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VERTICAL PHOSPHORUS DISTRIBUTION IN THE BOTTOM SEDIMENTS OF THE SOLINA–MYCZKOWCE RESERVOIRS

The analysis of total phosphorus content and its bioavailable forms in the bottom sediment profiles of the cascade of the Solina–Myczkowce dam reservoirs was carried out. It has been found that first of all phosphorus occurring in organic compounds must be considered to be more mobile. The increase of the total phosphorus and organic matter contents in the upper layers of the lacustrine zone sediments can indicate a slow increase of fertility in both reservoirs.

1. INTRODUCTION

As early as the reservoir had been created, its basin started to fill with sedimenting matter produced in aquatic environment (autochthonous) as well as with sedimenting matter drifted from the catchment (allochthonous). Together with the increase of the amount of sediments their chemical composition also used to change [11]. It has not been determined precisely how a thick layer of sediments exchanges phosphorus with water; however, it is suspected that it can reach on an average approx. 10 cm. The proportion of phosphates decreases with the thickness of sediments, while that of insoluble phosphorus forms (apatite fraction), which are permanently removed from the biological cycle, increases [1].

The aim of investigation was to analyse the vertical distribution of the bioavailable phosphorus in the bottom sediments of the cascade of the upper San River dam reservoirs.

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2. MATERIALS AND METHODS

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 (figure 1) that serves the complex of Hydroelectric Power Stations of Solina–Myczkowce S.A. The Solina–Myczkowce cascade 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 (90% of which are derived from the hypolimnion of the Solina reservoir) form the main tributary feeding the Myczkowce reservoir [5], [8].

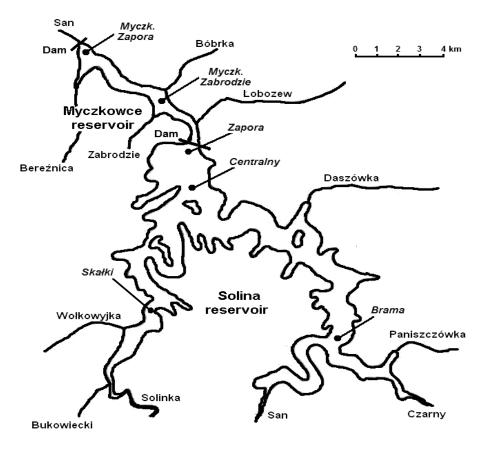


Fig. 1. Sampling locations at the Solina and Myczkowce reservoirs

The samples of bottom sediment were collected at four stations around the Solina reservoir, i.e. 1. Centralny, 2. Zapora, 3. Brama, 4. Skałki (average depths of approx. 45, 60, 14 and 15 m, respectively), as well as at two stations in the Myczkowce reservoir, i.e. 5. Myczk. Zapora and 6. Myczk. Zabrodzie (the depth of approx. 11 and 3 m, respectively) in August 2006. The upper 15-cm layer of the sediment core (divided

into 5-cm thick sections) was analyzed. The interstitial water was separated by centrifugation (at 4000 r.p.m.). The residue obtained 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 [2], [7]. The fractions obtained were as follows: inorganic phosphorus (IP), organic phosphorus (OP), apatite phosphorus (AP, calciumassociated 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 HNO₃ (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. The content of other elements in the solutions of mineralized bottom sediments involved colorimetric methods complying with: PN-ISO 6332:2001 (iron), PN-ISO 6058:1999 (calcium), DIN ISO 10566E30 (aluminium) and DIN 38406E2 (manganese). An Aquamate spectrophotometer (Thermo Spectronic, United Kingdom) was used for colorimetric determinations. The organic matter (OM) content in bottom sediments was determined by dry sediment calcination at 550 °C.

Table 1

Parameter	Solina reservoir	Myczkowce reservoir			
Area (ha)	2200	200			
Maximal 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			

Morphometric parameters of the cascade of the Solina-Myczkowce reservoirs

3. RESULTS AND DISCUSSION

The total phosphorus content decreases with the depth of the examined layer in the deposits from the following stations: Centralny, Zapora, Myczk. Zapora (table 2). A similar tendency was observed for organic matter, iron and calcium in the sediments collected in the lacustrine zone. Less clear tendencies were revealed in the sediments being under the riverine zone influence. The content of total phosphorus slightly decreased with the depth of the layer; however, at the Brama station, the total phosphorus concentration increased with the sediment thickness, while the content of organic matter, manganese and calcium decreased. OP fraction decreased with the depth of the sediment layer at all the stations analysed (figure 2), which was also

