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ANALYSIS OF THE SPATIAL DISTRIBUTION OF PHOSPHORUS FRACTIONS IN THE BOTTOM SEDIMENTS OF THE SOLINA–MYCZKOWCE DAM RESERVOIR COMPLEX

The statistical analysis was performed to compare average contents of phosphorus fractions in the bottom sediments between the lacustrine zone and the riverine zone in the Solina Reservoir, between the main object and the retarding one as well as between all the research stations of the analysed reservoirs. It was found that the deposits from the stations localized in the lacustrine zones of both reservoirs did not differ significantly in regards to total phosphorus content, inorganic phosphorus, and non-apatite, inorganic phosphorus fractions, however, they were characterized by significantly different contents of organic phosphorus.

1. INTRODUCTION

The concentrations of biogenic substances determine trophic conditions of a reservoir [1–3]. High content of phosphorus in the bottom sediments testifies to intensive primary production that is connected with high trophy of waters.

Phosphorus compounds deposit in the bottom sediments of reservoirs due to sedimentation processes. Along the axis of dam reservoirs, the following zones can be distinguished: the riverine, transitional and lacustrine zones differing in phosphorus circulation. In the riverine zone, mainly sedimentation of phosphorus compounds, associated with thick mineral and organic suspension, as well as dragging of deposit deep inside the reservoir over the bottom take place. Sedimentation of little loamy and organic particles, containing phosphorus, occurs together with a decrease of the water flow speed in the transitional zone. The conditions in this zone, decreasing water flow, and a high content of mineral salts in water are favourable to primary production. Periodic internal supply of phosphates can occur in this zone because of fine-grained deposit easily undergoing resuspension. Biological circulation and sedimentation with

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decayed organic remains as well as periodic release of the dissolved phosphates from the sediments, in favourable conditions, are considered significant elements of the phosphorus circulation within the dam in the lacustrine zone [4, 5].

Decomposition processes are intensive in the bottom sediments. Emission and movement of the released phosphates into other layers and zones of the reservoir can be stimulated by currents in the active bottom zone, by weak water movements in the metalimnion and hypolimnion, by fish activity, bentos, and bentoplancton as well as by gases released from the deposits [6]. Variability of phosphorus respective fractions in different places of the sediments can reflect differences in the sources of phosphorus. Relatively more iron-phosphorus compounds are met in the deposits of these reservoirs which are more subject to greater inflow of sewage [7, 8].

The aim of the work was to analyse the spatial distribution of the phosphorus fraction content in the bottom sediments of the upper San dam reservoirs complex (the main reservoir – the retarding one).

2. EXPERIMENTAL

The Solina Reservoir is the most voluminous and the deepest body of water behind a dam in Poland. Together with the Myczkowce Reservoir it forms a cascade (Fig. 1) that serves the complex of Hydroelectric Power Stations of Solina –Myczkowce S.A. The Solina–Myczkowce complex of dam reservoirs is constituted of two bodies of water that are very different in terms of their morphometric parameters (Table 1). The waters of the San River (of which 90% are derived from the hypolimnion of the Solina Reservoir) form the main tributary feeding the Myczkowce Reservoir [9].

The samples of bottom sediment were collected at four stations around the Solina Reservoir, i.e. : Centralny (1), Zapora (2), Brama (3), Skałki (4), of average depths of ca. 45, 55, 14 and 15 m, respectively, as well as at two stations in the Myczkowce Reservoir, i.e. Myczkowce Zapora (5), Myczkowce Zabrodzie (6). of approximate depths of 11 and 3 m, respectively. Sampling was carried out 1–2 times a month from May to November 2005 (9 samples) and once a month (except in May) between April and November 2006 (7 samples). The 0–5 cm superficial layer was taken for analysis, averages being calculated for three sediment cores sampled with a gravity corer. The interstitial water was separated by centrifugation (at 4000 r.p.m.). The obtained residue was air dried at room temperature and at 60 °C, and then ground and sieved. The fraction of <0.9 mm grain size was stored for examination in hermetically closed PE bags at a temperature of 4 °C in the dark. The harmonized SMT protocol was applied in analysing the fractionation of phosphorus in the sediments [10–12]. The fractions obtained were as follows: inorganic phosphorus (IP), organic phosphorus (OP), apatite phosphorus (AP, calcium-associated forms) and non-apatite inorganic phosphorus

