Environment Protection Engineering

Vol. 33 2007 No. 2

LILIANNA BARTOSZEK*, JANUSZ A. TOMASZEK*

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

The analyses of phosphorus content and its bioavailable forms in the bottom sediments of the Solina–Myczkowce reservoirs falling in cascade were carried out. It has been found that the apatite fraction constitutes the biggest portion of total phosphorus in shallower parts of the Solina reservoir and Myczkowce reservoir. In deeper parts of Solina, an inorganic fraction of phosphorus constitutes a slightly bigger part of total phosphorus than the apatite fraction. The fraction containing non-apatite inorganic phosphorus, despite the greatest differentiation among the stations, constitutes the smallest part of total phosphorus in the bottom sediments of both reservoirs.

1. INTRODUCTION

Phosphorus in bottom sediment has been the subject of investigations due to its role in the eutrophication of surface waters. The phosphorus content in the sediments is 1000 times higher than in the lake waters and its release depends on the concentration and distribution in the sediments, the degree of saturation of exchangeable phosphorus, the intensity of biological and chemical processes taking place at the water–sediment interphase and hydrological conditions [3], [7].

The studies of the occurrence of bioavailable phosphorus forms are of great importance for the evaluation of quantities of phosphorus which can be released from the sediments. Phosphorus mobility is related to its interaction with different components of sediment matrix, thus the knowledge of different forms of phosphorus in sediments is necessary. Phosphorus is found both in organic and inorganic forms in the sediments. Fractionation of inorganic phosphorus provides more information about its potential bioavailability than total mineralisation resulting in separation of the resources, which are not readily soluble in water under natural conditions and thus they are bioavailable [2], [4]. The most important inorganic forms of phosphorus are as follows: unstable phosphorus (exchangeable forms weakly bounded with the sediment

* Rzeszów University of Technology, Department of Environmental and Chemistry Engineering, ul. Wincentego Pola 2, 35-959 Rzeszów, Poland. Tel: +48 17 8651361, e-mail: bartom@prz.rzeszow.pl

matrix), phosphorus associated to with oxides and hydroxides of aluminium, iron and manganese, phosphorus associated with calcium minerals, and residual inorganic phosphorus (included in very resistant minerals and crystal structures of some silicates) [6].

Many year application of different fractionation methods has shown that the distribution of phosphorus fraction depends on the fractionation procedure. On the basis of the existing fractionation schemes of phosphorus in the bottom sediments and interlaboratory studies involving the expert laboratories the SMT protocol has been developed within the Standards, Measurements and Testing Programme of the European Commission [11], 13].

The ability of a sediment to accumulate or release phosphorus affects the nutrient level in the reservoir and its productivity. The study of the phosphorus behaviour in the sediment is therefore the key factor in the understanding of this nutrient cycle in rivers and reservoirs. It is also of prime importance in the planning of water management and restoration of reservoirs [10].

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

2. EXPERIMENTAL

The Solina reservoir is the biggest in terms of volume and also the deepest dam reservoir in Poland. Together with the Myczkowce reservoir it constitutes a cascade (figure 1) which is the element of the Complex of Hydro-Electric Power Stations of Solina–Myczkowce S.A. The stilling basin for the top-pumping performance of this power station was located in Myczkowce.

The cascade of the Solina–Myczkowce dam reservoirs is constituted by two reservoirs, being very different in terms of morphometric parameters (table 1). The San River waters coming from the hypolimnion of the Solina reservoir (over 90%) are a main tributary of the Myczkowce reservoir [8], [9].

For the analyses, the samples were collected from the bottom sediments (0–5 cm layer) at four stations of the Solina reservoir: 1. Centralny, 2. Zapora, 3. Brama, 4. Skałki, (average depth of approx. 45, 60, 14, 15 m, respectively) and at two stations of the Myczkowce reservoir: 5. Myczkowce-Zapora, 6. Myczkowce-Zabrodzie (approx. 11 and 3 m, respectively) 1–2 times a month from May to November 2005. The interstitial water was separated by centrifugation of the sediment sample. The bottom sediments dried at 60 °C were mineralized in a concentrated HNO_3. The harmonized SMT protocol was applied to analyse the fractionation of phosphorus in the sediments [5], [6], [7], [10], [11], [13]. The following fractions were obtained: 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 aluminium, iron and manganese). Phosphorus forms in the solutions of extracts and mineralized bottom sediments were analysed colorimetrically in agreement with PN-EN 1189:2000 standard.