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Vertical distribution of the content of some elements and phosphorus fractions (mg $P.g^{-1}$ of d.w.; OM - %), sediment pH, and fraction proportion (%) in P_{tot} in the profiles of the bottom sediments of the Solina–Myczkowce reservoirs

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Profiles	P _{tot.}	Fe	AI	Mn	Ca	MO	Fe/P	pH _{KCl}	NAIP	Ы	AP		OP		P	
IIV IIV 0.890 46.5 45.5 2.72 8.24 9.47 52.2 6.62 0.232 24.9 0.366 34.4 0.8806 44.3 41.8 2.49 5.75 9.28 51.1 6.31 0.236 41.4 0.228 26.5 0.860 44.3 48.5 2.64 4.81 8.57 51.5 6.34 0.277 32.0 0.316 33.4 0.948 45.1 42.4 2.90 6.88 9.89 47.6 6.48 0.277 31.6 0.316 33.4 0.9255 42.6 40.3 2.74 4.78 8.51 48.8 6.10 0.261 28.2 0.316 33.4 0.9255 42.6 40.0 44.1 1.30 9.64 6.47 0.277 31.6 0.316 33.4 0.8873 40.0 44.1 1.30 9.65 8.54 7.56 0.316 32.4 0.8873 23.5 <td< td=""><td>(cm)</td><td>(mg g⁻¹ of d.w.)</td><td>(mg g⁻¹ of d.w.)</td><td>(mg g⁻¹ of d.w.)</td><td>(mg g⁻¹ of d.w.)</td><td>(mg g⁻¹ of d.w.)</td><td>(%)</td><td></td><td></td><td>(mg g⁻¹ of d.w.)</td><td>(%)</td><td>(mg g⁻¹ of d.w.)</td><td> </td><td>(mg g⁻¹ of d.w.)</td><td>(%)</td><td>(mg g⁻¹ of d.w.)</td><td>(%)</td></td<>	(cm)	(mg g ⁻¹ of d.w.)	(%)			(mg g ⁻¹ of d.w.)	(%)	(mg g ⁻¹ of d.w.)		(mg g ⁻¹ of d.w.)	(%)	(mg g ⁻¹ of d.w.)	(%)				
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Centralny																
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0-5	0.890	46.5	45.5	2.72	8.24	9.47	52.2	6.62	0.222	24.9	0.346	38.9	0.306	34.4	0.573	64.4
5 0.860 44.3 48.5 2.64 4.81 8.57 51.5 6.34 0.277 32.2 0.356 41.4 0.228 2.65 0 9.948 45.1 42.7 2.69 5.16 8.61 48.4 6.10 0.261 28.2 0.356 36.9 0.316 33.1 0 9.955 44.7 42.7 2.69 5.16 8.61 48.4 6.10 0.261 28.2 0.356 33.4 0.256 29.3 0 9.815 47.9 7.04 0.179 22.0 0.355 38.4 0.256 29.3 0 8.816 6.90 0.221 26.9 0.316 32.4 0.256 30.3 0 0.825 23.7 9.05 8.38 8.76 6.90 0.216 32.4 0.256 30.3 0 0.825 23.7 39.9 0.74 0.111 15.3 0.234 46.2 0.188 26.9	5-10	0.876	44.8	41.8	2.49	5.75	9.28	51.1	6.31	0.238	27.1	0.330	37.6	0.287	32.8	0.585	66.7
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10-15	0.860	44.3	48.5	2.64	4.81	8.57	51.5	6.34	0.277	32.2	0.356	41.4	0.228	26.5	0.625	72.7
	Zapora																
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0-5	0.948	45.1	42.4	2.90	6.88	9.89	47.6	6.48	0.224	23.6	0.350	36.9	0.316	33.4	0.613	64.7
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5-10	0.925	44.7	42.7	2.69	5.16	8.61	48.4	6.10	0.261	28.2	0.353	38.2	0.306	33.1	0.623	67.3
	10-15	0.875	42.6	40.3	2.74	4.78	8.51	48.8	6.24	0.277	31.6	0.336	38.4	0.256	29.3	0.605	69.2
	Brama																
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0-5	0.816	39.1	37.4	1.80	10.92	9.01	47.9	7.04	0.179	22.0	0.325	39.8	0.261	32.0	0.522	64.0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5-10	0.823	40.0	44.1	1.30	9.65	8.38	48.7	6.90	0.221	26.9	0.316	38.4	0.253	30.8	0.567	68.9
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10-15	0.859	23.7	39.9	0.77	4.72	7.03	27.6	6.07	0.276	32.2	0.237	27.6	0.247	28.8	0.538	62.7
