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Speciation forms of phosphorus in bottom sediments of three selected anthropogenic reservoirs with different trophy degree

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Abstract: The study presents the results of the research into different phosphorus forms in the bottom sediments of anthropogenic limnic ecosystems i.e. the reservoirs of Pławniowice, Rybnik and Goczałkowice (SP). The bottom sediments of dam reservoirs were investigated by chemical extraction procedure for phosphorus forms. The lowest value of the mean AAP form percentage in the Pławniowice bottom sediments reflected the effect of reclamation with the hypolimnetic removal that had been conducted in the reservoir since 2003. The highest percentage of the RDP form (2%) was found in the Goczałkowice bottom sediments. The order of the specific speciation forms in the bottom sediments of the examined reservoirs was:

Rybnik: AAP > EP > WDP > RDP; 4,630> 3,740 > 117 > 65 > 3.5 mgP/kg
Pławniowice: AAP > EP > WDP > RDP; 916 > 783 > 107 > 15 > 1.4 mgP/kg
Goczałkowice: AAP > WDP > EP > RDP; 686 > 628 > 51 > 7 > 0.14 mgP/kg

The mutual correlations between the phosphorus speciation forms (AAP : EP : WDP : RDP) were as follows:
Rybnik: 1,323 : 1,068 : 33 : 18 : 1;
Pławniowice: 654 : 559 : 76 : 11 : 1;
Goczałkowice: 4,900 : 4,485 : 364 : 50 : 1.

The comparison of the mean concentration values for specific phosphorus forms in the bottom sediments of the three investigated reservoirs demonstrated that the Rybnik sediments had the highest contents of phosphorus. The contents in Pławniowice and Goczałkowice were 5–7 times lower.

Introduction

The complexity of the environmental conditions and the differences between particular reservoirs (even similar ones) result in the fact that the diversification of the bottom sediment compositions (with consideration for the speciation phosphorus forms) is researched and compared (Gonsiorczyk et al. 1998, Kaiserli et al. 2002, Zhou 2001. Phosphorus and its compounds are believed to be essential to comprehend the transformation cycle of this element, which is necessary for the protection and reclamation of limnic ecosystems (Zhou et al. 2005, Psenner 1988). Specific speciation phosphorus forms are responsible for the phosphorus release process from bottom sediments to water (according to the conditions in a given reservoir). They also define the phosphorus bioavailability for living organisms (Bostrom et al. 1998, Kowalczewska-Madura et al. 2005, Petterson et al. 1988).

Not all the phosphorus forms are released from bottom sediments to the same extent and with the same intensity (Bartoszek et al. 2007, Gonsiorczyk et al. 1998, Bartoszek and Koszelnik 2016). The limnic ecosystem ability for storing or releasing phosphorus is an effect of its various characteristics, particularly supply water quality, depth (ability to stratify, oxygen conditions), or retention time (Kostecki 2014, Psenner 1988). Those characteristics decide on the influence of the phosphorus loads deposited in the sediments on the trophic condition of a water reservoir. The principle for searching and comparing the differences was used in the research into the bioavailable phosphorus fractions in the anthropogenic Silesian reservoirs affected by diversified human impact.

The following study presents the results of the research into the speciation phosphorus forms in three dammed reservoirs of Southern Poland, i.e. Pławniowice, Rybnik and Goczałkowice.

Research objective and scope

The research aim was to investigate the variability and mutual relations between the specific phosphorus forms in the bottom sediments of the anthropogenic reservoirs under different human impact. It was also conducted to define the abundance of the bottom sediments with phosphorus and to set the grounds for comparing the discussed reservoirs with natural lakes in terms of the phosphorus speciation.

Research areas

Three anthropogenic water reservoirs (i.e. Pławniowice, Rybnik and Goczałkowice) were researched. (Tab. 1).