(NAIP, the forms associated with oxides and hydroxides of Al, Fe and Mn). The bottom sediments were mineralized in concentrated HNO_3 (microwave digestion method – UniClever II Plazmatronika). Phosphorus forms in the solutions of extracts and mineralized bottom sediments were analysed colorimetrically in accordance with the PN-EN 1189:2000 standard. An Aquamate spectrophotometer (Thermo Spectronic, UK) was used for colorimetric determinations.

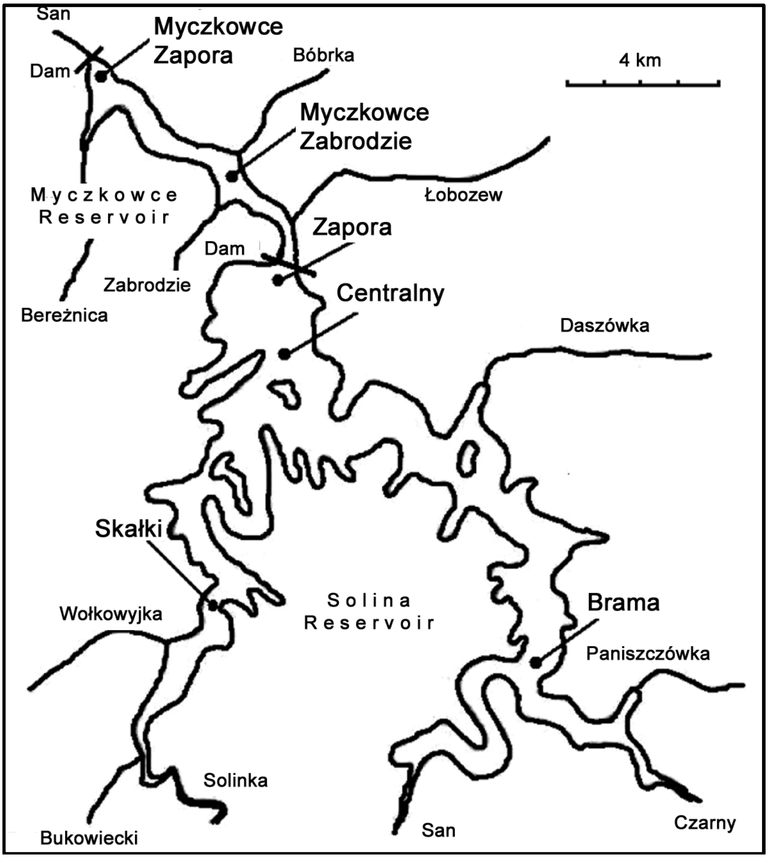

Fig. 1. Sampling locations at the Solina and Myczkowce Reservoirs

The t-Student test, the test of Cochran–Cox (the so called t test with a separate variance analysis) and the nonparametric test of Kolmogorov–Smirnov were applied to compare the average values of the two groups. The variance analysis (ANOVA – the normality test of Shapiro–Wilk, the test of Levene of variance uniformity, Fisher–Snedecor's test, the parametric test of Scheffe and the nonparametric test of Kruskal–Wallis) was used to evaluate the differences between the average values in a few groups, at the assumed significance level $\alpha = 0.05$ [13].