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Skałki																
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	0-5	0.726	44.0	39.3	1.69	13.57	8.99	60.7	7.44	0.111	15.3	0.308	42.5	0.220	30.3	0.449	61.9
39.3 42.9 1.60 14.57 9.84 56.4 7.45 0.138 19.8 0.355 51.0 0.187 26.9 35.9 33.2 1.88 11.44 12.08 39.3 6.97 0.251 27.6 0.309 33.9 0.327 35.8 27.8 38.4 0.89 9.07 6.59 43.7 6.90 0.139 21.9 0.268 42.2 0.149 23.5 26.4 30.6 0.94 6.59 43.7 6.99 0.139 24.3 0.268 42.2 0.149 23.5 26.4 30.6 0.94 6.59 43.7 6.99 0.139 24.3 0.278 48.6 0.129 22.6 25.0 27.0 1.936 33.1 6.74 0.180 23.9 0.258 34.1 25.5 25.7 0.75 12.52 7.98 35.4 7.22 0.229 31.8 0.129 21.6 26.4 25.7	5 - 10	0.723	35.4	40.6	1.40	14.46	9.37	48.9	7.35	0.131	18.1	0.334	46.2	0.188	26.0	0.494	68.4
35.9 33.2 1.88 11.44 12.08 39.3 6.97 0.251 27.6 0.309 33.9 0.327 35.8 27.8 38.4 0.89 9.07 6.59 43.7 6.90 0.139 21.9 0.268 42.2 0.149 23.5 26.4 30.6 0.94 6.59 5.90 46.1 6.99 0.139 24.3 0.278 48.6 0.129 23.5 26.4 30.6 0.94 6.59 5.90 46.1 6.99 0.139 24.3 0.278 48.6 0.129 22.6 25.0 27.0 1.95 10.71 9.36 33.1 6.74 0.180 23.9 0.278 36.7 0.258 34.1 25.5 25.7 0.75 12.52 7.98 35.4 7.22 0.229 31.8 0.327 45.4 0.164 22.9 26.4 25.7 0.77 10.35 7.23 32.8 7.14 0.294 36.4 0.159 19.7	10-15	0.697	39.3	42.9	1.60	14.57	9.84	56.4	7.45	0.138	19.8	0.355	51.0	0.187	26.9	0.512	73.5
35.9 33.2 1.88 11.44 12.08 39.3 6.97 0.251 27.6 0.309 33.9 0.327 35.8 27.8 38.4 0.89 9.07 6.59 43.7 6.90 0.139 21.9 0.268 42.2 0.149 23.5 26.4 30.6 0.94 6.59 5.90 46.1 6.99 0.139 24.3 0.268 42.2 0.149 23.5 26.4 30.6 0.94 6.59 5.90 46.1 6.99 0.139 24.3 0.278 48.6 0.129 23.6 25.0 27.0 1.95 10.71 9.36 33.1 6.74 0.180 23.9 0.258 34.1 25.5 25.7 0.75 12.52 7.98 35.4 7.22 0.229 31.8 0.327 45.4 0.164 22.9 26.4 25.7 0.77 10.35 7.23 32.8 7.14 0.294 36.4 0.159	Myczk. Z	apora															
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26.4 30.6 0.94 6.59 5.90 46.1 6.99 0.139 24.3 0.278 48.6 0.129 22.6 25.0 27.0 1.95 10.71 9.36 33.1 6.74 0.180 23.9 0.278 36.7 0.258 34.1 25.5 25.7 0.75 12.52 7.98 35.4 7.22 0.229 31.8 0.327 45.4 0.164 22.9 26.4 25.7 0.77 10.35 7.23 32.8 7.14 0.294 36.4 0.159 19.7	5 - 10	0.636	27.8	38.4	0.89	9.07	6:59	43.7	6.90	0.139	21.9	0.268	42.2	0.149	23.5	0.448	70.4
25.0 27.0 1.95 10.71 9.36 33.1 6.74 0.180 23.9 0.278 36.7 0.258 34.1 25.5 25.7 0.75 12.52 7.98 35.4 7.22 0.229 31.8 0.327 45.4 0.164 22.9 26.4 25.7 0.77 10.35 7.23 32.8 7.14 0.294 36.4 0.159 19.7	10-15	0.571	26.4	30.6	0.94	6.59	5.90	46.1	6.99	0.139	24.3	0.278	48.6	0.129	22.6	0.418	73.1
0.756 25.0 27.0 1.95 10.71 9.36 33.1 6.74 0.180 23.9 0.278 36.7 0.258 34.1 0.719 25.5 25.7 0.75 12.52 7.98 35.4 7.22 0.229 31.8 0.327 45.4 0.164 22.9 0.807 26.4 25.7 0.73 32.8 7.14 0.294 36.4 0.159 19.7	Myczk. Z	abrodzie															
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0.807 26.4 25.7 0.77 10.35 7.23 32.8 7.14 0.294 36.4 0.320 39.6 0.159 19.7	5 - 10	0.719	25.5	25.7	0.75	12.52	7.98	35.4	7.22	0.229	31.8	0.327	45.4	0.164	22.9	0.548	76.2
	10-15	0.807	26.4	25.7	0.77	10.35	7.23	32.8	7.14	0.294	36.4	0.320	39.6	0.159	19.7	0.609	75.5