Pławniowice is under the influence of an agricultural catchment area. The Ruda River catchment area that supplies Rybnik reservoir has an urban-industrial catchment area. It is a part of the technological system of the Rybnik Power Station and functions under the thermal pollution conditions. Goczałkowice is a reservoir used for drinking water supply and part of the anti-flood protection system. The location of the sampling points is presented in Figs. 1–3.

Research methodology

The reservoir research was conducted in 2012–2014. In Pławniowice, the bottom sediments were sampled nine times (in 2012 and 2013). In Rybnik, the samples were collected in two transects due to the characteristic oblong and transverse asymmetry of the reservoir depth. In 2012, the bottom sediments were sampled seven times in 1-month intervals (between May and December). In 2013, the bottom sediments were sampled twelve times in 1-month intervals (between January and December). In Goczałkowice, the sampling points were determined in two transects (the Vistula River – sampling points 1–5; the Bajerka River – sampling points A–D) (Fig. 3).

The sediments were collected with the Birge-Eckman sampler. In Pławniowice and Rybnik, the samples were taken from the surface sediment layer (5-cm thickness) and lower layer (15–20 cm of the sediment core thickness). In Goczałkowice, the bottom sediment samples were collected from the surface sediment layer due to their low thickness. The sampling points were located with consideration for the water mass movements.

The chemical extraction procedure for the phosphorus forms and bioavailability analysis principles were used in the investigation (Recknagel et al. 1995). The following bioavailable speciation phosphorus forms were determined in the bottom sediments: AAP (algal available phosphorus), representing phosphorus bound to metals (mainly aluminium and iron) and organic matter (defined as the availability measure for algae, particularly under anoxic conditions); EP (Olsen-P, extracted phosphorus), treated as an indicator for soil (and sediment) abundance with phosphorus, i.e. a quantitative factor for the available phosphorus, and fraction helping to make conclusions on the critical level for the plant production (not necessarily in the water environment) (Olsen et al. 1954); WDP (water dissolved phosphorus), defined as the most bioavailable phosphorus fraction, extracted with water; RDP (readily desorbable phosphorus), defining phosphorus desorbed from the surface of the bottom sediment particles during the extraction with calcium chloride. The pH and Eh (redox potential) of the bottom sediments were measured.

The phosphorus extraction from the wet sediment was conducted with the following reagents: sodium hydroxide 0.1 mole (AAP), acidic sodium bicarbonate 0.5 mole and pH=8.5 (Olsen-P), distilled water (WDP), calcium chloride 0.01 mole (RDP) (Zhou et al. 2001).

The following proportions of the sediment to the applied reagent/extraction time were used: 200 ml of sodium hydroxide per 0.8 g of the wet sediment – 4 h; 50 ml of acidic sodium bicarbonate per 2.5 g of the wet sediment – 30 min; 100 ml of distilled water per 1 g of the wet sediment – 2 h; 50 ml of calcium chloride per 2 g of the wet sediment – 1 h.

Table 1. Characteristics of the research areas

Reservoir	Reservoir type	Supply	Area [ha]	Volume [mln m^3]	Depth max.	Axis length [m]	Year of establishment
Pławniowice	Flooded sand mine pit working	Toszecki Stream	225	29	16	2.500	1974
Rybnik	Dammed	Ruda River	450	21	10	4.100	1971
Goczałkowice	Dammed	Vistula River	3.200	110	10	16.000	1956

