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An attempt to describe the correlation between granulometric structure and the concentration of speciated forms of phosphorus and selected metals in the bottom sediments of a thermally contaminated dam reservoir

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Abstract: An attempt was made to determine the correlation between the granulometric structure of bottom sediments and the content of speciation forms of phosphorus and selected metals. Using the sedimentation method, the bottom sediments of a thermally contaminated dam reservoir were divided into fast and slow-draining fractions. Measurements of granulometric composition were made, determining the volume proportions of sediment particles in the range of 0.1 m to 650 m. Particle share sizes were determined in the size range: 0.1–50 m (F1), 50–100 m (F2), 100–200 m (F3), 200–400 m. (F4). The study showed that the content of speciation forms of phosphorus and selected metals remains related to the granulometric structure of bottom sediments. The content of organic matter in sediments is determined by the proportion of the smallest particles, from 0.1 to 50 µm, at the same time these particles most strongly affect the reduction conditions of sediments. According to Gilford›s correlation thresholds, there was no correlation between the proportion of sediment particles with dimensions of 0.1–50 µm and the concentration of speciation forms of phosphorus. For particles with dimensions of 50–100 µm, the strongest correlation was observed for the concentration of the EP fraction and for the WDP fraction (r2 = 0.4048, r2 = 0.3636). A strong correlation between the size of sediment particles and the concentration of speciated forms of phosphorus was noted for particles with dimensions of 100–200 µm and 200–400 µm. The coefficient of determination was for AAP, EP, WDP and RDP, respectively: 0.8292, 0.891, 0.7934, 0.47. The relationship between particles in the 0.1–50 m range and iron (Fe) concentration, R2 – 0.3792, aluminum (Al) R– 0.3208, and zinc (Zn) R2 – 0.4608, was classified as medium. For particles in the 50–100 m range, a medium correlation with calcium (Ca) and magnesium (Mg) concentrations is apparent, R2 0.4443 and 0.3818, respectively. For particles 100–200 mm and 200–400 mm, an almost full correlation is noted for iron (Fe) R2 – 0.9835, aluminum (Al) R2 – 0.9878, calcium (Ca) R2 – 0. 824, very strong for manganese (Mn) R2 – 0.6817, and zinc (Zn) R2 – 0.7343. There is a very strong correlation between the concentration of the AAP fraction with the concentration of iron (Fe) R2 – 0.8694 and a strong correlation between the concentration of EP with the concentration of iron (Fe) R2 – 0.609. There is a strong correlation between the concentration of the AAP and EP fractions with the concentration of aluminum (Al) R2 – 0. 6253 and 0.8327. The concentration of AAP and EP fractions with the concentration of calcium (Ca) R2 – 0.5941 and 0.7576 remains in a strong relationship. The correlation between the concentration of RDP fractions and the concentration of magnesium (Mg) and manganese (Mn) remains in a medium relationship. The concentration of the EP fraction (Olsen-P) is in a strong relationship with the concentration of organic matter (R2 –.0.6763). No correlation was found between the concentration of the residuum form and the concentrations of organic matter, iron (Fe) and aluminum (Al). A medium correlation was found between the concentration of the residuum form and the concentration of calcium (Ca), magnesium (Mg), manganese (Mn) – R2 = 0.4206 and zinc (Zn).

Introduction

Bottom sediments are an integral part of limnic aquatic ecosystems. They are suspended solids, accumulated over the years, at the bottom of lakes (Gierszewski 2018, Jancewicz et al. 2012). Bottom sediments are formed as a result of complex processes, the type and intensity of which remain related to environmental conditions. (Qixing Zhou et al. 2001, Kostecki 2003, Sedlaczek 2017). These determinants include catchment factors, the quality of the water supply and the morphometric conditions of the ecosystem. Each catchment has peculiar morphological and morphometric conditions affecting the process of transport of pollutants (suspended and dissolved) from the source of their generation to flowing waters and then to the bottom sediments of lakes and reservoirs (Jancewicz et al. 2012, Grochowska 2016, Gierszewski 2008, Moses et al. 2011).

Phosphorus is transported to bottom sediments mainly by coagulation, under the influence of iron, aluminum and magnanium hydroxides (Augustyniak et al. 2019, Grochowska et al. 2004). Suspensions of an organic nature are sorbents that promote sedimentation (Aimin Zhou et al. 2005, Grochowska et al. 2004). The literature data highlight the major role of iron, aluminum, magnesium, and calcium components of the sorption complex, binding phosphorus and determining the amount of phosphorus deposited in sediments (Aidin Isil et al. 2009, Canavan et al. 2007, Grochowska et al. 2016, Wojtkowska 2005). The instability of connections to iron, due to the variability of iron valency, and the transition to the reduced form results in the release of phosphorus from sediments into water (Gierszewski 2008, Kostecki 2003, Machowski et al. 2019).

An important factor affecting the formation and subsequent movement of suspended solids within the ecosystem is the movement of water masses, both in the vertical profile, caused by the influence of wind, and horizontal movements along the axis of a large flowing limnic ecosystem (Gierszewski 2018, Stoker et al. 2003). The morphometric features of the lake that shape the retention time are the degree of extension, surface area, depth, and volume. They affect the linear velocity of water flow, the conditions of thermal and oxygen stratification of water masses, and thus the conditions of suspended solids sedimentation (Anishchenko et al. 2015, Kostecki 2003, Moses et al. 2011, Siedlaczek 2017).

Increasing the retention time, reducing the linear velocity of water flow, creates conditions for physical and chemical processes that cause the deposition of suspended solids in the bottom sediments of the limnic ecosystem (Sojka et al. 2019, Sedlaczek et al. 2017, Kostecki 2014).

In turn, the chemical composition of the feeding waters is not without influence – in a manner specific to the hydrochemical, hydrodynamic and morphometric conditions of a given ecosystem – on the process of bottom sediment formation, both on its quality and quantity (Kostecki 2014, Moses et al. 2011, Rzętała 2008, Suresh et al. 2012).

In the case of flowing lakes, linear velocity is affected by morphometry, i.e., the cross-sectional area of the lake basin in the direction of water flow. As soon as water masses are diverted into the lake, the linear velocity of water flow is sharply reduced. This causes a decrease in transport capacity and sedimentation of allochthonous suspended solids in the estuarine zone of the watercourse feeding the lake (Jancewicz 2012, Kostecki 2014, Kostecki 2003, Stoker et al. 2003). Another factor affecting the sedimentation process is water temperature, generally higher in the lake than in the feeder watercourse. In this case, changes in water density and viscosity also affect the dynamics of the suspended sedimentation process (Kostecki 2021).

Within the lake, due to the extended retention time of water masses, microbiological, physical, chemical, and biochemical processes are activated, resulting in the formation of autochthonous suspensions (Agiyah et al. 2014). Particularly important are the processes of transition of water-soluble forms of pollutants to precipitated insoluble forms, and the process of primary production resulting in an increase in the biomass of planktonic organisms (Aimin et al. 2005, Grochowska et al. 2016, Tarnawski et al. 2012, Tuszyńska et al. 2011).

A factor that influences the directions and intensity of these processes is thermal-oxygen relations, in particular, the occurrence of stratification. The partitioning of water masses into layers differentiated by temperature and oxygen concentration implies processes affecting the formation of suspended solids. Intense photosynthesis in the trophogenic zone can induce physical (temperature, transparency, pH) and chemical changes in water quality. In turn, low temperature and oxygen deficits in the bottom layers of water cause the growth of anaerobic bacteria, the reduction of sulfates to sulfides, the lowering of pH and the release of phosphorus from bottom sediments (Kostecki 2021, Ligęza et al. 2002.

Phosphorus is introduced into the limnic ecosystem (lake or anthropogenic reservoir) with waters of the feeder watercourse in dissolved and suspended forms (Hudon et al. 2008, Jaguś et al. 2011). Intra-reservoir processes allow phosphorus to pass from dissolved to undissolved forms, precipitated from the water.

The process of phosphorus transfer from water to bottom sediments occurs as a result of coagulation and sorption on aluminum, iron, and manganese hydroxide particles, forming a sorption complex (Aimin et al. 2005, Augustyniak et al. 2019 Quixing Zhou et al. 2001). Added to this is sedimentation of organic, allo- and autochthonous matter and minerals, especially calcium (Grochowska et al. 2004). In turn, depletion and oxygen deficiencies in the hypolimnion cause a threat from the activation of the internal enrichment process (Koc et al. 2003, Machowski et al. 2019, Kostecki 2014). The problem becomes not only the concentration of phosphorus in the bottom sediments, but the amount of sediment accumulation. With the deposition of successive sediment layers, the total phosphorus load and the loads of individual speciation forms are magnified. An increase in the overall phosphorus abundance of the ecosystem does not directly translate into trophic status (Jancewicz et al. 2012). What matters are the forms of phosphorus in which it is deposited in bottom sediments and their bioavailability (Quixing Zhou et al. 2001). Therefore, it is important to know what forms of phosphorus are present, and where they come from, which promotes their formation.

Purpose of the study

Literature data draw attention to the variation of contaminant content depending on the size of soil particles, especially agricultural soils, pointing to the special role of the clay fraction (0.1 to 2 mm) of mineral formations in the accumulation of contaminants (Wojtkowska 2005, Polish Standards 1998). However, there is much less information on these correlations in bottom sediments (Adiyah 2014, Aydin et al. 2009, Ligęza et al. 2003, Tuszyńska et al. 2011)). As a rule, the correlations of heavy metals in sediments are studied (Anishchenko et al. 2015, Gierszewski 2008, Machowski et al. 2019). In contrast, there are no data on the relationship between the granulometric structure of sediments and the content of speciated forms of phosphorus.