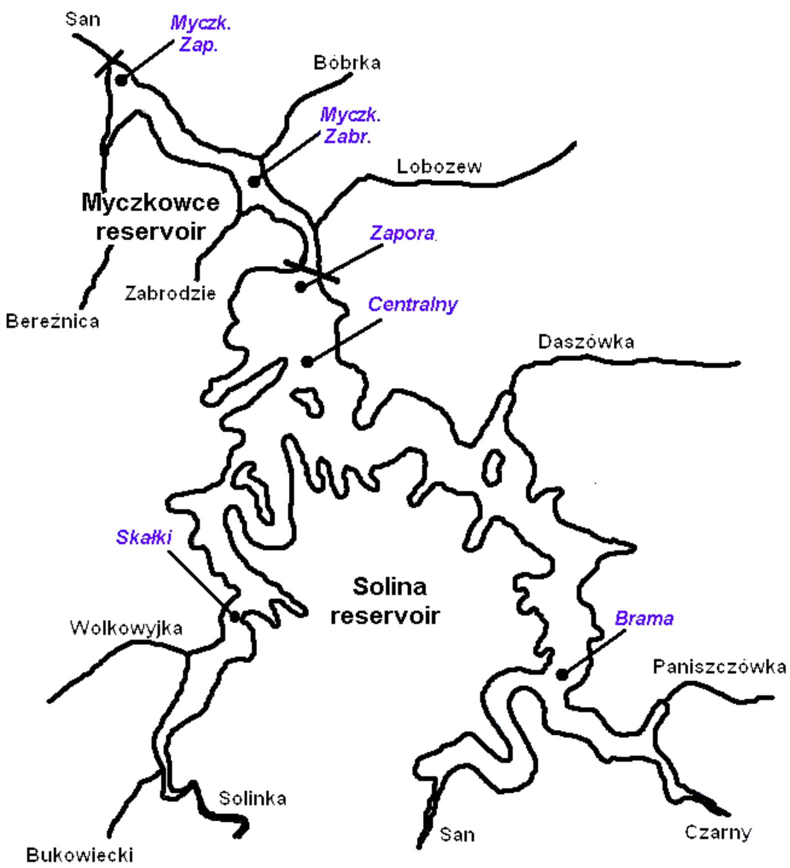

Fig. 1. The location of sampling places in the Solina and Myczkowce reservoirs

Table 1

Morphometric parameters of the cascade of the Solina–Myczkowce reservoirs

Parameter	Solina reservoir	Myczkowce reservoir
Area [ha]	2200	200
Maximal volume [mln m^3]	502	10
Average depth (max) [m]	22 (60)	5 (15)
Catchment area [km^2]	1174.5	1248
Hydraulic retention time [d]	215	6

3. RESULTS OF INVESTIGATION

Sedimentation processes result in more or less stable accumulation of phosphorus compounds in the bottom sediments. The content of total phosphorus in the sediments of the Solina reservoir and the Myczkowce reservoir ranged from 0.650 to 1.007 mg P g^{-1} of d.w. and from 0.702 to 0.950 mg P g^{-1} of d.w., respectively. The concentration of total phosphorus in the bottom sediments of both reservoirs varied slightly. Relatively greater variability of total phosphorus was observed at the Centralny and the Zapora stations in deeper parts of the Solina reservoir and at the Myczkowce–Zapora station in the Myczkowce reservoir (figure 2a, b, e).

