

RELATIONSHIPS BETWEEN PHOSPHORUS DISTRIBUTION AND
MAJOR COMPONENTS IN THE BOTTOM SEDIMENTS OF THE
SOLINA-MYCZKOWCE RESERVOIRSLILIANA BARTOSZEK¹, JANUSZ A. TOMASZEK¹

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Abstract: The contents of total P and its bioavailable forms, as well as of Fe, Al, Mn, Ca, and OM in the bottom sediments of the Solina-Myczkowce (S-E Poland) cascade of reservoirs, are presented. Notwithstanding a relatively low calcium content, it is the apatite fraction that accounts for the largest share of total phosphorus in the shallower parts of the Solina and Myczkowce Reservoirs. In turn, while contents of iron and aluminium (and manganese in the Solina Reservoir) are high, the fraction containing non-apatite inorganic phosphorus accounts for the smallest portion of the total phosphorus in the bottom sediments of both reservoirs. Bottom sediments of the Solina Reservoir are also characterised by significant correlations between total phosphorus content and aluminium content. Otherwise, significant correlations are reported for only some of the stations at each of the reservoirs.

Keywords: phosphorus, fractionation, reservoirs, bottom sediments.

INTRODUCTION

Phosphorus limits the primary production in aquatic ecosystems to a much greater degree than other biogenic elements. The amount of phosphorus in such an ecosystem depends upon its import from the outside and upon export - with outflow and migrating organisms, and above all upon permanent accumulation in deep layers of bottom sediments (Kajak 1998).

The dominant aspect of the phosphorus cycle in dam reservoirs is the element's sedimentation. Phosphate ions easily undergo sorption on the surface of suspensions and sediments, and the sorption properties of suspended matter and sediment particles are more enhanced the greater the abundance in water of iron, manganese, aluminium or calcium, as well as organic matter, since all of these manifest considerable sorption capacity. The biological and chemical processes taking place at the water-sediment interface provide for the release of a certain amount of phosphate from sediments, this becoming available to algae and macrophytes (Golterman 2001).

In the presence of oxygen, phosphorus combines with the oxidized form of iron $\text{Fe}(\text{OH})_3$ to form an insoluble complex which undergoes sedimentation. In sediments with a low concentration of oxygen (approx. 0.1 mg-dm^{-3}), reduction of Fe^{3+} to Fe^{2+} takes place, resulting in dissolution of the aforementioned complex and return of phosphorus to the water (O'Neill 1998).

Redox conditions also control the sorption of phosphorus onto oxides and hydroxides of manganese (Gonsiorczyk *et al.* 1998). However, Mn is usually only found in small amounts in sediments, hence the usual view that its role in the phosphorus cycle is of less relevance than those of Fe and Al (Pardo *et al.* 2003). Phosphorus sorption by aluminium compounds is pH-sensitive, whereas under reducing conditions Al maintains its adsorptive capacity. Aluminium compounds in insoluble forms occur at pH values in the range 6-8. The amounts of the forms dissolved in water increase with both lower and higher pH (Lossow and Gawrońska 2000).

Calcium can also make a considerable contribution to the removal of phosphorus from the water column, and to the element's permanent accumulation in sediments (Gonsiorczyk *et al.* 1998). However, the precipitation involving calcium is reaction-dependent, being more intensive in an alkaline environment. Apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})(\text{F})$) formation takes place in these circumstances, through direct precipitation or co-precipitation with CaCO_3 , or else via adsorption onto CaCO_3 particles. When anaerobic conditions prevail in sediments, an automatic decrease of pH in the interstitial water takes place through CO_2 generation. This decrease can bring about the dissolution of apatite (Serrano *et al.* 2003; Golterman 2004).

The mineralisation of organic substances allows for the direct release of phosphorus into the water column and can also affect release indirectly. Organic matter is a donor of electrons and its mineralisation causes a decrease in both redox potential and pH. The results are the dissolution of redox-sensitive phosphorus compounds such as those associated with Fe or Mn, as well as the dissolution of apatite, this being sensitive to a decrease in pH (Gonsiorczyk *et al.* 1998; Serrano *et al.* 2003; Golterman 2004).

