952	0.961	0.832	1.000

Correlations significant at $p < 0.05$ are marked in red

Table 8
Spearman's correlation matrix for analysis among total contents of analyzed pollutants and sediments particle size

	0.1–50 μm	50–100 μm	100–200 μm	200–400 μm	400–650 μm	DMP	DEP	DBP	BBP	DEHA	DEHP	DOP
0.1–50 μm	1.000											
50–100 μm	−0.538	1.000										
100–200 μm	−0.925	0.504	1.000									
200–400 μm	−0.954	0.431	0.934	1.000								
400–650 μm	−0.797	0.345	0.742	0.877	1.000							
DMP						1.000						
DEP	0.092	−0.606	−0.051	−0.051	−0.051		1.000					
DBP	0.706	−0.517	−0.704	−0.676	−0.691	0.220	1.000					
BBP	0.790	−0.364	−0.767	−0.851	−0.673	0.101	0.615	1.000				
DEHA	0.603	−0.270	−0.702	−0.676	−0.565	−0.093	0.503	0.720	1.000			
DEHP	0.629	−0.517	−0.588	−0.541	−0.427	0.110	0.657	0.566	0.208	1.000		
DOP	0.521	−0.021	−0.589	−0.677	−0.749	−0.102	0.479	0.718	0.809	0.275	1.000	
∑PAEs	0.755	−0.503	−0.774	−0.744	−0.680	0.147	0.846	0.783	0.612	0.853	0.662	
4tOP	0.545	−0.477	−0.285	−0.433	−0.295	0.280	0.164	0.345	−0.148	0.392	−0.186	
4nNP	0.408	−0.416	−0.138	−0.333	−0.326	0.351	0.176	0.232	−0.251	0.289	−0.184	
BPA												
∑phenols	0.465	−0.401	−0.194	−0.384	−0.333	0.287	0.162	0.268	−0.251	0.338	−0.191	
Cd	0.483	0.266	−0.501	−0.591	−0.342	−0.376	0.070	0.483	0.395	−0.028	0.345	
Cr	0.839	−0.182	−0.876	−0.897	−0.712	−0.211	0.524	0.769	0.832	0.329	0.718	
Cu	0.979	−0.545	−0.949	−0.954	−0.776	0.147	0.769	0.846	0.620	0.657	0.542	
Ni	0.881	−0.294	−0.872	−0.947	−0.797	−0.156	0.594	0.839	0.790	0.434	0.718	
Pb	0.895	−0.483	−0.960	−0.947	−0.755	0.110	0.671	0.846	0.616	0.629	0.599	
Zn	0.671	0.021	−0.680	−0.751	−0.481	−0.248	0.203	0.741	0.678	0.231	0.613	
∑heavy metals	0.958	−0.490	−0.914	−0.975	−0.826	0.147	0.706	0.902	0.620	0.615	0.620	

	∑PAEs	4tOP	4nNP	BPA	∑phenols	Cd	Cr	Cu	Ni	Pb	Zn	∑heavy metals
0.1–50 μm												
50–100 μm												
100–200 μm												
200–400 μm												
400–650 μm												
DMP												
DEP												
DBP												
BBP												
DEHA												
DEHP												
DOP												
∑PAEs	1.000											
4tOP	0.146	1.000										
4nNP	0.063	0.946	1.000									
BPA				1.000								
∑phenols	0.092	0.975	0.986		1.000							
Cd	0.112	0.203	0.070		0.162	1.000						
Cr	0.608	0.178	0.035		0.092	0.748	1.000					
Cu	0.804	0.488	0.359		0.408	0.469	0.825	1.000				
Ni	0.671	0.324	0.211		0.261	0.699	0.965	0.867	1.000			
Pb	0.776	0.377	0.254		0.310	0.524	0.818	0.944	0.860	1.000		
Zn	0.434	0.206	0.014		0.106	0.867	0.888	0.650	0.846	0.685	1.000	
∑heavy metals	0.783	0.505	0.394		0.444	0.510	0.825	0.979	0.888	0.951	0.699	1.000

Correlations significant at $p < 0.05$ are marked in red

analyzed phthalates and phenol derivatives in the separated sedimentation fractions did not allow for a clear indication whether any of this fraction is responsible for the accumulation of these pollutants in an increased amount than the others.

All of the tested pollutants were characterized by spatial variability and their concentrations increased with increasing depth of the reservoir, towards the dam, where organic matter accumulates in the reservoir basin. This confirms the influence of the reservoir morphometry on the distribution of tested pollutants.

The grain size of the sediments changes in the longitudinal profile of the reservoir and was related to the chemical composition of the sediments. The obtained correlations confirm that the increased participation of the small particles (size 0.1–50 μm) and the increased content of organic matter in sediments are related to the increased content of the tested pollutants, namely selected heavy metals and phthalates.

The dominant share in the environment of bottom sediments of bis(2-ethylhexyl) phthalate and dibutyl phthalate shows the influence of anthropopressure on the pollution of the aquatic environment. Moreover, the concentration of bis(2-ethylhexyl) phthalate in the sediments of the Rybnik Reservoir does not pose a threat to the benthic organisms of the studied ecosystem. In the case of analyzed heavy metals, the opposite results were obtained. Only lead does not adversely affect aquatic organisms. Results of the ecological risk analysis indicate that the highest risk for fauna and flora of the Rybnik Reservoir may pose presence of Cd, Cu, Zn and Ni. The most dangerous might be Cd and Zn, whose share in the mobile forms (most bioavailable) was the highest.

The result of statistical analysis shows a strong correlation between the analyzed heavy metals, as well as some phthalates. Moreover, strong mutual correlations between these groups of pollutants were also found, which indicates that they may come from the same origin. In the case of phenol derivatives, the observed correlations indicated that some of the analyzed alkylphenols may have a similar source of origin, but different from heavy metals or phthalates.

Acknowledgements

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