An average content of total phosphorus in the sediments, in the whole period of its investigation at individual stations, was slightly higher in the sediments collected from deeper parts of the Solina reservoir than that in the sediments from the shallower parts. The same situation arose in the Myczkowce reservoir. This leads to the conclusion that phosphorus retention in the sediments of both reservoirs can increase together with the depth. Higher total phosphorus content in the sediments collected from deeper parts can be caused by the increased sedimentation in the central part of the reservoir, connected with a decrease in water flow (lake area) [15].

Difficulties in estimating the quantities of phosphorus, which is exchanged in the processes of its releasing and depositing in the sediments, arise from the simultaneity of these processes at the water–sediment interphase under natural conditions. Therefore the studies of the occurrence of bioavailable forms of phosphorus differing in solubility (mobility) are of great importance [6].

The highest variability of individual phosphorus fractions in the analysed period of investigation was observed in the sediments collected from the Centralny and the Zapora stations, while the lowest one was observed in the sediments from the Skałki and the Myczkowce-Zabrodzie stations (figure 2a, b, d, f) in spite of the fact that in shallower parts of the reservoir the processes of phosphorus release from the sediments can be significantly influenced by the resuspension of bottom sediments [14]. However, in deep parts of the reservoirs, faster sedimentation and better mineralisation of organic matter besides phosphorus release from organic compounds (OP fraction) can be responsible for local oxygen deficiencies right under the sediments surface. Moreover, redox potential decreases resulting in the decomposition of Fe-P and Mn-P compounds (NAIP fraction) [6]. The excretion of organic acids and CO_2 by bacteria during decomposition of organic matter and the concurrent decrease in pH of interstitial water can affect the solubility of pH-sensitive phosphorus fractions as those associated with $CaCO_3$ and apatite [3].

The higher average content of AP fraction was observed at the stations in shallower parts of the reservoir, the lower one was observed in its deeper parts (table 2). In the case of NAIP fraction, an opposite tendency is observed (a similar phenomenon is recorded for phosphorus content), i.e., its contribution to total phosphorus increases along with the depth of the sediments in the Solina and the Myczkowce reservoirs.