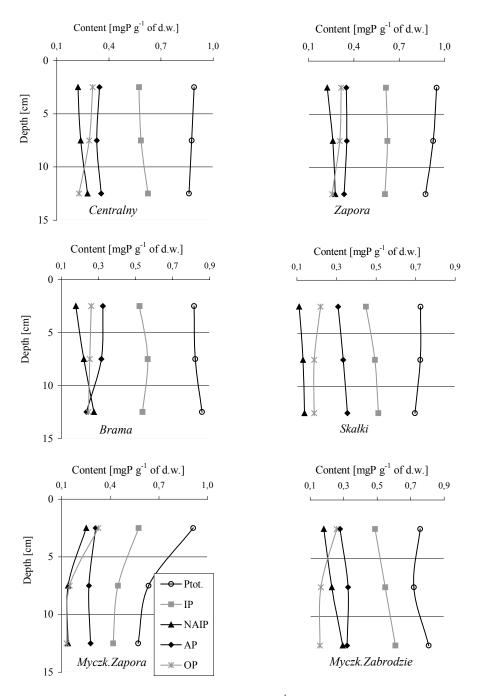


Fig. 2. Vertical phosphorus distribution (mg P g⁻¹ of d.w.) in the bottom sediments of the Solina–Myczkowce reservoirs

observed for the content of organic matter, except the deposits of the Skałki station, where the organic matter content in the 0–5-cm layer and in the 10–15-cm layer of the sediment profile was respectively the lowest and the highest. The chemical analysis of the individual layers of bottom sediment in Lake Dołgie Wielkie showed the greatest accumulation of total phosphorus and organic matter in the 0–5-cm surface layer. The content of these elements in the individual layers decreased with the sediment thickness [10].

The content of NAIP fraction increased with the sediments thickness at all the stations except the deposits collected at the Myczk. Zapora station (lack of trend). Although no analogical tendency was observed in the case of iron, aluminium and manganese, their relatively high content allowed us to presume that organic compounds released phosphorus that is bound to these metals. The AP fraction content in all three sediment layers was slightly different but with no distinct tendency to change. The proportion of apatite compounds in total phosphorus was the greatest in the deepest layer of sediment profiles (10-15 cm) of all stations except the Brama station. In the deepest layer of deposits from the Brama station, the NAIP fraction proportion was the highest. The content of inorganic phosphorus compounds (IP fraction) visibly increased deep into the sediment profile from the stations: Centralny, Skałki and Myczk. Zabrodzie, and decreased at the Myczk. Zapora station. In the sediments from other two stations, such definite tendencies were not revealed. It is also difficult to identify a distinct tendency, analysing the content of phosphorus forms which are considered to be more mobile (NAIP+OP). The content of a potentially mobile phosphorus decreased in the deposits from the Centralny and the Myczk. Zapora stations, and increased in the deposits from the Brama station. The deposits collected at the Brama station were characterized by lower hydration and high consolidation which might have impeded phosphorus release from the deep layers of the sediment.