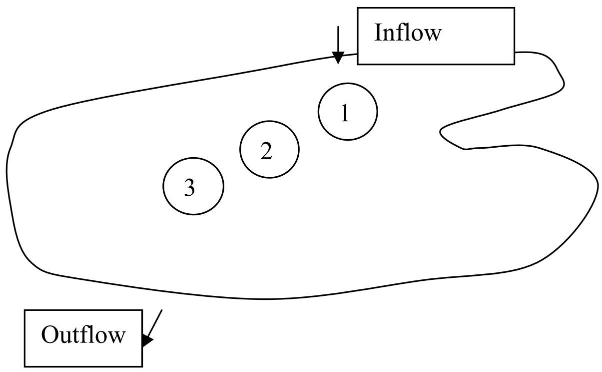

Fig. 1. Pławniowice – sampling points for bottom sediments

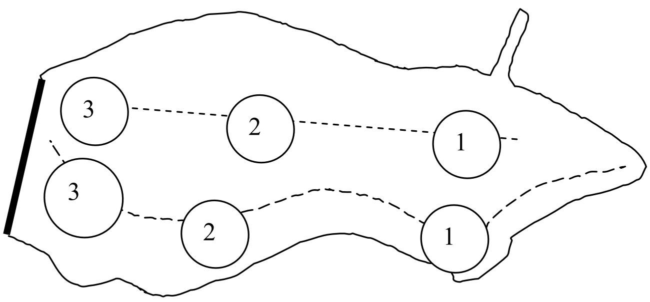

Fig. 2. Rybnik – sampling points for bottom sediments

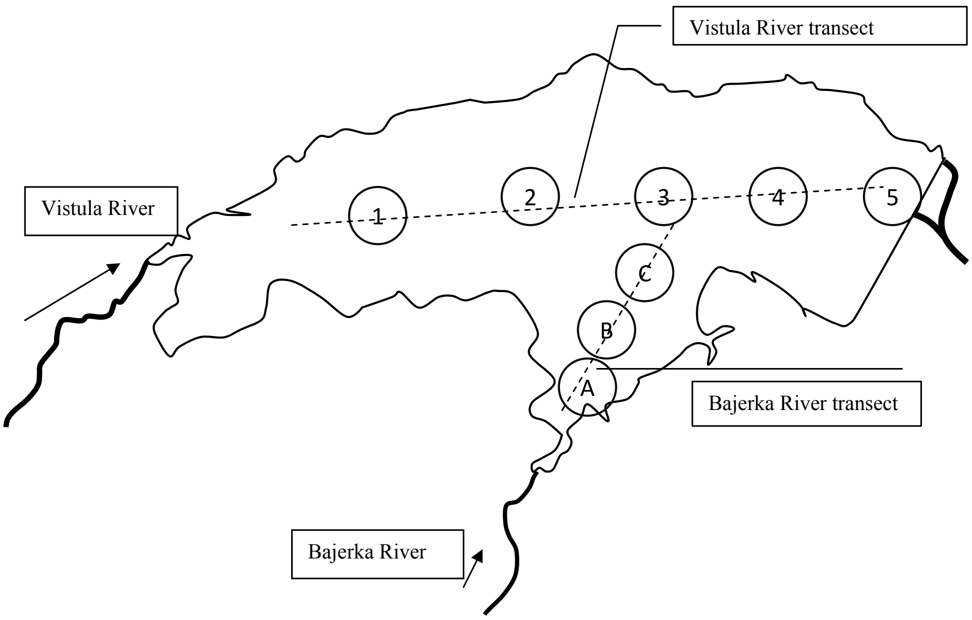

Fig. 3. Goczałkowice – sampling points for bottom sediments

Results

Redox potential and pH

The pH (measured in H_2O) differences between particular sampling points and bottom sediment layers were small. The change range was 0.6–0.7.

The redox potential value decreased with the rising pH. With similar ranges of the pH changes, the redox potential values indicating the reduction environment were found in Rybnik and Pławniowice, but not in Goczałkowice.

Organic matter

The organic matter content and bottom sediment hydration in particular reservoirs indicated the differences in the trophy level characteristic for each reservoir (Fig. 8). The highest organic matter content (25%) was determined for Rybnik. The organic matter percentage in the Pławniowice bottom sediments was 14%. The reservoir has been reclaimed for 10 years and is presently at the stage of passing from the eutrophy state to the a-mesotrophy state[6]. The lowest organic matter content was determined for Goczałkowice (2.2%).