Table 1

Morphometric parameters of the cascade of the Solina–Myczkowce Reservoirs

Parameter	Solina Reservoir	Myczkowce Reservoir
Area [ha]	2200	200
Maximum volume [Mm^3]	502	10
Average depth (max) [m]	22 (60)	5 (15)
Catchment area [km^2]	1174.5	1248
Hydraulic retention time [d]	155–273	2–6

3. RESULTS AND DISCUSSION

The analysis of phosphorus fractionation in the bottom sediments with the SMT method allowed one to separate four fractions: NAIP, AP, OP and IP. The content of the NAIP fraction containing the forms associated to oxides and hydroxides of Al, Fe and Mn ranged from 0.096 to 0.316 mg $P\cdot g^{-1}$ of d.w. in the sediments of the Solina Reservoir and from 0.123 to 0.331 mg $P\cdot g^{-1}$ of d.w. in the sediments of the Myczkowce Reservoir (Table 2).

The content of the AP fraction (the forms associated with calcium) varied in a rather wide range from 0.199 to 0.414 mg $P\cdot g^{-1}$ of d.w. in deposits of the Solina Reservoir in comparison to the range of this fraction from 0.255 to 0.332 mg $P\cdot g^{-1}$ of d.w. in deposits of the Myczkowce Reservoir. Organic phosphorus – OP, the fraction covering all organic compounds in which phosphorus can occur in the bottom sediments, varied in a similar range from 0.189 to 0.385 mg $P\cdot g^{-1}$ of d.w. and from 0.188 to 0.327 mg $P\cdot g^{-1}$ of d.w. (Solina, Myczkowce respectively). The IP fraction (inorganic phosphorus) informs on a general content of inorganic compounds with phosphorus. The IP fraction content ranged from 0.407 to 0.685 mg $P\cdot g^{-1}$ of d.w. in the Solina Reservoir and from 0.446 to 0.644 mg $P\cdot g^{-1}$ of d.w. in the Myczkowce Reservoir.

The average content of the NAIP, OP and IP fractions showed the trend of increase similarly as the average of total phosphorus with the depth of the reservoirs from which the sediments were collected. The statistical analysis (based on the tests: Cochran–Cox and Kolmogorov–Smirnov) confirmed the significance of differences (p <0.05) of the average contents of the above mentioned phosphorus fractions between the deposits of zones: the lacustrine zone and the zone being under the influence of tributaries in the shallower parts of the Solina Reservoir.

A detailed test of Kruskal–Wallis, on account of similar values of the average contents of NAIP fractions, distinguished two groups of sediments: (1) at the Centralny, Zapora and Myczkowce Zapora stations as well as (2) at the Skałki and Myczkowce Zabrodzie stations. The deposits collected at the Brama station placed themselves, from the point of view of similarities, between these groups, not showing statistically significant differences with respect to the sediments from the stations: Centralny and Skałki as well as Myczkowce Zabrodzie (Fig. 2).

Table 2

Content of phosphorus and its fractions [mg P·g^{-1} d.w.] and fractions contribution [%] in P_{tot} in the bottom sediments of the Solina – Myczkowce Reservoirs