In a limnic, flowing ecosystem, water masses move in the inflow-drainage direction, so there is a change in conditions along the great lake axis, both for the production of suspended solids and their sedimentation (Kostecki 2014, Stoker et al. 2003).

Taking into account the role of phosphorus, as a factor specifically threatening aquatic limnic ecosystems, an attempt was made to study the interdependence between granulometric structure and the pollution status of bottom sediments, taking into account speciation, bioavailable forms of phosphorus and selected heavy metals that form connections with phosphorus.

Object of study

The study was performed on the material collected from the thermally contaminated, hypertrophic Rybnik Dam Reservoir, which is located in southern Poland in Upper Silesia. It was established in 1972 and is a technological facility of a power plant used to cool condensers of four 225 MW power units. The reservoir has a soil dam and is fed by waters of the Ruda River (SSQ flow of 1.23 m^3/s) and, incidentally, the Nacyna River (SSQ flow of 0.87 m^3/s), in the Oder River basin. (Rzętała M., Machowski R. 2018, Pohl A et al. 2022). The reservoir has an area of 465 hectares. At the normal level of damming (221.00 m above sea level), the volume of the reservoir is 22.099 million m^3, and at the maximum flood level (221.30 m above sea level) – 23.482 million m^3. The catchment area is 316.78km^2. The development of the catchment area comprises: agricultural land 41.7%, forested areas 33.6%, urbanized areas 22.6%, surface water 2.1%.

The choice of study site was made due to the long-standing thermal contamination of this ecosystem. For several decades, the reservoir has functioned as a component of power generation technology, used for surface cooling of water masses. Both water chemistry and movement, intensive evaporation from the water surface, hypertrophy, elevated water temperature and spatial variability of thermal relations influenced the process of creation and formation of the bottom sediment structure.

Research methodology

(a) Sampling

Bottom sediments were sampled with an Eckman-Birg scoop at three points determined along the 4.5 km – long major axis of the reservoir. The depth of the reservoir at each site was: Pkt 1. – 3 m, Pkt 2. – 5 m, Pkt 3. – 9 m (Figure 1).

(b) Separation of particle fractions

A sample of wet sludge diluted with water taken from the tank, at a ratio of 1:10, was placed in a Spilner funnel. The separation of the sediment mass into fractions was carried out by sedimentation method, using the sediment's natural tendency to sedimentation.

Separation of sedimentation fractions was made on the basis of observations of the propensity of the natural process of subsidence of suspensions, forming the bottom sediments of the studied reservoir. Sinking time intervals were adopted and four fractions F1–F4 of suspended solids were separated, after a sinking time of 2, 5, 15 and 30 minutes (Fig. 1). The use of the sedimentation method for sediment mass separation avoided disturbing the physical state of the sediment.

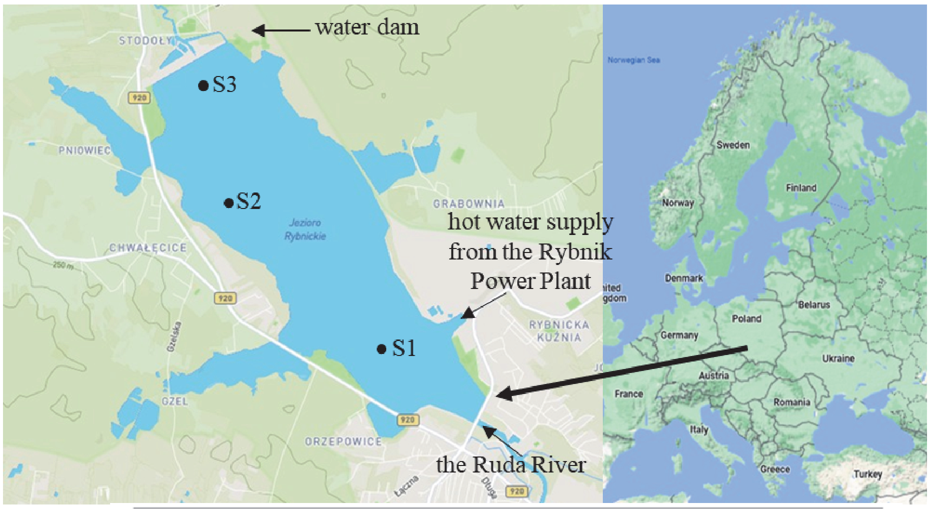
(c) Physical analysis of sediments – granulometry

The analytical material, obtained as described above, was subjected to granulometric analysis (Fritsch Laser Analyzer). Based on the results of measurements determining the percentages of particles in their total number, the fractions were adopted for further analysis: A – with particle size 01–50 mm, B – for particle size 500–100 mm, C – for particle size 100–200 mm, and D – for particle size 200–400 mm.

(d) Determination of speciation forms of phosphorus

Biologically available, speciation forms of phosphorus were determined in each of the separated sedimentation fractions (Quixin Zhou et al. 2001).

- AAP fraction (Algal Available Phosphorus) – phosphorus bound to metal oxides, mainly Al, and Fe, and organic



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. Rybnicki dam-reservoir – localization, sampling points [32]

matter, determined as a measure of availability to algae, (NaOH extraction)

- EP fraction (Extractable Phosphorus also referred to as Olsen-P) – treated as an indicator that speaks to the abundance of phosphorus in soils (and sediments), as a quantitative indicator for available phosphorus bound to calcium, and as a fraction to infer critical levels for crop production (not necessarily in aquatic environments), (Na_2HCO_3 extraction)
- WSP fraction (Water Soluble Phosphorus) – defined as the most biologically available fraction of phosphorus, extracted with water,
- RDP fraction (Readily Desorbable Phosphorus) – determining phosphorus desorbed from the surface of bottom sediment particles during extraction with calcium chloride ($CaCl_2$),
- the results of determination of phosphorus forms were correlated with the results of determination of metals with which phosphorus forms connections (Fe, Al., Ca, Mg, Mn, Zn),
- pH, Eh, rH, moisture content, and organic matter content were also measured.

Phosphorus extraction from wet sludge was performed using the following reagents: for the AAP fraction – sodium hydroxide 0.1 mole, for the EP (Olsen-P) fraction – sodium acid carbonate 0.5 mole pH 855, for the WDP fraction – distilled water, for the RDP fraction – calcium chloride 0.01 mole. The following ratios of sludge to reagent used/extraction time were used: sodium hydroxide 200 ml per 0.8 g wet sludge 4 h, sodium acid carbonate 50 ml per 2.5 g wet sludge 0.5 h, distilled water 100 ml per 1g wet sludge 2 h, calcium chloride 50 ml per 2 g wet sludge 1 h.

(e) Determination of heavy metals

In addition, the total concentration of the following selected metals was determined (ICP MS) in the collected sediment samples: iron (Fe), aluminum (Al), calcium (Ca), magnesium (Mg), manganese (Mn), zinc (Zn).

(f) Statistical elaboration

Based on the calculated (Statistica Program) regression coefficients (R2), an attempt was made to indicate the correlation between granulometric composition and the concentration of speciation forms of phosphorus, and between granulometric composition and the concentration of selected metals, as well as between the concentration of metals and the concentration of speciation forms of phosphorus. Correlation thresholds according to J.Guillforg were used: 0.0–0.1 – faint correlation, 0.1–0.3 – weak correlation, 0.3–0.5 – average correlation, 0.5–0.7 – high correlation, 0.7–0.9 – very high correlation, 0.9–1.0 – almost full correlation, 1 – full correlation (Guillford 1978).

Results

Different fractions of bottom sediments were characterized in terms of weight shares, granulometric structure, organic matter content, and redox potential.

Weight shares

Weight analysis showed that the dominant fraction, in terms of weight, at all three sites, is the first fraction (F1) separated after two minutes of sedimentation (Fig. 2).

The highest proportion of the F1 fraction, amounting to 65%, was recorded in the bottom sediments at site 1, in the upper part of the reservoir, in the zone of heated water discharge. At the other two sites, in the pelagic zone and in the dam zone, the weight share of the F1 fraction was equal and smaller, at 36% and 40% (Fig. 2). The share of the F2 fraction, falling within five minutes, decreased from 26% at site one to 24% at site two and 18% at site three. The share of the F3 fraction, separated after fifteen minutes of sedimentation, increased from 8% at site 1 to 30% at site 2 and 33% at site 3. The share of the F4 fraction was lowest at site 1, where it was only 0.2%. At site 2 and site 3, the share of this fraction was 10% and 9%. As can be seen, the larger the particle size of the suspensions, the smaller the weight share.