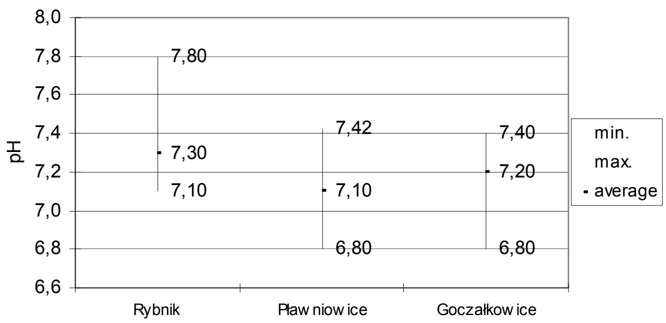

Fig. 4. Range of the pH changes for the bottom sediments of Rybnik, Pławniowice and Goczałkowice

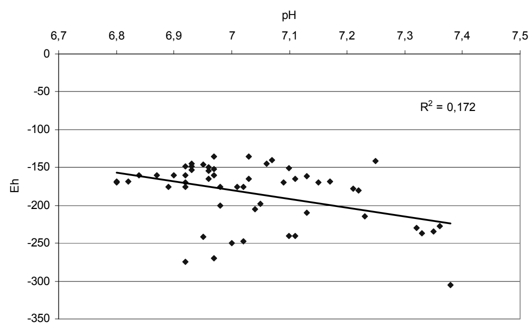

Fig. 5. Correlation between pH and Eh – Pławniowice

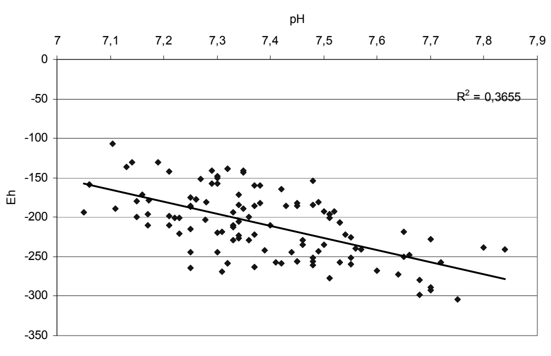

Fig. 6. Correlation between pH and Eh – Rybnik

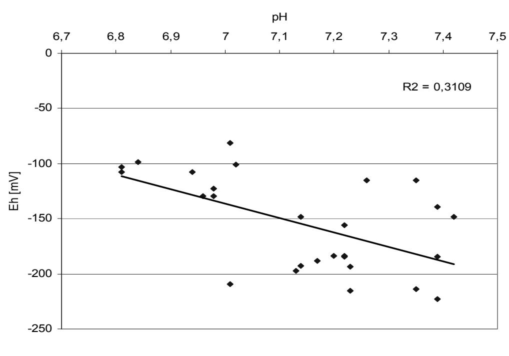

Fig. 7. Correlation between pH and Eh – Goczałkowice

The sediment humidity increased with the growing concentration of the organic matter (Fig. 9).

The correlations between the speciation phosphorus forms concentrations and the organic matter content in the bottom sediments of the investigated reservoirs are given below (Fig. 10).

The relatively low value of the mean AAP content in the Pławniowice bottom sediments could reflect the effect of the reservoir reclamation with the hypolimnetic removal conducted there since 2003 (Fig. 11, 12). The highest RDP percentage (2%) was found for the Goczałkowice bottom

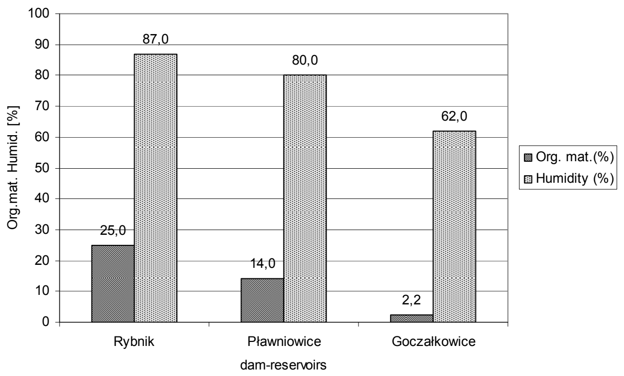

Fig. 8. Organic matter content and bottom sediment humidity in the investigated reservoirs– mean values