Station		$P_{tot.}$	NAIP		AP		OP		IP	
		[mg P·g^{-1} d.w.]		[%]	[mg P·g^{-1} d.w.]	[%]	[mg P·g^{-1} d.w.]	[%]	[mg P·g^{-1} d.w.]	[%]
Centralny $n = 16$	average	0.912	0.237	26.0	0.320	35.2	0.320	35.2	0.561	61.7
	median	0.894	0.235	25.6	0.333	36.6	0.311	34.5	0.570	62.4
	minimum	0.826	0.207	20.5	0.206	21.9	0.286	29.6	0.457	55.3
	maximum	1.009	0.316	33.5	0.370	40.3	0.385	44.5	0.603	66.1
	S.D.	0.05	0.03	3.0	0.05	5.3	0.03	3.6	0.04	3.5
Zapora $n = 15$	average	0.931	0.263	28.3	0.320	34.2	0.323	34.8	0.588	63.0
	median	0.928	0.262	27.8	0.350	36.2	0.326	33.4	0.594	64.5
	minimum	0.849	0.224	23.1	0.199	22.6	0.297	30.4	0.506	56.7
	maximum	1.014	0.306	34.8	0.414	40.8	0.365	39.7	0.685	69.9
	S.D.	0.05	0.03	3.1	0.06	5.5	0.02	3.0	0.06	4.0
Brama $n = 16$	average	0.857	0.196	22.9	0.339	39.7	0.291	34.0	0.537	62.7
	median	0.861	0.194	22.9	0.338	40.2	0.290	34.1	0.541	63.4
	minimum	0.766	0.153	17.6	0.288	31.1	0.245	30.8	0.481	55.6
	maximum	0.929	0.236	27.7	0.387	47.9	0.347	37.4	0.567	67.6
	S.D.	0.05	0.02	2.4	0.03	3.8	0.03	1.9	0.02	3.1
Skałki $n = 16$	average	0.689	0.126	18.3	0.306	44.5	0.218	31.7	0.438	63.5
	median	0.686	0.125	17.7	0.308	45.0	0.218	31.6	0.438	63.8
	minimum	0.650	0.096	14.1	0.278	39.5	0.189	27.7	0.407	58.4
	maximum	0.726	0.180	24.8	0.336	49.0	0.249	36.3	0.467	68.4
	S.D.	0.02	0.02	3.2	0.02	3.05	0.02	2.5	0.02	2.4
Myczkowce Zapora $n = 16$	average	0.869	0.259	29.6	0.294	34.0	0.288	33.1	0.556	64.0
	median	0.872	0.251	29.8	0.293	33.6	0.293	32.6	0.551	64.2
	minimum	0.724	0.179	24.4	0.255	29.5	0.198	27.4	0.454	58.9
	maximum	0.996	0.331	34.0	0.326	38.5	0.327	37.7	0.644	67.7
	S.D.	0.08	0.05	3.3	0.02	2.4	0.03	2.4	0.05	2.9
Myczkowce Zabrodzie $n = 15$	average	0.754	0.184	24.3	0.302	40.2	0.244	32.3	0.490	65.1
	median	0.756	0.181	24.4	0.297	39.6	0.258	32.7	0.486	65.0
	minimum	0.665	0.123	18.5	0.278	36.7	0.188	28.2	0.446	62.6
	maximum	0.826	0.224	27.6	0.332	49.9	0.289	36.1	0.556	67.5
	S.D.	0.04	0.03	2.6	0.02	3.5	0.3	2.5	0.03	1.5
Solina $n = 63$	average	0.846	0.205	23.8	0.321	38.5	0.288	33.9	0.530	62.7
	median	0.873	0.209	24.0	0.326	39.2	0.299	33.6	0.538	63.7
	S.D.	0.11	0.06	4.7	0.04	6.0	0.05	3.1	0.07	3.3
Myczkowce $n = 31$	average	0.813	0.222	27.0	0.298	37.0	0.267	32.7	0.524	64.5
	median	0.797	0.209	26.4	0.297	37.1	0.268	32.7	0.508	65.0
	S.D.	0.09	0.05	4.0	0.02	4.3	0.04	2.5	0.05	2.4

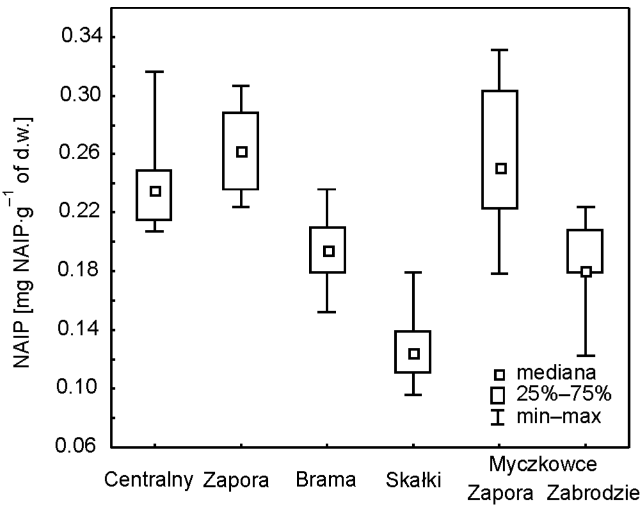

Fig. 2. Statistical distribution of NAIP fraction contents [mg P·g^{-1}of d.w.] in the bottom sediments of the Solina–Myczkowce Reservoirs