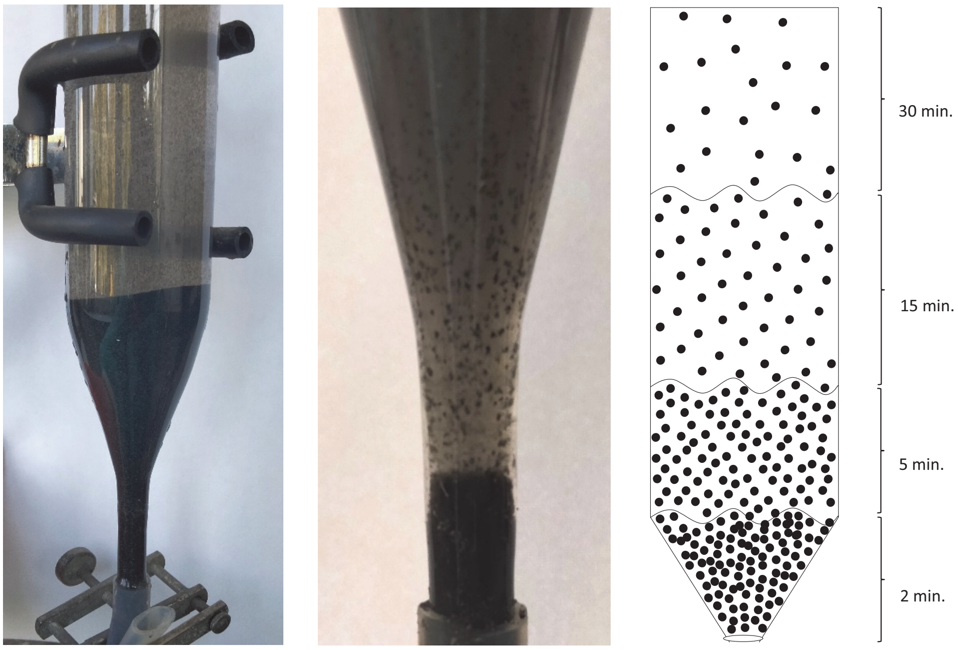


Fig. 2. Diagram of sedimentary separation of bottom sediments [32]

Granulometric structure

The granulometric composition of the separated sediment fractions at each site is shown graphically (Fig. 4).

Detailed measurement results are shown in Table 1.

Granulometric analysis showed characteristic differences in sediment composition (Tables 1–3). In terms of contribution to the total number of particles, the differences between individual fractions were small. In contrast, clear differences were noted

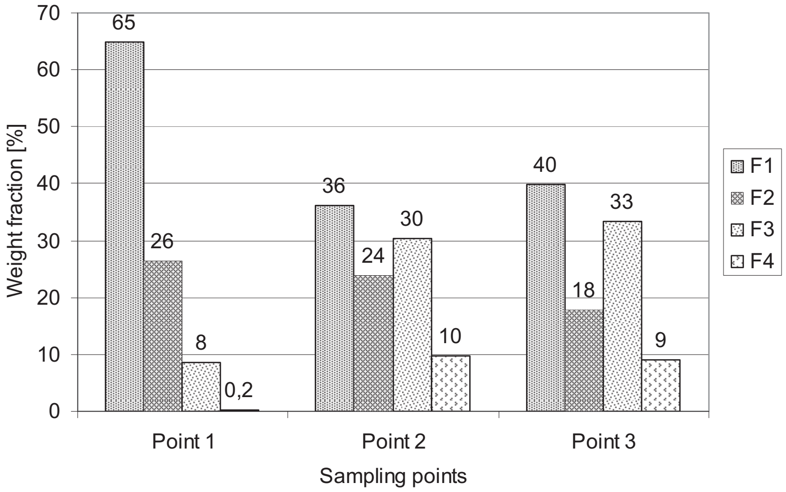


Fig. 3. The weight participation of sedimental fractions of bottom sediments

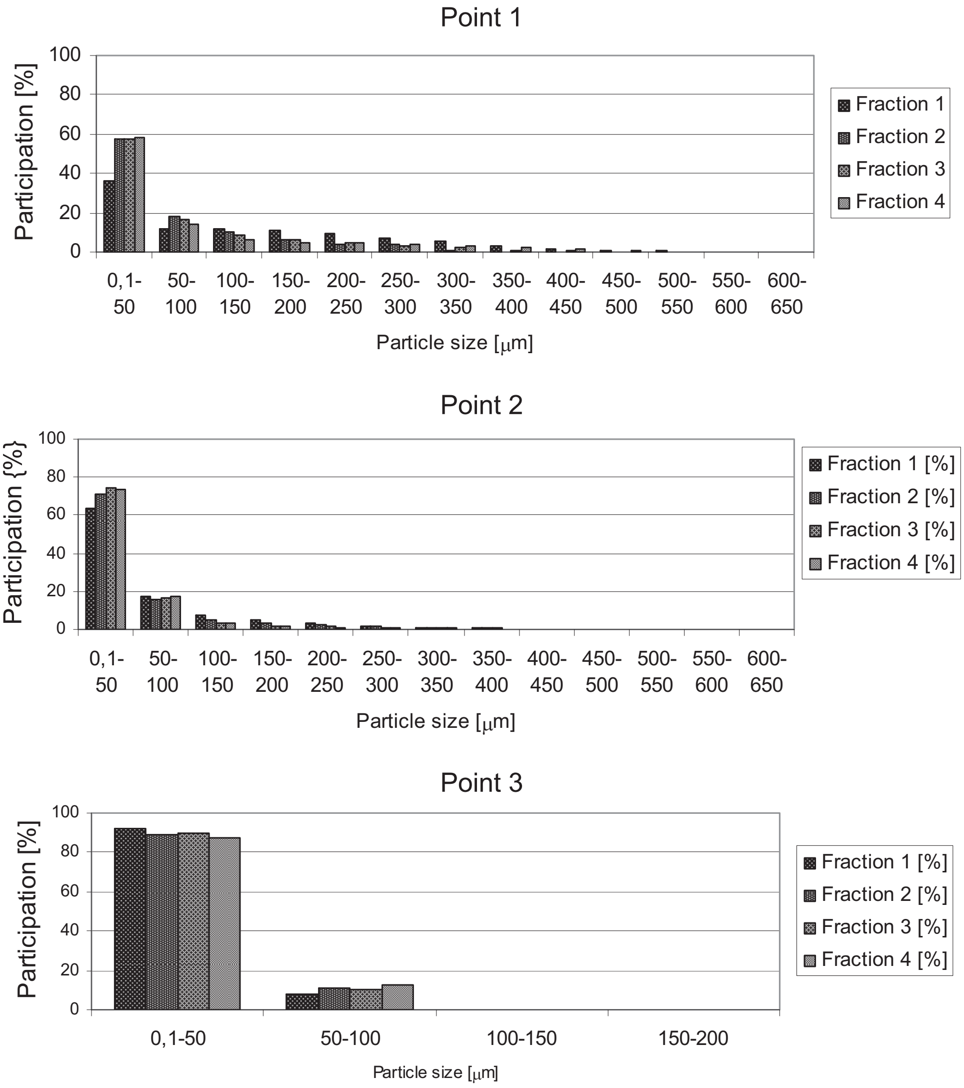


Fig. 4. The structure of the grain size composition of the separated fractions of bottom sediments Rybnik dam-reservoir

between successive sampling sites. The range of sediment particle diameter size decreases as one approaches the dam. At site 1, in the heated water discharge zone, the range of particle diameter size was from 0.1 m to 661 m, at the site in the middle zone, from 0.1 mm to 601 mm, and in the dam zone, from 0.1 m to 120 m.

At all three sites, the proportion of two fractions stood out. The dominant fraction was the fraction with particle diameter from 0.1–50 m, and the fraction with particle diameter from 50–100 m. At the site in the upper, shallowest part of the reservoir, in the heated water discharge zone, the proportion of particles with a diameter of 0.1–50 m ranged from 36% to 58%, in the middle zone of the reservoir, from 64% to 74%, and in the dam zone, from 87% to 92%. The proportion of particles with a diameter of 50–100 m was much smaller at all sites and ranged from 12% to 19% at the site in the heated water discharge zone, from 16% to 18% in the middle zone, and from 16% to 18% in the dam zone. The proportion of particles with a diameter of 100–150 m was even smaller, ranging from 6% to 12%, 3% to 7% and in the dam zone, from 0.01% to 0.17% at the following sites. Particularly noteworthy is the fact that in the bottom sediments in the dammed part of the reservoir, the proportion of sediment particles with a diameter of 0.1 to 100 mm is 99.8%, practically 100%. The shares of particles with a diameter of more than 100 m are minimal.

Table 1. The structure of the grain size composition of the separated fractions of bottom sediments Rybnik dam-reservoir – Point 1

Point 1 range [μm]	Fraction 1 [%]	Fraction 2 [%]	Fraction 3 [%]	Fraction 4 [%]
0,1–50	**36**	**58**	**57**	**58**
50–100	**13**	**19**	**16**	**14**
100–150	**12**	**11**	9	7
150–200	**11**	7	6	5
200–250	10	3	5	5
250–300	7	1	3	4
300–350	5	1	2	3
350–400	3	0	1	2
400–450	2	0	1	1
450–500	1	0	0	1

Table 2. The structure of the grain size composition of the separated fractions of bottom sediments Rybnik dam-reservoir – Point 2

Point 2 range [μm]	Fraction 1 [%]	Fraction 2 [%]	Fraction 3 [%]	Fraction 4 [%]
0,1–50	**64**	**71**	**74**	**74**
50–100	**17**	**16**	**17**	**18**
100–150	7	6	4	3
150–200	5	3	2	2
200–250	3	2	1	1
250–300	2	1	1	1
300–350	1	1	1	1
350–400	1	0	0	0

Table 3. The structure of the grain size composition of the separated fractions of bottom sediments Rybnik dam-reservoir – Point 3

Point 3 range [μm]	Fraction 1 [%]	Fraction 2 [%]	Fraction 3 [%]	Fraction 4 [%]
0,1–50	**92**	**89**	**89**	**87**
50–100	**8**	**11**	**11**	**13**
100–150	0,01	0,01	0,17	0,01
150–200	0,00	0,00	0,00	0,00
200–250				
250–300				

Organic matter

At sites 1 and 2, in the upper and middle parts of the reservoir, the content of organic matter in various fractions was similarly distributed. The lowest organic matter content was in the fastest falling fraction, where its share was 4% and 12%, respectively, and increased in subsequent fractions (Fig. 5).