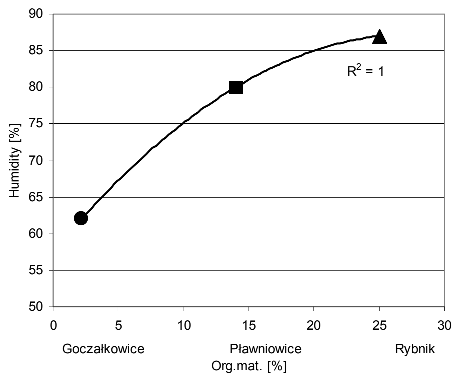

Fig. 9. Correlation between the organic matter content and bottom sediment humidity in the investigated reservoirs

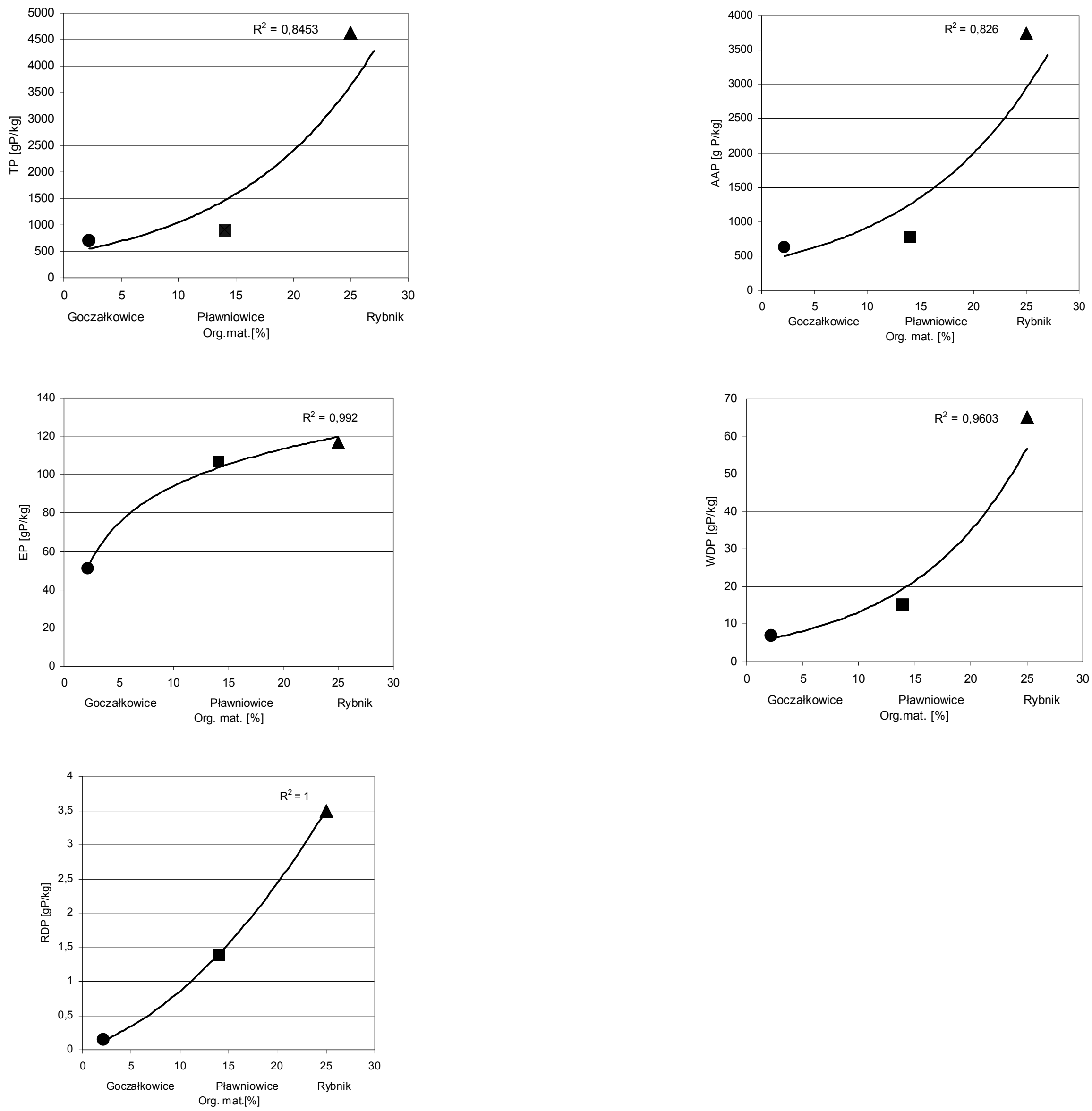

Fig. 10. Correlations between the organic matter content and concentrations of specific speciation phosphorus forms in the bottom sediments of the investigated reservoirs

sediments, which could indicate stronger sorption properties of the matter constituting these reservoir sediments.

In terms of the concentration quantities, the order of specific speciation phosphorus forms in the bottom sediments of the investigated reservoirs was as follows:

Rybnik: AAP > EP > WDP > RDP; 4,630> 3,740 > 117 > 65 > 3.5

Pławniowice: AAP > EP > WDP > RDP; 916 > 783 > 107 > 15 > 1.4

Goczałkowice: AAP > EP > RDP > WDP; 686 > 628 > 51 > 7 > 0.14

For Goczałkowice, the higher mean value for WSP than for EP indicated the low accumulation potential of the sediments. The estimated phosphorus loads in the bottom sediments of particular reservoirs are given in Table 2.

The researchers found correlations between the total iron concentration and AAP, and between the phosphorus content and calcium concentration in the bottom sediments (Fig. 13).