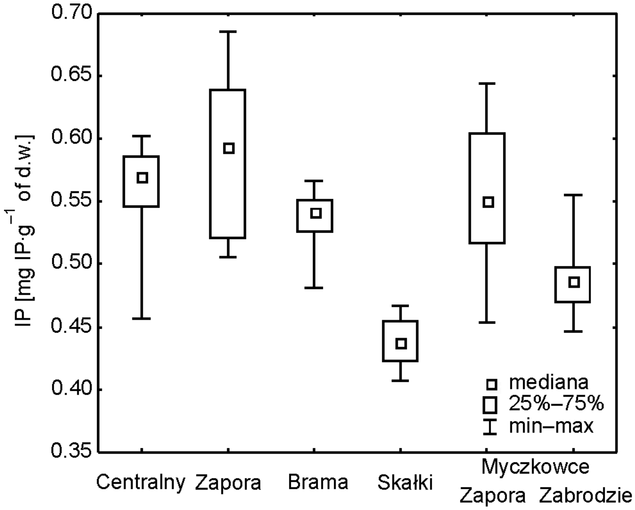

Fig. 3. Statistical distribution of IP fraction contents [mg P·g^{-1}of d.w.] in the bottom sediments of the Solina–Myczkowce Reservoirs

Statistically similar differentiation of the average contents was observed in the IP fraction, however, the sediments from the Brama station showed similarity to all deposits of the first group with statistically significant difference with the sediments from the Skałki station (Fig. 3). The evaluation of statistical significance of OP fraction average values (by means of Scheffe's parametric test) showed rather considerable differentiation of organic phosphorus among the deposits from particular stations.

The deposits from the stations: Centralny, Zapora and Brama did not show statistically significant differences, however, the deposits from the Myczkowce Zapora station showed similarity to those of the Brama station in the content of OP fraction. From the statistical point of view, the deposits from the Skałki and Myczkowce Zabrodzie stations, characterized by the lowest content of organic compounds with phosphorus, clearly differed from other deposits (Fig. 4).

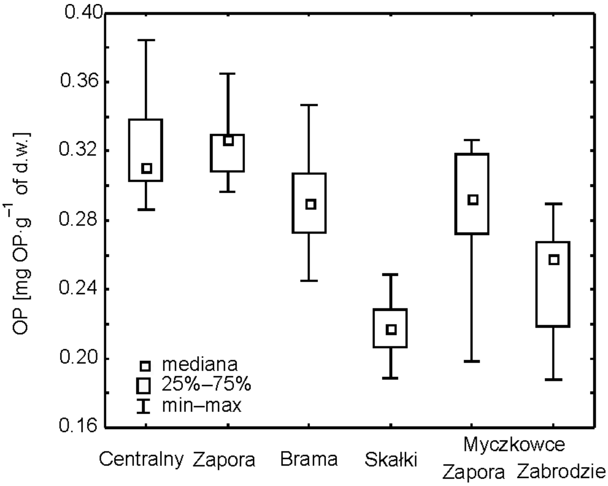

Fig. 4. Statistical distribution of OP fraction contents [mg P·$g^{-1}$of d.w.] in the bottom sediments of the Solina–Myczkowce Reservoirs