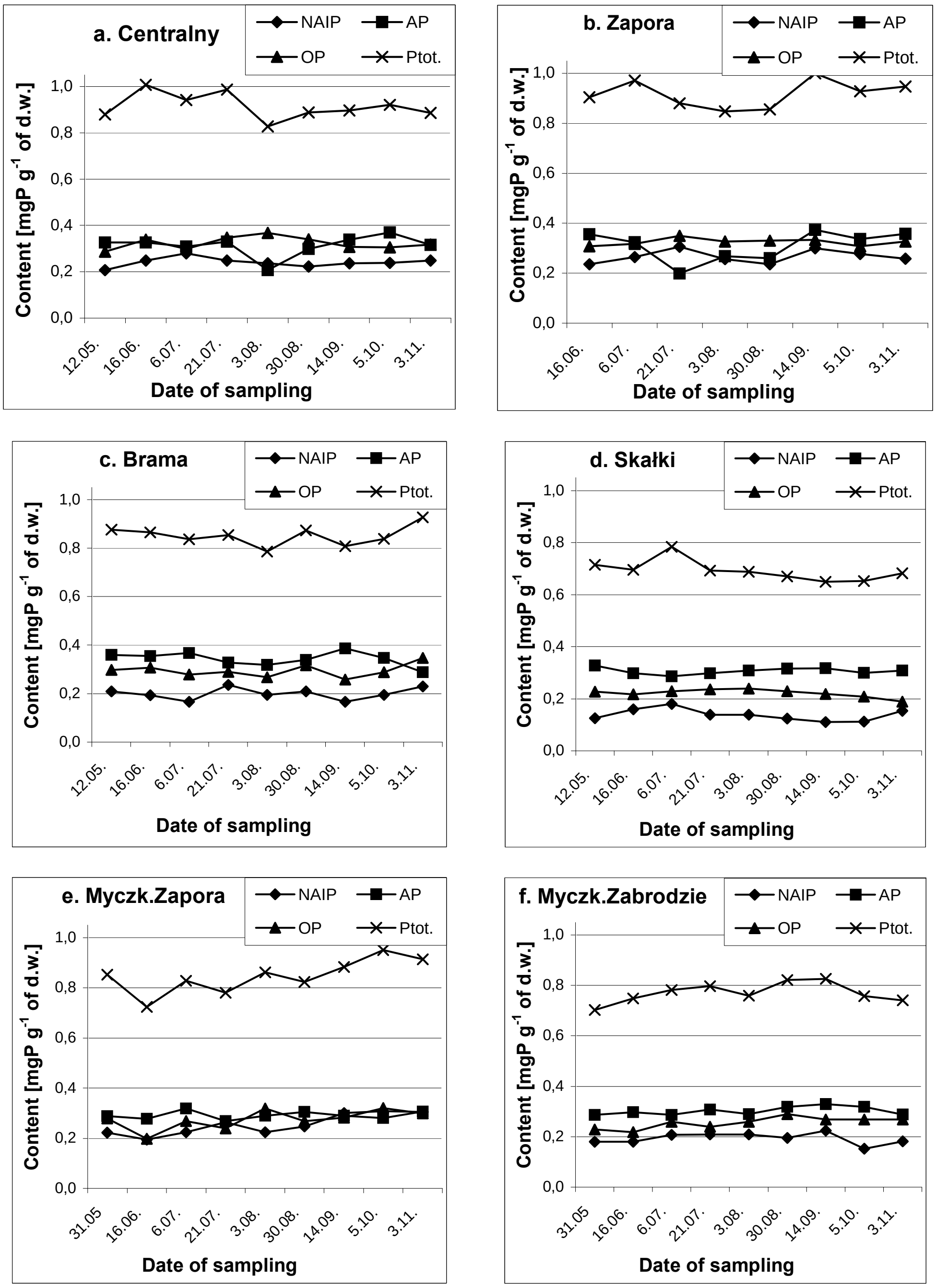

Fig. 2. The variability of fractions of NAIP, AP, OP and $P_{tot.}$ [mg P g^{-1} of d.w.] in bottom sediments of the Solina and Myczkowce reservoirs

Figure 3 presents an important negative correlation between the average contents of NAIP and AP fractions in the sediments ($r = -0.94$; $p < 0.01$).

Table 2

Average contents of NAIP, AP, OP [%] fractions in P_{tot}
in bottom sediments of the Solina and Myczkowce reservoirs

Station	NAIP	AP	OP
Centralny	26.37	34.24	35.48
Zapora	29.10	33.58	35.57
Brama	23.49	40.47	34.55
Skałki	19.89	44.47	32.05
Average	**24.59**	**38.32**	**34.38**
Myczk-Zapora	29.94	34.60	32.35
Myczk-Zabrodzie	25.05	39.28	33.14
Average	**27.50**	**36.94**	**32.74**

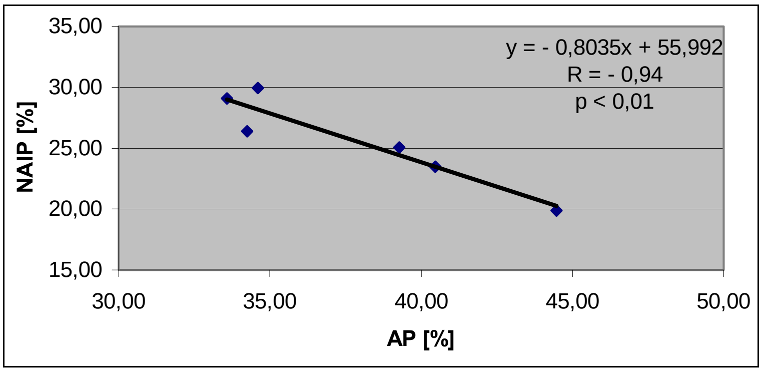

Fig. 3. Relationship between average contents of NAIP [%] and AP [%] fractions
in bottom sediments of the Solina and Myczkowce reservoirs