The most available form of phosphorus in the bottom sediments is considered (Pacini and Gächter 1999; Kaiserli *et al.* 2002) to be that loosely adsorbed onto the surface of sediment particles (e.g. as the $\text{NH}_4\text{Cl-P}$ fractions separated by the methods of Psenner, as well as Hietjes and Lijklema).

The phosphorus occurring in compounds with iron is also very mobile, while biological availability is much lower where phosphorus is present in compounds with aluminium, or else in organic matter. The remaining phosphorus occurs in compounds with calcium and in other practically insoluble compounds of a mineral and organic character. The contribution of these forms of phosphorus in the exchange processes between sediment and water is considered negligible (Ting and Apan 1996; Rydin and Welch 1998; Kentzer 2001).

In turn, the release of the phosphorus present in bottom sediments is capable of determining a body of water's trophic state, as well as the time delay with reconstructing the ecosystem.

The aim of this study was to describe how the distribution of phosphorus was related to the presence of selected components in the bottom sediments of the Upper San cascade of dam reservoirs.

MATERIALS AND METHODS

Location of sampling sites

The Solina Reservoir is Poland's most voluminous and deepest body of water behind a dam. Together with the Myczkowce Reservoir it forms a cascade (Fig. 1) that serves the complex of Hydroelectric Power Stations of Solina–Myczkowce S.A.

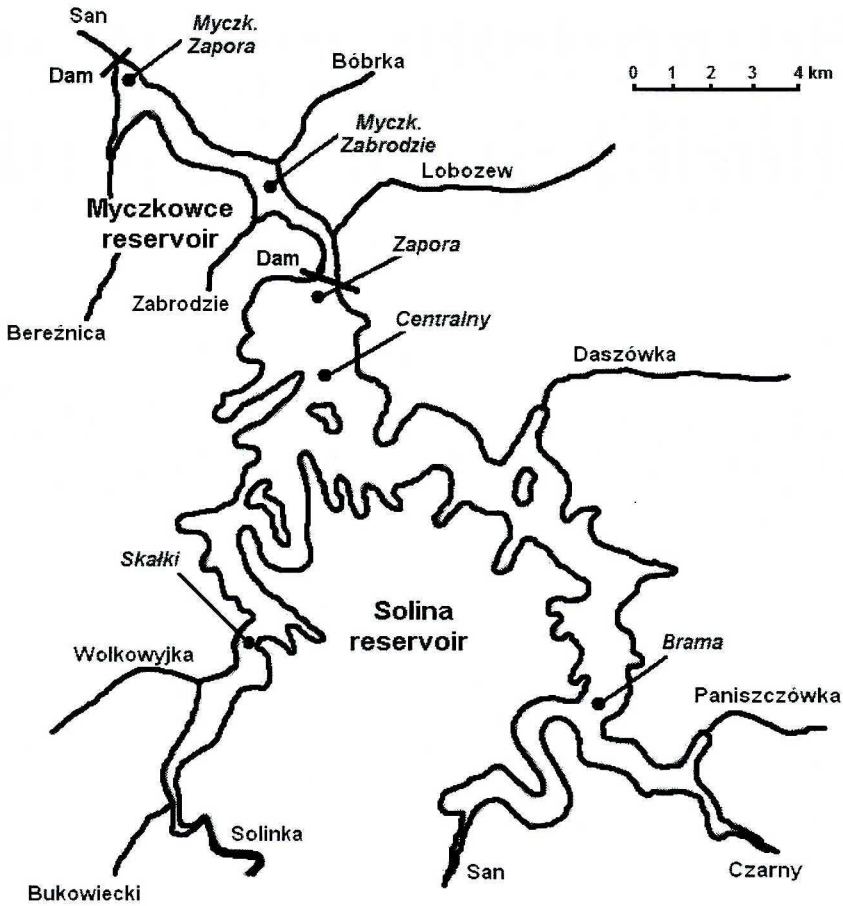


Fig. 1. Sampling locations at the Solina and Myczkowce Reservoirs.

The stilling basin for the top-pumping performance of this power station has been located in Myczkowce. 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 River San (of which 90% are derived from the hypolimnion of the Solina Reservoir) form the main tributary feeding the Myczkowce Reservoir (Płuzański *et al.* 1990).