The average content of the AP fraction seemed to be similar in the deposits from almost all the stations. No statistically significant differences were found in the content of the apatite fraction in the sediments within reservoirs. The variance analysis (ANOVA) showed only statistically significant differences in the content of apatite compounds among the deposits from the Myczkowce Zapora (the lowest AP) and Centralny as well as Brama stations and also among the deposits from the Myczkowce Zabrodzie and Brama stations (Fig. 5). However, the comparison between the averages in the two examined groups (by means of the Kolmogorov–Smirnov's test) did not show statistically significant differences (p <0.05) considering AP fraction content between the sediments of the zones: the lacustrine zone and the one being under the influence of tributaries in the shallower parts of the Solina Reservoir.

The deposits of the Myczkowce Reservoir were characterized by the higher average content of the NAIP fraction and by the lower one of AP and OP in comparison to the deposits of the Solina Reservoir. The content of IP fraction was comparable in the deposits of both reservoirs (Table 2). Statistical analysis (based on the tests: t-Student, Cochran–Cox and Kolmogorov–Smirnov) confirmed the occurrence of significant differences between the averages in the two examined groups ($p < 0.05$), between the content of AP and OP fractions in the deposits of the main reservoirs and the retarding one and it did not show statistically significant differences considering the contents of NAIP and IP fractions in the deposits of both reservoirs.

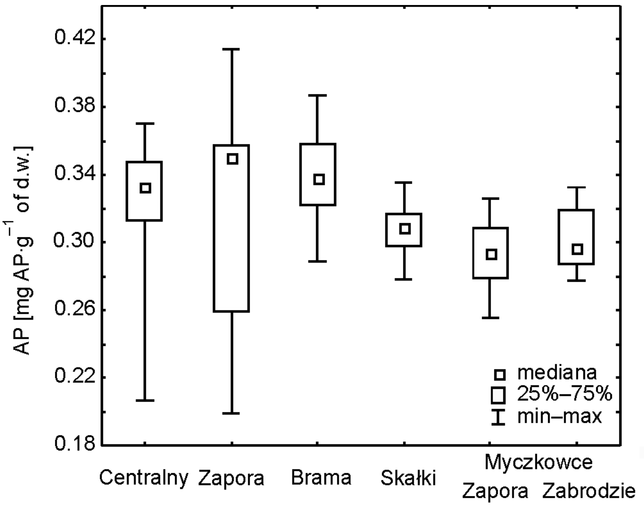

Fig. 5. Statistical distribution of AP fraction contents
[mg P·g^{-1} of d.w.] in the bottom sediments of the Solina–Myczkowce Reservoirs

Considering spatial differentiation of phosphorus content in the sediments of the discussed reservoirs more information about the distribution of phosphorus is provided by the proportion of particular fractions in total phosphorus. The proportion of the NAIP fraction in total phosphorus was the smallest (on the average from 18.3% to 29.6%) in the deposits of both reservoirs (Table 2). The proportion of AP fraction in total phosphorus was highest in the deposits of the Solina Reservoir riverine zone (on average 39.7% – Brama, 44.5% – Skałki) and in the deposits of the Myczkowce Reservoir (34.0% – Myczkowce Zapora, 40.2% – Myczkowce Zabrodzie). The percentage content of the AP fraction was comparable to the OP fraction (35.2% – Centralny, 34.2% – Zapora) in the deposits of the Solina Reservoir lacustrine zone. The average percentage contents of IP and NAIP fractions was higher in the deposits of the retarding reservoir and those of OP and AP fractions lower than in the deposits of the main reservoir.