The greatest contribution of AP fraction to total phosphorus is found in shallower parts of the Solina reservoir and the Myczkowce reservoir. OP fraction shows slightly greater contribution to total phosphorus than AP fraction in deeper parts of the Solina reservoir (figure 4). NAIP fraction constitutes the smallest part of total phosphorus in the bottom sediments of both reservoirs in spite of the greatest differentiation between the stations. The resuspension of the bottom sediments can be responsible for the smaller content of NAIP fraction as well as for total phosphorus in shallower parts of the reservoir. Relatively higher concentration of NAIP fraction can be found in the sediments subject to greater sewage inflow [12]. Considerable differences between the content of total phosphorus and its individual fractions in the sediments collected from the shallower parts of the Solina reservoir, slightly differing in depth (Brama, Skałki), probably result from differentiation of the sediment structure and hydration. Moreover, the Skałki station was located at the arm of the Solina reservoir not far from the estuary of the Solinka River, which is considered to be the purest tributary of the reservoir on the basis of many year studies that have been carried out so far. However, the Brama station was located at the second arm of the reservoir not far from the estuaries of the San River and the Czarny Stream, which carry a considerable load of biogens [1].

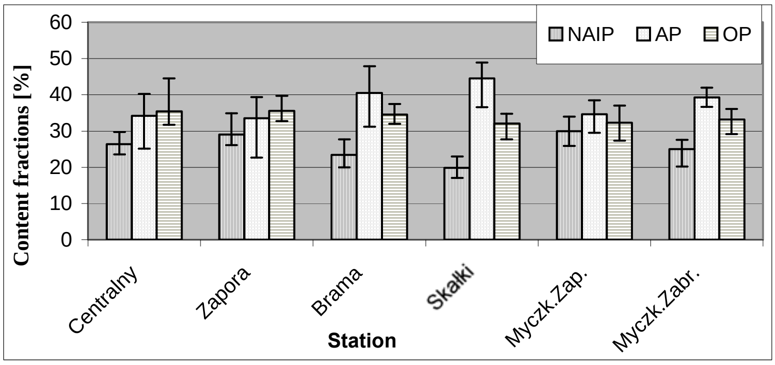

Fig. 4. The average contents of NAIP, AP, OP [%] fractions in $P_{tot.}$
in bottom sediments of the Solina and Myczkowce reservoirs
(minimum and maximum values were marked)

4. CONCLUSIONS

- In the bottom sediments of both reservoirs, a slight increase of phosphorus retention with depth has been observed. The resuspension of the bottom sediments can be responsible for the lower content of the NAIP fraction in shallower parts of the reservoir.
- A considerable contribution of the apatite fraction to total phosphorus in the bottom sediments suggests that calcium can have significant influence on the sediments retention ability of both reservoirs.
- In the case of possible nutrient level increase in both reservoirs due to supplying them with considerable loads of pollutants, especially organic ones, more indissoluble Ca-P compounds seem to protect better the reservoirs against internal feeding than the compounds comprising manganese and iron (NAIP) which are not resistant to oxidation–reduction conditions in the above-bottom zone.

LITERATURE

[1] BARTOSZEK L., KOSZELNIK P., TOMASZEK J., *Dynamika zmian fosforu w dopływach zbiornika solińskiego*, I Kongres Inżynierii Środowiska, Monografie Komitetu Inżynierii Środowiska PAN, Lublin, 2002, 11, 233–249.

[2] GOLTERMAN H.L., *The Chemistry of Phosphate and Nitrogen Compounds in Sediments*, 2004, 277 p.

[3] GOLTERMAN H.L., *Phosphate release from anoxic sediments or "What did Mortimer really write?"*, Hydrobiologia, 2001, 450, 99–106.

[4] KENTZER A., *Fosfor i jego biologicznie dostępne frakcje w osadach jezior różnej trofii*, habilitation, Wydawnictwo UMK, Toruń, 2001.

[5] PARDO P., RAURET G., LOPEZ-SANCHEZ J.F., *Shortened screening method for phosphorus fractionation in sediments. A complementary approach to the standards, measurements and testing harmonized protocol*, Analytica Chimica Acta, 2004, 508, 201–206.