No differences were revealed in the content of the apatite compounds containing phosphorus between 0-5, 5-10, 10-15-cm layers of the core in the bottom sediments of the Bort–Les–Orgues reservoir (France). However, there was observed a slight increase in OP fraction content deep into the sediment. The lowest content of the NAIP fraction was found in a 10-15-cm layer [9]. The studies of the bottom sediment vertical profiles revealed that phosphorus released from organic matter recently deposited was its main source in the eutrophic lakes [4].

The analysis of the selected elements in the sediment core profiles showed that the changes of total phosphorus content were correlated, in a positive statistically significant way, upon the changes of manganese content in the cores of the Solina reservoir sediments and organic matter content of the Myczkowce reservoir sediments (table 3). A positive significant correlation was also found between the IP fraction content and the manganese content in the layers of the Solina reservoir sediments. Because of higher manganese potential in the redox reactions and slower kinetics of its oxidation in comparison with iron, the phosphorus–manganese compounds occurring deep inside a highly reducing sediment could have been dissolved more easily than those with iron [3]. Iron(III) controls the process of phosphorus solubility in the superficial layer of the sediments, whereas the flux of phosphorus from deeper layers of the sediments is probably affected by vivianite forming (iron(II)) [6]. A visible increase of NAIP fraction content in deeper sediment core layers of the Solina reservoir, in spite of theoretically more reducing conditions prevailing there, can testify to the movement of phosphorus forms within the same fraction but in the different deposit layer. A positive correlation between the content of organic matter and total phosphorus and also OP fraction in the sediment cores as well as the highest content of organic matter and OP fraction in the superficial layer of deposits (0–5 cm) suggest that the deposition of phosphorus in the form of organic compounds occurred more intensively in the Myczkowce reservoir for the last years.

Table 3

Relationships between content of total phosphorus, its fractions (mg P g⁻¹ of d.w.) and some selected parameters (mg g⁻¹ of d.w.; OM in %) in the profiles of the bottom sediments of the Solina–Myczkowce reservoirs (r – coefficient of correlation; p – significance level)

	Solir	na reserv	oir		Myczkowce reservoir					
У	f(x)	r	п	р	у	f(x)	r	n	р	
	Mn	0.64		< 0.05		OM	0.86		< 0.05	
р	pH _{KCl}	-0.88		< 0.001	р	NAIP	0.81		< 0.05	
P _{tot.}	NAIP	0.82		< 0.001	P _{tot.}	OP	0.80		< 0.05	
	OP	0.91	12	< 0.001				6		
IP	Mn	0.71		< 0.05	OP	OM	0.98		< 0.001	
	pH _{KCl}	-0.82		< 0.01						
NAIP	pH _{KCl}	-0.96		< 0.001	AP	pH _{KCl}	0.82		< 0.05	

The changes of the content of NAIP and OP fractions, which are considered to be more mobile fractions of phosphorus, had a quite significant influence on total phosphorus content variability in the sediment layers of both reservoirs. The negative correlations between total phosphorus content, IP and NAIP fractions and the sediment pH were found only for the Solina reservoir. In the sediments, whose capability for accumulating this element is mostly determined by the phosphorus– iron(III) interaction, pH decrease probably causes a significant phosphorus accumulation in deposits, whereas in the sediments rich in calcium, low pH should increase the phosphorus release from deposits [1]. A positive correlation between AP fraction content and pH changes in the sediment cores was, however, observed in the Myczkowce reservoir whose deposits are more abundant in calcium compared to those in the Solina reservoir.

4. SUMMARY

It has been found, based on the examinations of the Solina–Myczkowce reservoirs bottom sediments, that first of all phosphorus occurring in organic compounds, i.e. as OP fraction, must be considered to be more mobile. NAIP fraction seems to be less mobile in comparison with OP fraction in the reservoirs characterized by the high content of iron, aluminium and manganese in the bottom sediments. The increase of the total phosphorus and organic matter content in the upper layers of the lacustrine zone sediments can testify to a slow increase of fertility of the reservoirs analysed. The deposits in deeper parts reveal more autochthonous character and are slightly influenced by the catchment. Phosphorus occurs mostly in organic form on the surface of deposits, where it settles together with sedimenting remains of aquatic organisms. The processes of organic matter decomposition, taking place in the bottom sediments, lead to mineral phosphorus being bonded to the metal ions.

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