In the bottom sediments of the Bort-Les-Orgues Reservoir (France) the percentage obtained by SMT method was: 59% NAIP fraction, 25% OP and 16% AP (of total phosphorus) [8, 14]. The average proportion of NAIP fraction in the bottom sediments from four stations of the Chinese lake was 72%, 41%, 24% and 12% (in total phosphorus). The proportion of OP and AP fractions varied from 12% to 24% and from 11% to 70% respectively, in total phosphorus. Generally, IP fraction was higher than the OP one [15]. Alkalization of lakes admittedly progresses together with the increase of lakes trophy, therefore the increase of the proportion of the apatite fraction in total phosphorus could be theoretically treated as an indicator of the eutrophication of reservoirs [16]. However, as per Kaiserli et al. [17], the AP fraction was the predominant phosphorus fraction in the deposits of mesotrophic lakes. Jin et al. [15] also found, that the NAIP fraction content was higher than the AP fraction content in the deposits (from the two research stations) of the Chinese Taihu Lake, more contaminated with sewage and the opposite situation: AP > NAIP was observed in the deposits (from other two stations) less subject to anthropogenic contaminations. Perrone et al. [18] observed higher percentage of the NAIP fraction in the deposits collected from the deeper lake part and the higher content of AP and OP fractions in the deposits of the shallower parts.

In the Bort-Les-Orgues Reservoir, phosphorus mainly came from anthropogenic contamination (NAIP and partially OP) whereas the apatite fraction (AP) coming from the detritus was lower than 20%. Thus the highest amount of phosphorus, in the reservoir deposits, was of allochthonous origin [8, 14]. Brigault and Ruban [19] found that from the allochthonous sources of phosphorus, ca. 30% comes from domestic and industrial effluents (mainly NAIP), 60% from agriculture (NAIP + OP).

Significant proportions of the apatite and organic compounds in the total phosphorus content were found in the deposits of the Solina and Myczkowce Reservoirs, however, taking into consideration generally low content of this element in the deposits, they testify to low trophy level of the analysed reservoirs.

4. CONCLUSIONS

By means of the statistical analysis, the comparison of the phosphorus fraction average contents in the bottom sediments was made between the lacustrine and riverine zones in the Solina Reservoir, between the main reservoir and the retarding one as well as among all the research stations of the Solina–Myczkowce dam reservoirs complex. It has been found that the deposits of the lacustrine zone and the one being under the influence of tributaries are significantly different in relation to the content of NAIP, IP and OP fractions, whereas the deposits from the stations localized in the lacustrine zones of both reservoirs (Centralny, Zapora, Myczkowce Zapora) did not differ significantly in regards to the total phosphorus content of IP and NAIP fractions, however, they were characterized by significantly different contents of organic phosphorus (OP). The deposits collected at the Brama station showed great similarity to deposits of the lacustrine zone and the deposits from the Skałki and Myczkowce Zabrodzie stations clearly differed from other deposits. Statistically significant differences in the apatite fraction content were found neither in the deposits within reservoirs nor between the sediments of the lacustrine zone and the one being under the influence of tributaries in the shallower parts of the Solina Reservoir. However, it has been observed that the deposits of the main reservoir and the retarding one differ significantly between themselves in the content of apatite (AP) and organic (OP) compounds with phosphorus. The retention of phosphorus in the deposits of dam reservoirs, especially spatially extensive ones, can take place by means of various mechanisms. As it results from the carried out analysis, the different distribution of phosphorus fraction in the bottom sediments does not necessarily have to be caused by the different character of deposits, connected with the depth changes along the longitudinal axis of the reservoirs.

The differentiation between the content of total phosphorus and the content of particular fractions in the deposits collected in the zone being under the influence of tributaries in the shallower parts of the Solina Reservoirs (Brama and Skałki), resulted presumably from different management and use of the catchment of the Solinka River, the San River and the Czarny Stream [20]. Bottom sediments of the central parts of both reservoirs as well as the sediments affected by the San River and the Czarny Stream could have been subject to greater sewage inflow resulting in the higher content of NAIP fraction. The proportion of the NAIP fraction in total phosphorus was the smallest in the deposits of both reservoirs that can suggest that the catchment of the Solina–Myczkowce dam reservoirs complex is not so much subject to anthropogenic contaminants inflow as the catchments of other reservoirs, especially lowland ones, usually are.

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