The organic matter content at site 3, in the dam zone, was the highest (30%) and virtually the same in all four separated sediment fractions (Fig. 4).

Moisture

The moisture content of all four sediment fractions increases along the axis of the large reservoir, in the direction of water flow (Fig. 6). The average moisture content was 54% in the upper zone of the reservoir, 70% in the pelagic zone, and 85% in the dam zone. "Very high" degree of sediment moisture correlates with organic matter content (R^2 = 0.8701), the content of which is determined by 0.1 50m particles. "Very high" is also the degree of correlation between moisture content and the proportion of particles with a diameter of 0.1–50 m (R^2 = 0.7843). For particles with a diameter of 50–100 mm, the correlation was determined as "weak" (R^2 = 0.228).

Redox potential of separated fractions of bottom sediments

Oxidation-reduction conditions in the bottom sediments of limnic ecosystems affect the processes taking place in them, including the process of internal enrichment, i.e., phosphorus release. Based on the results of pH and Eh measurements (Figs. 7, 8), the values of Clark's hydrogen exponent, rH, were calculated, determining the nature of the sediment environment within each of the separated fractions at each site.

The values of the hydrogen exponent rH, calculated for each sediment granulometric fraction, differed slightly (Fig. 9). At site 1, where the depth was 3m, the value of rH was the highest at 15. At the other two sites, the bottom sediments produced reducing conditions (rH below 15), intensifying as the control sites moved toward the dam. For the relationship between rH and pH, the correlation coefficient R2 was 0.8828, and for the relationship between rH and Eh, R2 was 0.57579.

Specialized forms of phosphorus in separated fractions of bottom sediments

The concentration of speciation forms of phosphorus in the sedimentation-separated bottom sediment fractions of

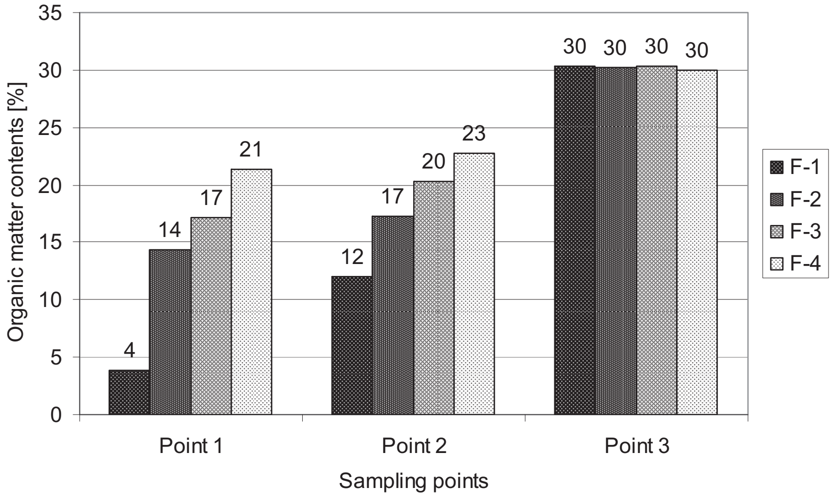


Fig. 5. The organic matter contents in the four fractions of bottom sediments

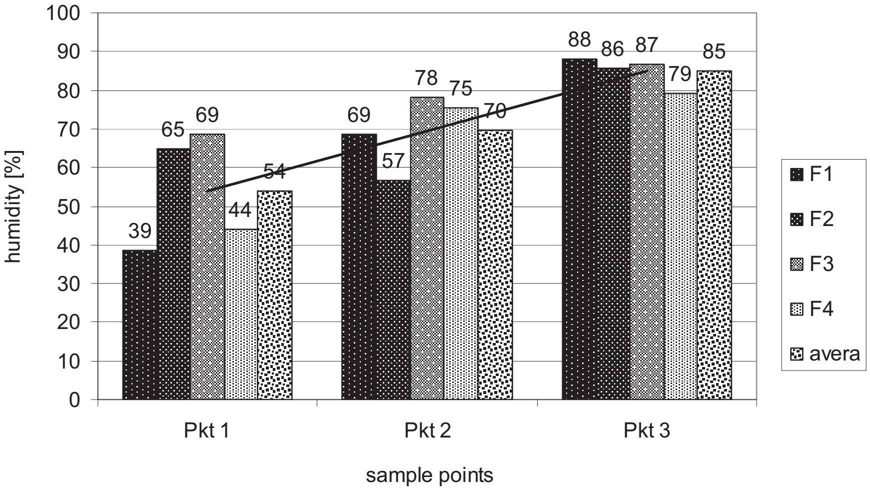


Fig. 6. The moisture of bottom sediments

the Rybnik reservoir is shown in Fig. 10. Detailed data are presented in Table 4.

Relationship between the concentration of speciated forms of phosphorus and reservoir water temperature

In the case of water reservoirs, which are part of the cooling system of a power generation plant, the main anthropopressure element causing thermal contamination is temperature. In these (flow-through) reservoirs, the highest water temperatures occur in the upper, shallow part of the reservoir, in the zone of the power plant's heated water discharge. As water masses move through the reservoir, the water cools down. The lowest, and at the same time elevated compared to natural lakes, temperature occurs in the deepest part of the reservoir, in the dam zone. The temperature of the water affects its density. Below (Fig. 10) is an example of the seasonal variation in water density of the Rybnik Dam Reservoir in 2015 (Kostecki 2022, Mazierski et al. 2021).

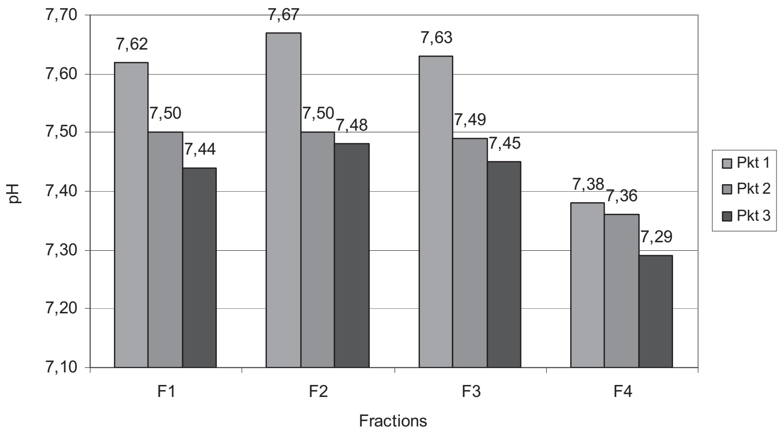


Fig. 7. pH of granulometric fractions of bottom sediments Rybnik dam-reservoir

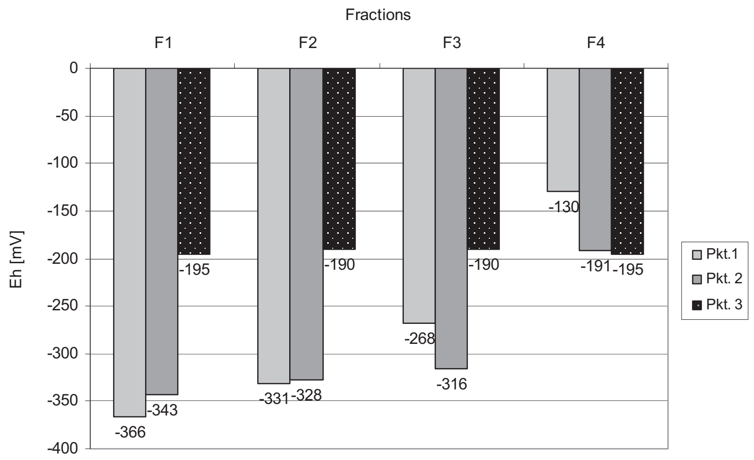


Fig. 8. Eh of granulometric fractions of bottom sediments Rybnik dam-reservoir

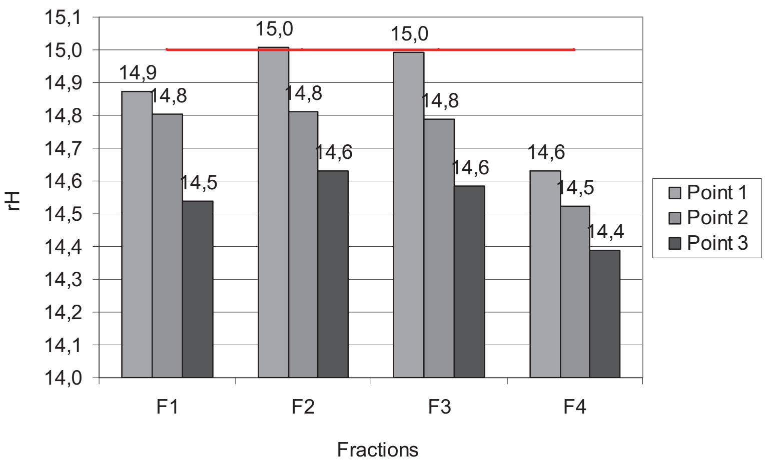


Fig. 9. The hydrogen exponent rH – Clarck

Over the spring and summer, the density of water decreases. The calculated magnitudes of the constant decrease in density were: at the site in the heated water discharge zone, at the surface 0.0267 g/m^3*d^{-1}, at the bottom 0.0171 g/m^3*d^{-1}, in the middle zone, at the surface 0.0191 g/m^3*d^{-1} and 0.0173 g/m^3*d^{-1} at the bottom, and in the dam zone, at the surface 0.0258 g/m^3*d^{-1} and 0.0150 g/m^3*d^{-1} at the bottom. The graphs show the periods of the thermocline occurrence during summer stagnation.