Table 1. Morphometric parameters of the cascade of the Solina-Myczkowce Reservoirs.

Parameter	Solina reservoir	Myczkowce reservoir
Area [ha]	2200	200
Maximal volume [M 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

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 15m respectively), as well as at two stations in the Myczkowce Reservoir, i.e. 5. Myczkowce-Zapora and 6. Myczkowce-Zabrodzie (approx. depths 11 and 3m respectively).

Sample collection, preparation and analysis

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 (Tomaszek 1988). 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. Prior to analyses, sediments were re-dried for 2h at a temperature not exceeding 60°C, to ensure organic compounds with phosphorus were retained. The harmonized SMT protocol was applied in analysing the fractionation of phosphorus in the sediments (Ruban *et al.* 1999; Ruban *et al.* 2001; Pardo *et al.* 2004). The fractions obtained were 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 0.2g aliquot of the dried sediment was extracted by shaking (16h) with 20 ml of 1 mol dm⁻³ NaOH, the supernatant solution being separated after centrifugation (as extract I), and the residue being re-extracted with 20 ml of 1 mol dm⁻³ HCl (16h). AP was determined in extract II. 4 ml of 3.5 mol dm⁻³ HCl was then added to a sample containing 10 ml of extract I (with 1 mol dm⁻³ NaOH), and left for 16h to precipitate organic matter. NAIP was determined in the supernatant solution. IP was determined in the supernatant solution obtained after repeated extraction through shaking of a 0.2g aliquot of the dried sediment with 20 ml of 1 mol dm⁻³ HCl (16h). The residue after extraction was placed in a porcelain crucible and calcinated for 3h at 450°C. The residue was then re-extracted by shaking (16h) with 20 ml of 1 mol dm⁻³ HCl. After centrifugation, OP was determined in the extract. 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. Analysis of other parameters 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 (aluminum) and DIN 38406E2 (manganese). An Aquamate spectrophotometer (Thermo Spectronic, United Kingdom) was used for colorimetric determinations. Determinations were carried out in triplicate with each sample; the final result was taken to be the average of results differing by not more than 5% of the lowest result. The organic matter (OM) content in bottom sediments was determined by dry sediment calcinations at 550°C.

RESULTS AND DISCUSSION

The substantial thickness of bottom sediments ensures their capacity to accumulate considerable resources of various elements (Kajak 1998). Through the whole period of investigation at individual stations, the average content of total phosphorus was slightly higher in sediments collected from the deeper parts of the Solina Reservoir than from the shallower parts (Table 2).

Table 2. Average contents of analysed components in bottom sediments of the Solina and Myczkowce Reservoirs (average \pm S.D.).

Station	P _{tot} [mgP g ⁻¹ of d.w.]	Al [mg g ⁻¹ of d.w.]	Fe [mg g ⁻¹ of d.w.]	Mn [mg g ⁻¹ of d.w.]	Ca [mg g ⁻¹ of d.w.]	OM [%]
Centralny (n=16)	0.91 ± 0.05	40.5 ± 4.5	44.6 ± 5.7	2.82 ± 1.07	7.67 ± 1.48	8.86 ± 0.63
Zapora (n=15)	0.93 ± 0.05	39.9 ± 3.8	45.6 ± 2.1	3.05 ± 0.79	5.56 ± 1.62	8.48 ± 0.94
Brama (n=16)	0.86 ± 0.05	38.9 ± 5.0	43.3 ± 2.7	2.10 ± 0.47	11.96 ± 3.28	8.81 ± 0.56
Skalki (n=16)	0.69 ± 0.02	35.8 ± 2.6	39.8 ± 2.5	1.66 ± 0.34	14.25 ± 3.43	8.19 ± 0.52
Average (n=63)	0.85 ± 0.11	38.8 ± 4.4	43.3 ± 4.1	2.40 ± 0.90	9.93 ± 4.29	8.59 ± 0.72
Myczk-Zapora (n=16)	0.87 ± 0.08	34.2 ± 4.1	35.9 ± 2.9	1.37 ± 0.32	12.90 ± 6.16	11.52 ± 2.51
Myczk-Zabrodzie (n=15)	0.75 ± 0.04	29.7 ± 3.6	30.0 ± 3.5	1.35 ± 0.31	20.81 ± 7.47	9.74 ± 1.95
Average (n=31)	0.81 ± 0.09	32.0 ± 4.4	33.0 ± 4.4	1.36 ± 0.31	16.73 ± 7.82	10.66 ± 2.40