Discussion

Large loads of the organic carbon compounds, mineral and organic phosphorus compounds and nitrogen are accumulated in the bottom sediments of limnic ecosystems. For phosphorus, the loads accumulated in the bottom sediments may be a few thousand times higher than in the reservoir water (Bostrom et al. 1998, Kaiserli et al. 2002, Zhou et al. 2001). Their load may largely exceed the load coming from the external supply (Kostecki 2014). The discussed substances may be recovered into the internal ecosystem circulation under anoxic conditions in the bottom water layer (Bartoszek 2007, Gonsiorczyk 1998, Kostecki 2014). Consequently, it is necessary to know the morphometric conditions and thermal and oxygen conditions to appropriately assess the threats for the limnic ecosystem.

The comparison of the mean values for specific phosphorus forms in the bottom sediments of the investigated reservoirs showed that the Rybnik bottom sediments were the

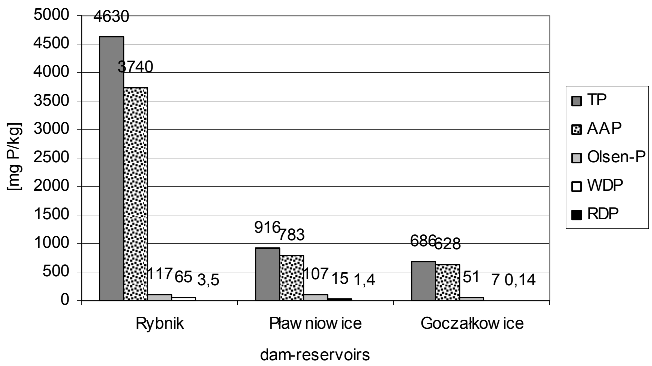

Fig. 11. Concentrations of the speciation phosphorus forms in the bottom sediments of the investigated reservoirs – mean values