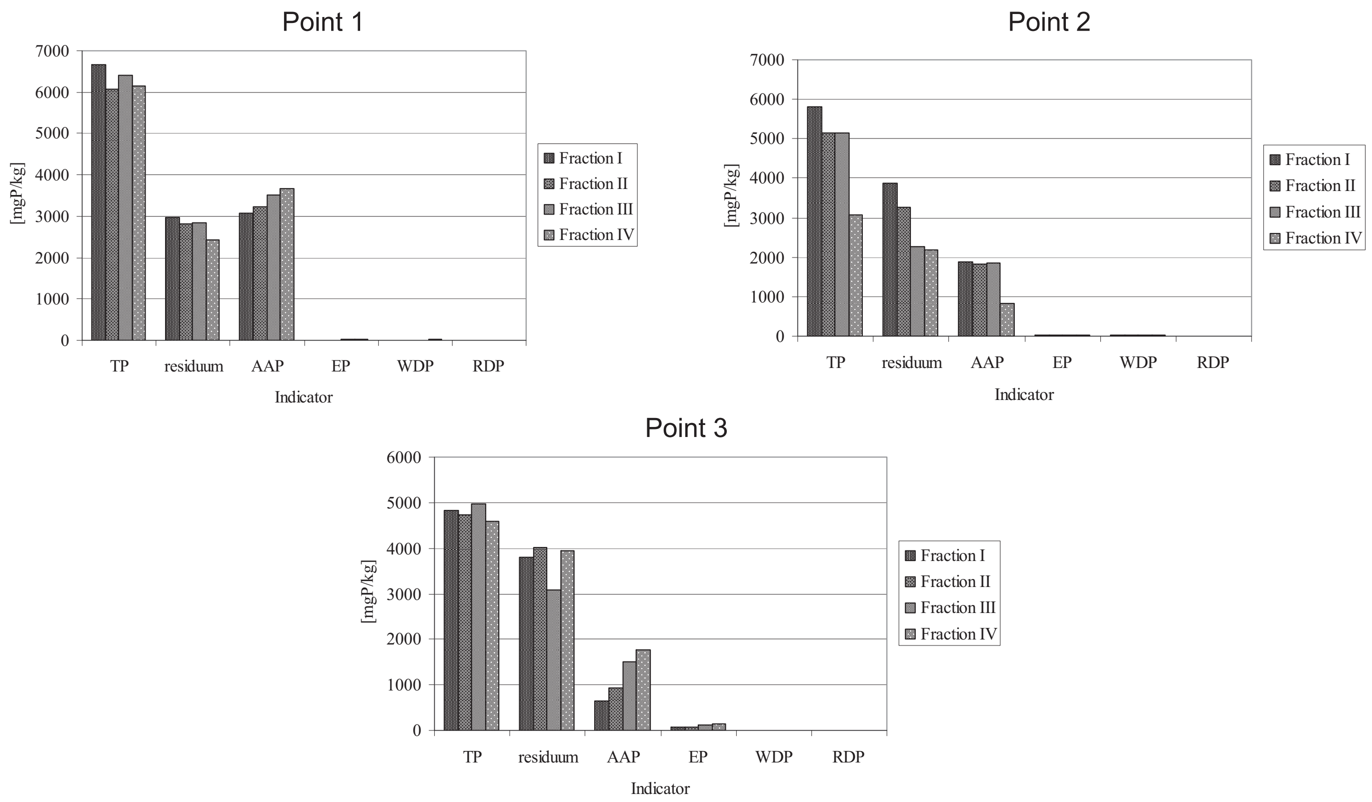


Fig. 10. Concentration [mgP/kg] of speciation forms of phosphorus in separated fractions of bottom sediments of Rybnik dam reservoir

Table 4. Concentration [mgP/kg] of speciated forms of phosphorus in the separated fractions of the bottom sediment of the Rybnik dam reservoir.

	Fraction 1	Fraction 2	Fraction 3	Fraction 4
		TP		
Point 1	6653	6063	6396	6137
Point 2	5798	5139	5151	3077
Point 3	4820	4738	4981	4584
		AAP		
Poin 1	3078	3241	3518	3669
Point 2	1894	1822	1842	835
Point 3	654	934	1504	1765
		EP		
Poin 1	3.1	8.4	16.7	19.3
Point 2	18.4	24.4	21.9	30.8
Point 3	60.2	80.4	117.3	136.9
		WDP		
Poin 1	7.3	8.1	9.7	16.8
Point 2	15.8	16.3	27.2	19.4
Point 3	8.2	3.4	5.6	6.3
		RDP		
Poin 1	0.5	0.7	0.7	1.0
Point 2	0.5	0.6	1.2	1.15
Point 3	1.0	0.6	0.3	0.1

Certainly, the temperature of the water creating the reaction environment, plays an important role in the formation and behavior of suspended solids in the water tone. In the annual limnological cycle, the highest water temperatures are recorded between May and September. In the case of the studied reservoir, three factors overlap – water temperature, which varies along the large axis of the reservoir, depth and water flow. Below (Figure 11) are presented the average values of water temperature of the studied reservoir for the multi-year period 2004–2021, at sites along the major axis. Analysis of the average water temperature values shows that for the maximum values (surface water layer), the difference between the upper reservoir zone and the dam zone is 6.3°C, whereas for the lowest values (bottom water layer), the difference is 3.6°C. It would be very interesting to determine the influence of the role of the thermics of water masses on the formation of suspended solids of certain dimensions in the water tone, but according to the author, this would require a separate study. An attempt to determine the relationship and formulate conclusions about the influence of water temperature on the formation of suspensions and the formation of fractions of particles of different sizes in the bottom sediments, based on the results obtained, would be subject to great error.