A similar tendency was observed for the iron and aluminium contents, while the opposite situation applied to calcium content. The same was true for the Myczkowce Reservoir. It appears from this that iron and aluminum contents can influence the retention of phosphorus in the sediments of both reservoirs significantly. The higher phosphorus content in the sediments collected from deeper parts may reflect increased sedimentation in the reservoir's central part, in connection with a reduced flow of water (lake area) (Wiśniewski 1995).

The content of manganese in the bottom sediments of the Solina Reservoir is also clearly depth-dependent (being lower in the shallows and higher in the deep parts). Such differentiation was not noted in the Myczkowce Reservoir, which is, however, characterized by a higher average content of organic matter and calcium, and a lower one for iron, aluminium and manganese. The contents of phosphorus in the sediments of the two reservoirs are comparable (Table 2). The high content of iron, aluminium and manganese in the sediments of the Solina Reservoir (and of iron and aluminium in the Myczkowce Reservoir) seems to be characteristic for the Solina-Myczkowce cascade. Nevertheless, the NAIP (non-apatite inorganic phosphorus) fraction accounts for the smallest share of total phosphorus in the bottom sediments of both reservoirs (Table 3).

Table 3. Average contents of NAIP, AP, OP, IP fractions in total phosphorus (P_{tot}) in bottom sediments of the Solina and Myczkowce Reservoirs (average \pm S.D.).

Station	NAIP [%]	AP [%]	OP [%]	IP [%]
Centralny	26.0	35.2	35.2	61.7
(n=16)	± 3.0	± 5.3	± 3.6	± 3.5
Zapora	28.3	34.2	34.8	63.0
(n=15)	± 3.1	± 5.5	± 3.0	± 4.0
Brama	22.9	39.7	34.0	62.7
(n=16)	± 2.4	± 3.8	± 1.9	± 3.1
Skalki	18.3	44.5	31.7	63.5
(n=16)	± 3.2	± 3.1	± 2.5	± 2.4
Average	23.8	38.5	33.9	62.7
(n=63)	± 4.7	± 6.0	± 3.1	± 3.3
Myczk-Zapora	29.6	34.0	33.1	64.0
(n=16)	± 3.3	± 2.4	± 2.5	± 2.9
Myczk-	24.3	40.2	32.3	65.1
Zabrodzie (n=15)	± 2.6	± 3.5	± 2.5	± 1.6
Average	27.1	37.0	32.7	64.5
(n=31)	± 4.0	± 4.3	± 2.5	± 2.4

The NAIP fraction showed similar tendencies to those found for the contents of phosphorus and iron, making a greater contribution to total phosphorus at greater depths of sediment collection in both reservoirs. More intensive mineralisation of organic matter in reservoir deeps not only results in a release of phosphorus from organic compounds (the OP fraction), but also gives rise to local deficiencies of oxygen just beneath the surface of sediments, as well a decline in redox potential resulting in the decomposition of Fe-P and Mn-P compounds (the NAIP fraction) (Watts 2000). The resuspension of the bottom sediments may be responsible for the lower content of the NAIP fraction, as well as for total phosphorus in the shallower parts of the reservoir. In spite of the relatively low contents of calcium in sediments, the AP fraction (apatite) makes the greatest contribution to total phosphorus in the shallower parts of the Solina Reservoir and in the Myczkowce Reservoir, as well as only a slightly more limited contribution (after the AP fraction) where the deeper parts of the Solina Reservoir are concerned. A higher average content for the AP fraction was found at the stations in the shallower parts, and a lower one where water was deeper (Table III.). The excretion of organic acids and CO_2 by bacteria as they decompose organic matter combines with the concurrent decrease in the pH of interstitial water to affect the solubility of pH-sensitive Ca-P fractions - like those associated with $CaCO_3$ and apatite (Goedkoop and Pettersson 2000). The percentage of total P in the sediments of the two reservoirs accounted for by IP (inorganic phosphorus) is approximately twice as great as that in the case of the OP (organic phosphorus) fraction. This probably reflects the low content of organic matter and relatively high contents of iron, aluminium and manganese in the examined bottom sediments (the content of iron is four times as high than the average content in the bottom sediments of reservoirs in Poland (Wiechula 2004).