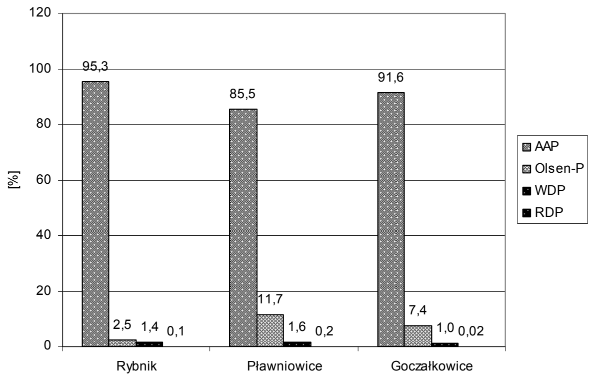

Fig. 12. Percentage of the speciation phosphorus forms in the bottom sediments of the investigated reservoirs – mean values

Table 2. Loads of the speciation phosphorus forms [Mg P] in the investigated bottom sediments

Reservoir/P load [Mg]	TP	AAP	EP	WSP	RDP
Rybnik	1,300	1,235	46	18	1
Goczałkowice	288	265	23	39	6
Pławniowice	212	178	27	7	0.2

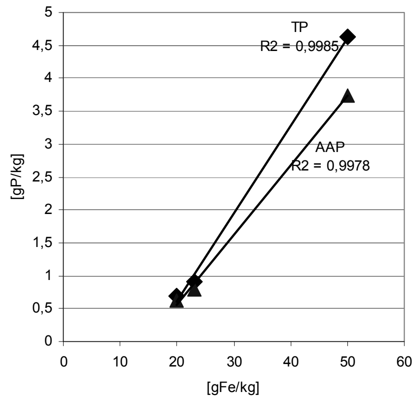

Fig. 13. Correlation between the iron and TP, and AAP concentrations in the bottom sediments of the investigated reservoirs

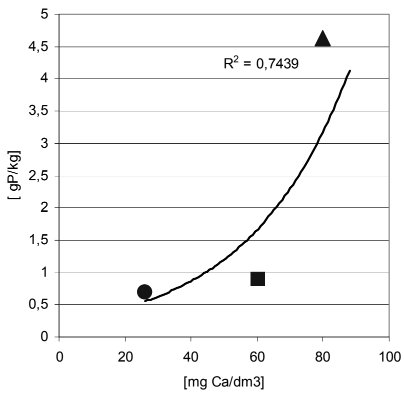

Fig. 14. Correlation between middle total phosphorus concentration in the bottom sediments and middle calcium concentration in the water of the investigated reservoirs

most abundant with phosphorus (Fig. 11). The Pławniowice and Goczałkowice bottom sediments contained 5–7 times less phosphorus than the Rybnik ones.

The mutual correlations between the speciation phosphorus forms were as follows:

AAP : EP : WDP : RDP

Rybnik: 1,323 : 1,068 : 33 : 18 : 1

Pławniowice: 654 : 559 : 76 : 11 : 1

In the Goczałkowice dam-reservoir – AAP : EP : RDP : WDP

Goczałkowice: 4,900 : 4,485 : 364 : 50 : 1

The WDP (dissolved in water) and RDP (easily desorbable) forms are the most bioavailable. They also pass from the bottom sediments into water in the easiest way (Gonsiorczyk et al. 1998, Kowalczewska-Madura et al. 2005, Kowalczewska-Madura et al. 2015). The results obtained for the three investigated anthropogenic reservoirs demonstrated diversified abundance with the bioavailable phosphorus forms. The threat of eutrophication was most likely for Rybnik due to its abundance with speciation phosphorus forms. For Pławniowice, the reclamation effects in this reservoir were visible. The most beneficial correlations between the speciation phosphorus forms were found for Goczałkowice.

The similar pH values determined for the bottom sediments of the reservoirs (differing in many aspects) indicated possible similarities in the type and character of the intra-reservoir processes (Bartoszek 2007, Bostrom et al. 1998).

The increase in the reservoir trophic level caused the increase in the organic matter in the sediments. The correlation between the organic matter content and concentration of the speciation phosphorus forms indicates the correlation between the trophic level and concentration of the speciation phosphorus forms in the bottom sediments.