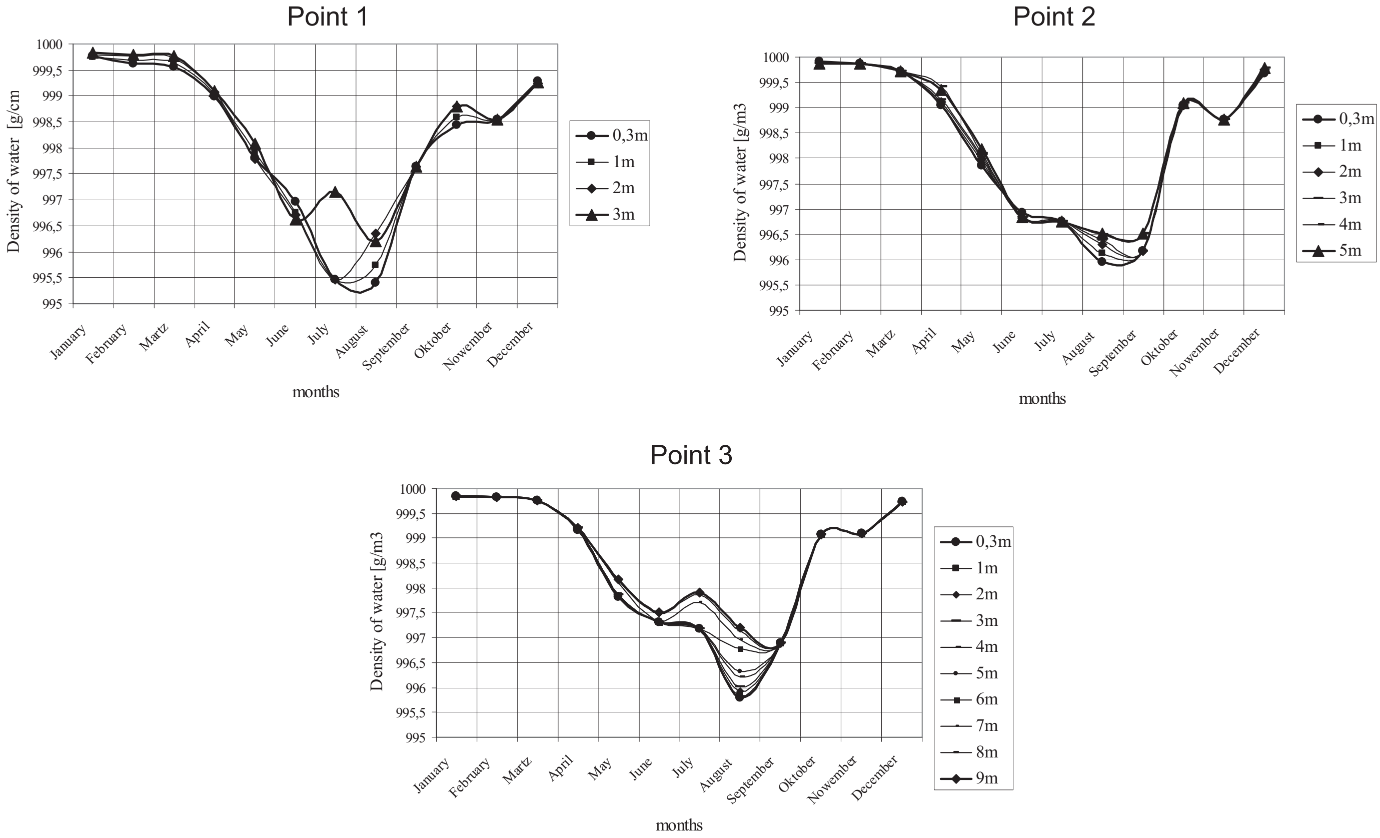


Fig. 11. The seasonal changes density of water Rybnik dam-reservoir

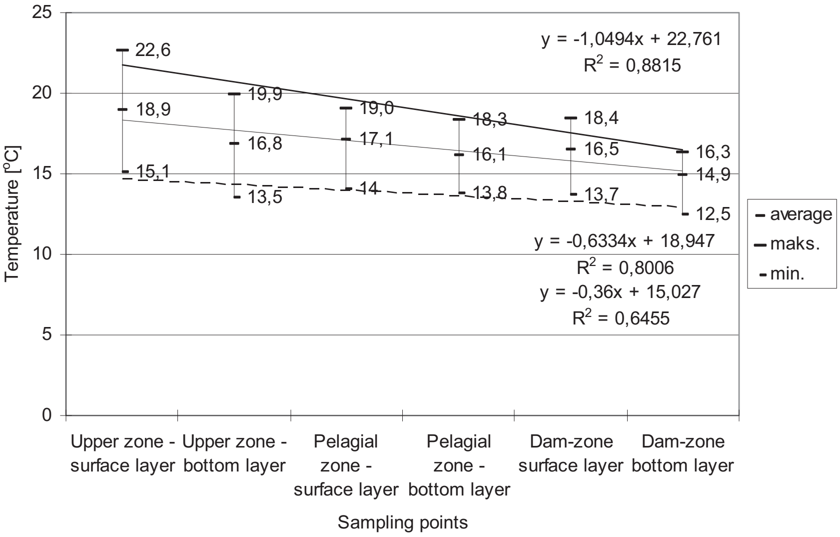


Fig. 12. Spatial variability of water temperature of Rybnik dam reservoir in the 2004–2021 multi-year period (own research) (Kostecki 2022, Mazierski et al. 2021]

Relationship between the concentration of speciation forms of phosphorus and reservoir morphometry

The conditions for the formation and sedimentation of suspended solids that form bottom sediments, are different in different zones of the limnic ecosystem (Anishchenko et al. 2015). In lowland dam reservoirs, morphometric conditions result from the shape and slope of the river valley, divided by the dam. There is a phenomenon of characteristic asymmetry of reservoir shape and depth. In its upper part, the reservoir is much narrower and shallowest. It reaches its greatest width at the crown of the dam. The depth of the reservoir increases along the axis of the large reservoir, in the direction of water flow, and is greatest in the dam zone. As the width of the reservoir increases, the depth increases, along the large axis of the reservoir, the linear velocity of water flow decreases. As the retention time increases, the conditions for the course of chemical reactions and the conditions for the formation and existence of plant and animal communities involved in the formation of bottom sediments change.

Among the separated granulometric groups of sediments, the particles with the smallest dimensions, in the range of 0.1–50 m, attract attention. The share of these particles is the highest at all three sites. At the same time, the share increases from 43% at the site in the heated water discharge zone to 68% in the middle zone of the reservoir and 92% in the dam zone (Fig. 12). The share of the other particle size groups decreases at all sites.

The concentration of speciated forms of phosphorus is related to both the depth from which the sediment samples were taken and the distance from the mouth of the waters feeding the reservoir. Three sampling sites were delineated at the depths of 3 m, 5 m, 9 m. along the reservoir's major axis of 4.5 km. The correlation coefficient for the relationship between the concentration of speciation forms of phosphorus and depth was determined. As can be seen (Table 4), the concentration of total phosphorus (TP) and speciation forms of phosphorus, was highest in the shallowest zone (the discharge of heated water), and decreased as we moved away from the discharge zone, with increasing depth.

The values of the correlation coefficient R2 indicate that the TP form deviates from this rule in the F-4 fraction, whereas the WDP form in the F-1 and F3 fractions. An "almost full" correlation was found for fractions F-1 for the TP, AAP, EP, and RDP forms. For fraction F-2, a correlation of "almost full" was found for the EP form, and "very high" for the TP and AAP forms. For the F-3 fraction, an "almost complete" correlation was found for the EP form, and a "high" correlation for the AAP form. For fraction F-4, an "almost Full" correlation was found for the EP form, and a "very high" correlation was found for the WDP and RDP forms. In each case, the correlation was negative.

Interrelationships between sediment granulometry and the concentration of speciation forms of phosphorus

The sizes of shares of sediment particles, in their total amount, were calculated for groups of 0.1–50 mm, 50–100 mm, 100–200 mm, 200–400 mm, 400–600 mm. The magnitudes of the shares were correlated with the concentration of

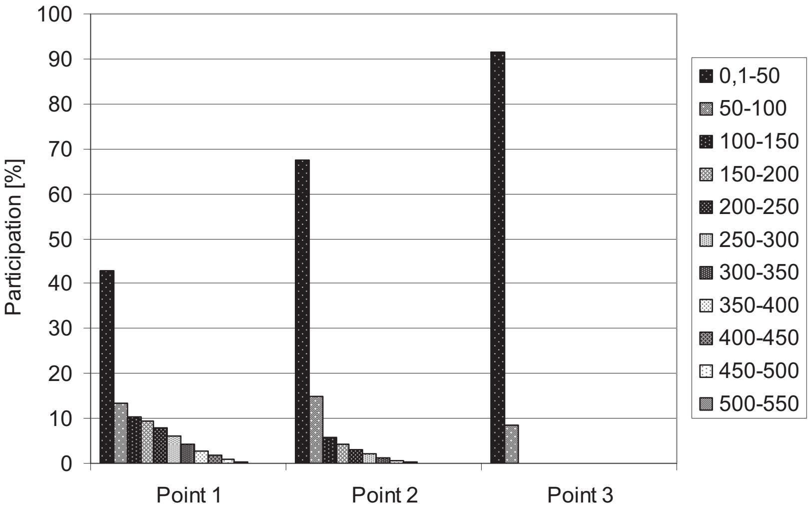


Fig. 13. The participation of fraction particie size

Table 5. Values of the correlation coefficient R2 for the relationship between the concentration of speciation forms of phosphorus and the depth of Rybnik Reservoir

Deepest	F1	F2	F3	F4
TP	**0.9773**	**0.838**	0.6779	0.1126
AAP	**0.9691**	**0.8997**	**0.7211**	0.2549
EP	**0.9946**	**0.9857**	**0.9197**	**0.9412**
WDP	**0.0086**	0.2834	0.1297	**0.7486**
RDP	**0.9085**	0.2891	0.298	**0.8096**

speciated forms of phosphorus by calculating R2 regression coefficients (Table 5). The existence of correlations between granulometric composition and concentration of speciation forms of phosphorus, between granulometric composition and concentration of selected metals, and between concentration of speciation forms of phosphorus and concentration of metals was indicated. Correlation thresholds were used according to J. Gillford (1978).

For particles with dimensions of 0.1–50 m, a very high correlation was found with the concentration of organic matter (R2 = 0.8701), and a high correlation with the value of the Clark hydrogen exponent (R2 = 0.5264). In contrast, a negligible correlation was found between the proportion of particles with dimensions of 0.1–50 m and the concentration of speciation forms of phosphorus. For particles with dimensions of 50–100 µm, an average correlation was noted for the concentration of EP fraction and for WDP fraction (R2 = 0.4048 and 0.3636). The largest, and at the same time the lightest, slowest falling sediment particles in the <100–200 m, <200–400 m, <400–600 m range are "responsible" for phosphorus content in bottom sediments. For particles <100–200 m, a very high correlation was found for the concentration of TP, AAP and WDP forms, and an average correlation was found for the RDP form. For particles <200–400 mm, high correlation was found for the TP form, and very high correlation for the AAP and EP forms. For particles <400–600 m, high correlation was found for the AAP and EP forms.

Correlation between sediment granulometry and concentration of selected metals

Table 7 shows the concentrations of selected metals in the separated bottom sediment fractions.

In the sedimentation-selected four sediment fractions , the order of the determined metals in terms of their concentrations was as follows: Fe>Al.>Ca>Mg>Zn>. In terms of the concentration of metals in the separated bottom sediment fractions, the order of the fractions for site 1 (heated water discharge zone) was as follows: F1>F2>F3>F4, while the reverse was true for site 2 (pelagial zone) and site 3 (dam zone), i.e., F4>F3>F2>F1. The magnitudes of the shares of each group of particles were correlated with the concentration of selected metals that can form connections with phosphorus (Table 8).