[6] PARDO P., LOPEZ-SANCHEZ J.F., RAURET G., *Relationships between phosphorus fractionation and major components in sediments using the SMT harmonized extraction procedure*, Anal. Bioanal. Chem., 2003, 376, 248–254.

[7] PARDO P., LOPEZ-SANCHEZ J.F., RAURET G., *Characterisation, validation and comparison of three methods for the extraction of phosphate from sediments*, Analytica Chimica Acta, 1998, 376, 183–195.

[8] PŁUŻAŃSKI A., PÓŁTORAK T., TOMASZEK J., GRANOPS M., ŻUREK R., DUMNICKA E., *Charakterystyka limnologiczna zbiorników kaskady górnego Sanu (Solina, Myczkowce), Funkcjonowanie ekosystemów wodnych ich ochrona i rekultywacja. Ekologia zbiorników zaporowych i rzek*. Część I, Materiały CPBP 04.10, SGGW, AR, Warszawa, 1990, 264–281.

[9] PŁUŻAŃSKI A., *Powierzchniowe spływy fosforu i azotu do zbiornika solińskiego i myczkowskiego, Funkcjonowanie ekosystemów wodnych, ich ochrona i rekultywacja. Ekologia zbiorników zaporowych i rzek*. Część I, Materiały CPBP 04.10, SGGW, AR, Warszawa, 1990, 254–263.

[10] RUBAN V., LOPEZ-SANCHEZ J.F., PARDO P., RAURET G., MUNTAU H., QUEVAUVILLER Ph., *Harmonized protocol and certified reference material for the determination of extractable contents of phosphorus in freshwater sediments – A synthesis of recent works*, Fresenius. J. Anal. Chem., 2001a, 370, 224–228.

[11] RUBAN V., LOPEZ-SANCHEZ J.F., PARDO P., RAURET G., MUNTAU H., QUEVAUVILLER Ph., *Development of a harmonized phosphorus extraction procedure and certification of a sediment reference material*, J. Environ. Monit., 2001b, 3, 121–125.

[12] RUBAN V., BRIGAULT S., DEMARE D., PHILIPE A.-M., *An investigation of the origin and mobility of phosphorus in freshwater sediments from Bort-Les-Orgues Reservoir*, France, J. Environ. Monit., 1999a, 1, 403–407.

[13] RUBAN V., LOPEZ-SANCHEZ J.F., PARDO P., RAURET G., MUNTAU H., QUEVAUVILLER Ph., *Selection and evaluation of sequential extraction procedures for the determination of phosphorus forms in lake sediment*, J. Environ. Monit., 1999b, 1, 51–56.

[14] WIŚNIEWSKI R., *Rola resuspensji osadów dennych w funkcjonowaniu ekosystemów wodnych*, Rozprawy UMK, Toruń, 1995a.

[15] WIŚNIEWSKI R.J., *Rola zasilania wewnętrznego w eutrofizacji zbiorników zaporowych. Procesy biologiczne w ochronie i rekultywacji nizinnych zbiorników zaporowych*, Biblioteka Monitoringu Środowiska, Łódź, 1995b, 61–70.

DYSTRYBUCJA FOSFORU W OSADACH DENNYCH ZBIORNIKÓW ZAPOROWYCH SOLINA–MYCZKOWCE

Określono zawartość fosforu całkowitego i jego biologicznie dostępnych form w osadach dennych kaskady zbiorników zaporowych Solina–Myczkowce. Stwierdzono, że frakcja apatytowa ma największy udział w fosforze całkowitym w płytszych partiach zbiornika solińskiego i w zbiorniku myczkowieckim. W głębszych partiach Soliny frakcja fosforu organicznego ma nieznacznie większy udział w fosforze całkowitym niż frakcja apatytowa. Frakcja zawierająca nieapatytowy, nieorganiczny fosfor mimo największego zróżnicowania pomiędzy stanowiskami ma najmniejszy udział w fosforze całkowitym w osadach dennych obu zbiorników.