The anthropogenic character and location of the reservoirs resulted in the fact that the material constituting the bottom might have a completely different character. Such a situation particularly concerns the reservoirs in which their cleaning, ordering and forming were not foreseen at the construction stage. The material (containing various pollutants) is going to affect the physical and biological intra-reservoir processes of transformations, including formation of bottom sediments, quality of water masses, microbiological processes, plant succession, and the exchange between water and bottom sediments.

Conclusions

The research into the compositions of the bioavailable speciation phosphorus forms in the bottom sediments of water ecosystems constitutes the basis for determining the threat of eutrophication.

1. The research into the abundance with speciation phosphorus forms in the bottom sediments is particularly important for a specific limnic ecosystem when the threat of the violent eutrophication process is taken into account.
2. The general abundance of the bottom sediments with phosphorus compounds, with consideration for its species, may be assessed with the mean concentration values. Nonetheless, it is only an estimation that solely defines the order of magnitude.
3. A proper assessment of the internal enrichment process risk requires determination of the ecosystem abundance with speciation phosphorus forms, which is done with defining the quantities of specific forms deposited in the bottom sediments. Such a process requires investigations enabling maximally exact determination of the bottom sediment amount in the examined ecosystem.
4. A proper assessment of the threat for the limnic ecosystem requires taking into account factors responsible for the internal enrichment process, which consists in the release of the phosphorus compounds from the bottom sediments. These factors include morphometric conditions and thermal and oxygen conditions of the reservoir.
5. Having in mind the anthropopressure scale and complexity, it is necessary to take into account the possible occurrence of a few factors affecting the extraction efficiency for the speciation phosphorus forms. The search for such factors may become the new direction in the research.

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Specjacyjne formy fosforu w osadach dennych trzech wybranych zbiorników antropogenicznych o różnym stopniu trofii

Streszczenie: Przedstawiono wyniki badań specjacyjnych form fosforu w osadach dennych antropogenicznych ekosystemów limnicznych. W badaniach wykorzystano chemiczną ekstraktację form fosforu oraz zasady analizy biodostępności. Osady zbiorników Pławniowice i Goczałkowice zawierają około 5–7 razy mniej fosforu niż zbiornik Rybnicki. Najniższa wartość średniego udziału formy AAP w osadach dennych zbiornika Pławniowice odzwierciedla skutek prowadzonej od 2003 roku rekultywacji tego zbiornika metoda usuwania hypolimnionu. Najwyższa ze wszystkich trzech zbiorników wartość udziału (2%) formy RDP, w osadach dennych zbiornika Goczałkowice może wskazywać na silniejsze właściwości sorpcyjne materii tworzącej osady tego zbiornika. Pod względem stężenia, kolejność form specjacyjnych w osadach dennych badanych zbiorników układała się:

Zbiornik Rybnicki: AAP > EP > WDP > RDP; 4630.> 3740 > 117 > 65 > 3,5 mgP/kg

Zbiornik Pławniowice: AAP > EP > WDP > RDP; 916 > 783 > 107 > 15 > 1,4 mgP/kd

Zbiornik Goczałkowice: AAP > WDP > EP > RDP; 686 > 628 > 51 > 7 > 0,14 mgP/kg

W zbiorniku Goczałkowice wyższe stężenie WDP od EP wskazuje niski potencjał kumulacyjny. Wzajemne relacje pomiędzy formami fosforu – AAP : EP : WDP : RDP – były następujące:

Zbiornik Rybnicki: 1323 : 1068 : 33 : 18 : 1, Zbiornik Pławniowice: 654 : 559 : 76 : 11 : 1, Zbiornik Goczałkowice: 4900 : 4485 : 364 : 50 : 1. Wartości potencjału redox wskazują na środowisko redukcyjne w osadach zbiorników Pławniowice i Rybnik. Średnie stężenia specjacyjnych form fosforu w osadach dennych wykazało, że najbardziej zasobne w fosfor są osady zbiornika Rybnickiego.