Table 6. Interrelationships between sediment particle size and concentration of speciated forms of phosphorus

range µm	Mat org.	TP	Res.P	AAP	EP	WDP	RDP	rH
0.1–50	**0.8701**	0.0656	0.0891	0.1194	0.1804	0.0056	0.0322	**0.5264**
50–100	0.2435	0.207	0.2772	0.0976	0.4048	0.3636	0.0814	0.1555
100–200	**0.6825**	**0.7863**	0.1265	**0.7163**	**0.621**	**0.7934**	**0.47**	0.235
200–400	0.3933	**0.6931**	0.0096	**0.8292**	**0.891**	0.4221	0.1955	0.0048
400–600	0.4913	0.2675	0.357	**0.5188**	**0.6643**	0.1272	0.0234	0.1479

Table 7. The concentrations of metals of the selected fractions of bottom sediuments

Point 1	F 1	F 2	F 3	F 4
Fe	39842.0	34615.0	32177.2	20260.9
Al.	19054.0	19443.4	17991.8	11535.1
Ca	7378.0	7903.4	7691.3	4310.5
Mg	2548.0	2411.3	2291.6	1460.8
Mn	1964.0	1621.4	1609.6	989.6
Zn	1730.0	1221.3	1122.1	650.1
Point 2	F 1	F 2	F 3	F 4
Fe	41211.7	48685.7	48050.9	52981.7
Al.	16557.8	21327.2	22431.1	25719.8
Ca	8926.5	11360.2	7123.2	12562.1
Mg	2081.9	2624.4	1500.5	2985.5
Mn	2033.4	1864.4	1848.4	1793.4
Zn	1052.3	1155.4	1214.3	1226.7
Point 3	F 1	F 2	F 3	F 4
Fe	48636.9	48526.6	48662.5	51026.1
Al.	27577.0	29061.8	28720.6	29886.3
Ca	18983.7	19262.4	17455.5	20734.9
Mg	3416.4	3332.8	3545.0	3627.3
Mn	1937.9	2075.9	2022.2	2406.8
Zn	1101.4	1095.4	1105.4	1195.7

For particles with a diameter of 0.1–50 m, an “average” correlation was found with iron (Fe), aluminum (Al.) and zinc (Zn). For particles with a diameter of 50–100 m, an “average” correlation was found with aluminum (Al.), calcium (Ca) and magnesium (Mg). For particles 100–200 m in diameter, a correlation of “very high” was found with iron (Fe), clay (Al) and calcium (Ca), and a correlation of “average” with magnesium (Mg) and zinc (Zn). For particles with a diameter of 200–400 m, an “almost complete” correlation was found for zinc (Zn), a “very high” correlation for calcium (Ca) and manganese, a high correlation, and a “weak” correlation for magnesium (Mg). For particles with a diameter of 400–600 mm, a correlation of “high” was found for iron (Fe), aluminum (Al.), manganese (Mn) and zinc (Zn), and “average” for calcium (Ca). The concentration of metals in the separated sediment fractions was generally presented as the sum of the six metals capable of forming connections with phosphorus (Fig. 13).

As highlighted above, the concentration of metals in individual fractions of bottom sediments at the site in the upper zone of the reservoir, in the zone of heated water discharge, is inversely related to the site in the middle zone and in the dam zone. At the site in the upper zone of the reservoir (Point 1), the concentration of the total amount of metals was highest in the F-1 fraction, and was lower and lower in subsequent fractions. At the site in the middle zone (Point 2), the lowest concentration of total metals was found in the F-1 fraction (the fastest falling). In subsequent fractions, the concentration of metals increased and the highest value was recorded for fraction F-4, falling the slowest. At the site in the dam zone (Point 3), the overall concentration of metals was the highest, while at the same time the differences in concentrations between individual sediment fractions were very small. The highest concentration of metals at this site was found in the F-4 fraction, falling the slowest. The distribution of metal concentrations shown highlights the difference between the upper zone of the reservoir and the middle zone and the dam zone.

Correlation between concentrations of selected metals and concentrations of speciation forms of phosphorus

The values of correlation coefficients for the concentrations of metals and concentrations of speciation forms of phosphorus in bottom sediments of the studied reservoir are presented below (Table 9).

For TP (total P), a high correlation was found with iron (Fe) and aluminum (Al.), and an “average” correlation with calcium (Ca). The correlation between TP and magnesium (Mg), manganese (Mn) and zinc (Zn) was determined to be “poor.” For the AAP form, there was a “very high” correlation with iron (Fe), a “high” correlation with aluminum (Al.) and calcium (Ca), an “average” correlation with magnesium (Mg) and manganese (Mn), and a “faint” correlation with zinc (Zn). For the EP (Olsen-P) form, there was an “almost full”

Table 8. Values of the coefficient of determination (R2) for the correlation between sediment particle size and metal concentration

range µm	Fe	Al.	Ca	Mg	Mn	Zn
0.1–50	0.3792	0.3208	0.179	0.1468	0.0365	0.4608
50–100	0.0007	0.2922	0.4443	0.3818	0.1264	0.0013
100–200	**0.7045**	**0.8231**	**0.8524**	0.4757	0.1717	0.3984
200–400	**0.9835**	**0.9078**	**0.6135**	0.2132	**0.6817**	**0.7343**
400–600	0.5918	0.5342	0.3965	0.0073	0.5626	0.5897

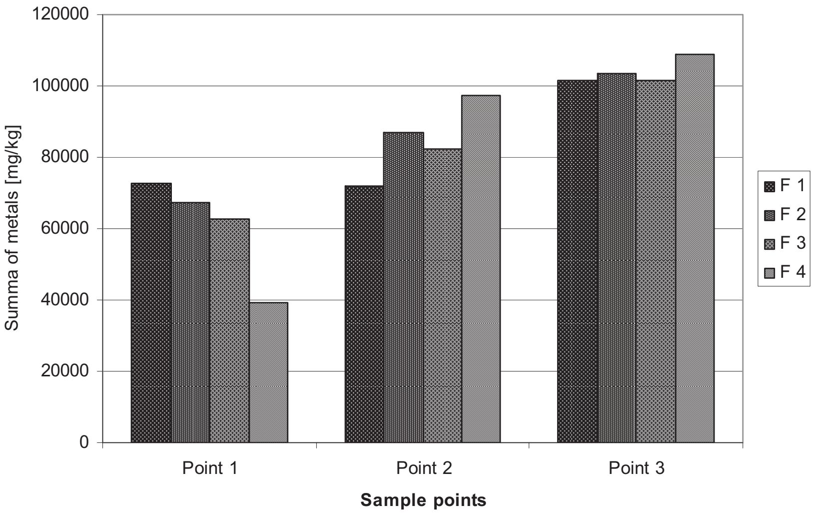


Fig. 14. The concentrations of summae six metals (Fe, Al., Ca, Mg, Mn, Zn) in the selected fraction of bottom sediments

Table 9. Values of the coefficient of determination (R2) for the correlation between the concentration of metals and the concentration of speciation forms of phosphorus

	TP	AAP	EP	WDP	RDP	Res.P
Fe	**0.6496**	**0.8694**	**0.609**	0.0169	0.0003	0.072
Al.	**0.5197**	**0.6253**	**0.8327**	0.153	0.0786	0.1802
Ca	0.4844	**0.5941**	**0.7576**	0.3123	0.1867	0.4569
Mg	0.1751	0.3602	**0.9307**	0.4927	0.2795	**0.5261**
Mn	0.0548	0.3613	0.3449	0.1251	0.3338	0.4206
Zn	0.0088	0.0046	0.0166	0.0354	0.0485	0.4478

correlation with magnesium (Mg), a "very high" correlation with aluminum (Al.), a "high" correlation with iron (Fe), an "average" correlation with manganese (Mn), and a "faint" correlation with zinc (Zn). For the WDP form, an "average" correlation was found with magnesium (Mg) and calcium (Ca), a "faint" correlation with iron (Fe), aluminum (Al.), manganese (Mn) and zinc (Zn). For the RDP form, there was an "average" correlation with manganese (Mg), a "weak" correlation with magnesium and calcium (Ca), and a "faint" correlation with iron (Fe), aluminum (Al.) and zinc (Zn).

Discussion of results

The results of the basic research presented here are an attempt to find a correlation between the granulometric structure of sediments and the concentration of the speciation forms of phosphorus and metals found in them, which can form insoluble combinations with phosphorus. The granulometric composition of soils and grounds is considered their basic physical property, taken into account in the study of other physical and chemical characteristics (Lamorski et al. 2014, Brogowski et al 2015). It is determined most often by sieve-sedimentation methods (Rząsa et al 2013). Two physical phenomena, sedimentation and wet and dry sieve analysis, are used to determine the granulometric composition of soil. Methods for studying the granulometric composition of soils and grounds have been applied over time to the bottom sediments of rivers and lakes and seas (Matijevic 2008). The Classification of Soil Granulometry uses a nomenclature that takes into account: loose sands, weakly loamy sands, loamy sands, sandy loams, ordinary loams, silty loams, silty loams, silty loams, clayey loams, silty loams, clayey loams, ordinary loams, and heavy loams (Polish PTG Standard 2008). Due to the specificity of the bottom sediments of limnic ecosystems, differentiating sediments from agrarian soils and soils, the author does not refer to the nomenclature of "soil types" but to particles of a certain size!

Researchers point to a number of correlations between the proportion of individual sediment fractions, especially clay, silt, and the pH and redox potential of sediments, decreasing as sampling points are brought closer to the reservoir dam (Ligęza et al. 2002, Martynow 2018). Studies on the occurrence and environmental impact of contaminants found in bottom sediments indicate a relationship between the clay fraction and dust fraction, with respect to metals (Machowski et al. 2019, Martynov 2018). A relationship is indicated between various lake characteristics and the formation of bottom sediments, including lake morphometry and the granulometric composition of bottom sediments (Moosem et al 2011, Ligęza et al 2003). Sediment particles are larger in the upper zone of the reservoir and smaller in the lower zone (Adiyah et al 2014, Sojka et al 2013). In addition, attention is paid to the relationship between sediment particle size and metal content, with the concentration of heavy metals in bottom sediments determined by the content of clay parts and organic matter, the depth of sampling and the distance from the reservoir recharge site (Fuentes 2000, Kos et al 2015, Tuszyńska et al 2011).

Bottom sediments are not a homogeneous formation, and their structure and chemical composition vary in different parts of the reservoir (Kostecki 2003, Matijevic et al. 2008, Martynov 2018). The factors shaping the spatial variability of the granulometric structure of bottom sediments, the spatial variability of the concentrations of speciation forms of phosphorus and metals in the separated, size-differentiated fractions of bottom sediments, are morphometric conditions, in particular, the length of the great axis, depth, vertical and horizontal movements of water masses and thermal relations. The results of the study show the structural, physical, chemical and spatial complexity of bottom sediments, as a formation resulting from intra-reservoir processes. The study of the correlation between granulometric composition and the concentration of contaminants contained in bottom sediments requires the separation of fractions that differ in size and density from the collected material (Lamorski et al. 2014, Polish Standard PTG 2008). Researchers use a number of methods: sieve, pipette, and areometric methods (Lamorski et al. 2014, Brogowski et al 2015, Rząsa et al. 2013). The sieve method, which requires drying and grinding of the material, carries the risk of affecting changes in the structure of the sediment. (Matijewic and all 2006). Sieve analysis was used by Wojtkowska, finding that the accumulation of zinc (Zn), copper (Cu) and lead (Pb) occurs mainly in the finest particles (Wojtkowska et al. 2016). The same was found for total phosphorus and iron-bound phosphorus (Matijevic et al. 2008). The difficulty in comparing and interpreting the obtained data is due, among other things, to the diversity of methods used to separate the granulometric fractions of bottom sediments.

The sedimentation method of separating sediment fractions based on the rate of their natural descent was used experimentally. This avoided physical interference with the shape and size of sediment particles, which is not provided by the sieve method, especially after the sediment has been dried and spread.

The synergism of environmental factors, such as the linear velocity of water flow, retention time and water temperature, viscosity and density, creates a transport mechanism that shapes the spatial variability of the granulometric structure and thus the chemical composition of sediments (Dunalska 2019, Ligęza et al. 2003, Mander et al. 1998, Martynov 2018). This mechanism applies to both limnetic and post-limnetic ecosystems. However, in the case of rivers, the trailing material forms unstable silts and nanos, the allocation of which changes under the influence of flood surges. The contamination status of these materials also changes (Alexander et al. 2004, Frankowski et al. 2005, Martynov 2018). The report on flood-affected soils emphasizes the importance of granulometric composition in the case of metals (lanthanides), in particular colloidal particles (clay), but also the possibility of a lack of correlation, in the case of soil aggregates, and a positive correlation with soil iron content (Martynov 2018).

Although marine and lake ecosystems differ in some respects, the results of studies indicate similar correlations between sediment granulometry and their chemical characteristics. Studies of marine bottom sediments conducted to assess the impact of anthropopressure increasing the threat of eutrophication showed that sediments from the area subjected to anthropogenic influence had the highest values of iron-bound P (Matijevic 2006, Matijevic 2008, Fuentez 2000). In the case of the iron-bound phosphorus (Fe) form, "finest fractions" are given as the location of this form, while particle sizes are not given (Matijevic et al. 2012). Studies in the Central Adriatic have shown maximum phosphorus accumulation in fine-grained sediments and in coastal zones subjected to anthropogenic influences (Matijevic et al. 2008). These observations correspond with the results obtained for the studied reservoir.

Summary

The study has highlighted the division of the bottom sediments of the studied reservoir into groups that vary in terms of particle diameter size, weight shares of particle groups of different sizes, and chemical composition. In the case of the thermally contaminated, hypertrophic Rybnik Dam Reservoir, the general range of particle size of bottom sediments ranges from 0.1 m to 660 m, but is different for each site. At site 1, in the heated water discharge zone, it ranges from 0.1 µm to 660 µm, at site 2, in the middle zone, from 0.1 mm to 600 m, and at site 3, in the dam zone, from 0.1 to 120 m.

The granulometric structure of the bottom sediments changes in the longitudinal profile of the studied ecosystem. Along the large axis of the dam reservoir, in the direction of water flow, with increasing depth, the proportion of the smallest particles, with a size of 0.1–50 µm, increases. The proportion of particles in the 50–100 µm range is stable, while the proportion of particles above 150 µm decreases. The larger the particle size of suspensions, the smaller the weight share. The spatial variation of weight shares indicates the influence of the movement of water masses along the large axis of the reservoir.

Based on the calculated regression coefficients (R2), the occurrence of correlations between granulometric composition and concentration of speciation forms of phosphorus, between granulometric composition and concentration of selected metals, between concentration of metals and concentration of speciation forms of phosphorus was indicated. Correlation thresholds were used (Guilford 1978). The correlation between the concentration of AAP, EP, WDP and RDP forms in particles with a diameter of more than 100m was classified as strong. The highest values of the regression coefficient R2 were: for AAP – 0.8292 (200 m–400 m), for EP – 0.891 (200 m–400 m), for WDP – 0.7934 (200 m–400 m), and for RDP – 0.47 (100 m–200 m). No correlation was found for sediment particles less than 100 m in diameter.

The correlation between particles in the 0.1–50 m range and the concentration of iron (Fe), R2 – 0.3792, aluminum (Al) R – 0.3208 and zinc (Zn) R2 – 0.4608, was classified as average.

For particles in the range of 50–100 m, a medium correlation is evident with the concentration of calcium (Ca) and magnesium (Mg), R2 0, respectively, 4443 and 0.3818. For 100–200 m and 200–400 m particles, a strong correlation is noted for iron (Fe) R2 – 0.9835, aluminum (Al) R2 – 0.9878, calcium (Ca) R2 – 0.824, manganese (Mn) R2 – 0.6817, and zinc (Zn) R2 – 0.7343.

The concentration of the AAP and EP fractions remains in a strong relationship with the concentration of iron (Fe) R2 – 0.8694 and 0.609. The concentration of the AAP and EP fractions remains in a strong relationship with the concentration of aluminum (Al) R2 – 0.6253 and 0.8327. In a strong relationship remains the concentration of AAP and EP fractions with the concentration of calcium (Ca) R2 – 0.5941 and 0.7576. In a medium relationship remains the correlation between the concentration of RDP fractions and the concentration of magnesium (Mg) and manganese (Mn). The concentration of EP fraction (Olsen-P) remains in a strong relationship with the concentration of organic matter (R – 0.6763).

No correlation was found between the concentration of the residuum form and the concentrations of organic matter, iron (Fe) and aluminum (Al). A medium correlation was found between the concentration of the residuum form and the concentration of calcium (Ca), magnesium (Mg), manganese (Mn) – R2 = 0.4206 and zinc (Zn).

In the bottom sediments of the studied reservoir, the dominant speciation form of phosphorus is AAP (Algal Available Phosphorus), in which phosphorus is associated with iron (Fe) and aluminum (Al.). The concentration of the other forms in the separated fractions is negligible. The most effective precipitation of phosphorus from water occurs in the upper zone of the reservoir. A feature of this zone is the highest water temperature. The spatial variability of the concentrations of phosphorus speciation forms is in interdependence with the spatial distribution of metal concentrations.

Presumably, the formation of phosphorus-metal combinations can be influenced by the temperature of the reaction environment. At the same time, the increased temperature of water in the zone of heated water discharge causes a reduction in its density and viscosity, which promotes the sedimentation process of the resulting suspensions. Probably, temperature also affects microbiological and biological processes involved in the formation of suspensions. The presented results are a starting point for further research.

They will also provide comparative material for the study of bottom sediments of reservoirs subjected to differential anthropopressure (Kostecki 2022, Mazierski et al. 2021).

Conclusions

Based on the results of the study, the following conclusions were made:

1. Bottom sediments of limnetic ecosystems are not a homogeneous creation, they are differentiated in terms of granulometric structure and the content of speciation forms of phosphorus and metals. The granulometric structure is related to the chemical composition and physical properties.
2. The abundance of phosphorus, including its bioavailable speciation forms remains related to the granulometric structure of bottom sediments. A strong correlation between sediment particle size and the concentration of speciation forms of phosphorus was noted for particles of 100–200 µm and 200–400 µm. The coefficient of determination was for AAP, EP, WDP and RDP, respectively: 0,8292, 0,891, 0,7934, 0,47.
3. Sediment particles with a size of 0.1–50 mm are not related to speciated forms of phosphorus.
4. The concentration of metals (Fe, Al, Ca, Mg, Mn, Zn) remains in correlation with the granulometric structure of sediments. In the case of 100–200 mm and 200–400 mm particles, an almost full correlation was recorded for iron (Fe) R2 – 0.9835, aluminum (Al) R2 – 0.9878, calcium (Ca) R2 – 0.824, a very strong one for manganese (Mn) R2 – 0.6817, and zinc (Zn) R2 – 0.7343.
5. The correlation between particles in the range of 0.1–50 m and the concentration of iron (Fe), R2 – 0.3792, aluminum (Al) R– 0.3208, and zinc (Zn) R2 – 0.4608 was classified as weak. For particles in the range of 50–100 m, a medium correlation with the concentration of calcium (Ca) and magnesium (Mg) is evident, R2 - 0.4443 and 0.3818, respectively.
6. The organic matter content of sediments is determined by the proportion of the smallest particles (from 0.1 to 50 µm), at the same time, these particles most strongly affect the reduction conditions of sediments.
7. Thermal contamination as an element of anthropopression is expressed in the spatial and seasonal variability of the thermics of water masses. It causes the formation of reservoir zones of varying water density, which can affect the sedimentation process.

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