A significant positive correlation between total phosphorus and levels of aluminium was found for the sediments from all the Solina stations (Fig. 2).

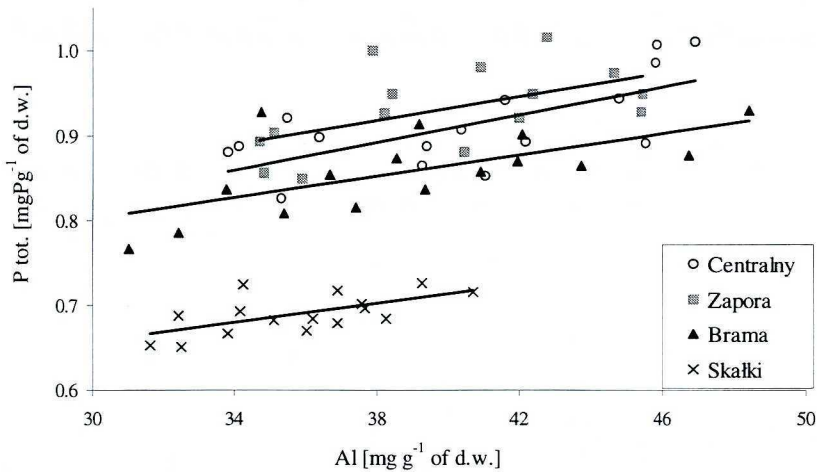


Fig. 2. Relationships between total phosphorus (P_{tot}) [mgP g^{-1} of d.w.] and aluminium [mg g^{-1} of d.w.] in bottom sediments at the Centralny ($r=0.68$, $n=16$, $p<0.01$), Zapora ($r=0.54$, $n=15$, $p<0.05$), Brama ($r=0.64$, $n=16$, $p<0.01$) and Skalki ($r=0.62$, $n=16$, $p<0.05$) sampling stations.

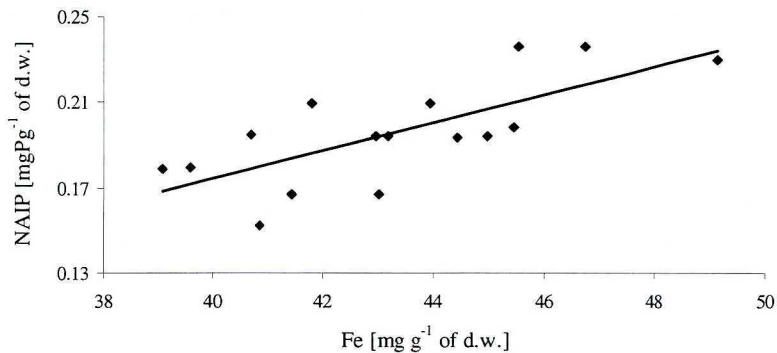


Fig. 3. Relationship between NAIP [mgP g^{-1} of d.w.] and iron [mg g^{-1} of d.w.] in bottom sediments at the Brama ($r=0.72$, $n=16$, $p<0.01$) sampling station.

A positive correlation between aluminium and the IP fraction was also found at the Solina Reservoir's Zapora and Brama stations ($r=0.52$, $p<0.05$; $r=0.68$, $p<0.01$ respectively). This confirms that aluminium can have a very significant influence on the retention of phosphorus in the Solina Reservoir where sediments form permanent compounds with this element. The amount of total phosphorus is also found to increase linearly with iron content at the Brama and Myczkowce-Zabrodzie stations ($r=0.68$, $p<0.01$; $r=0.64$, $p<0.01$ respectively). A similar correlation was found for iron versus the NAIP fraction at the Brama station (Fig. 3), and between iron and the IP fraction at the Myczkowce-Zabrodzie station ($r=0.66$, $p<0.01$).

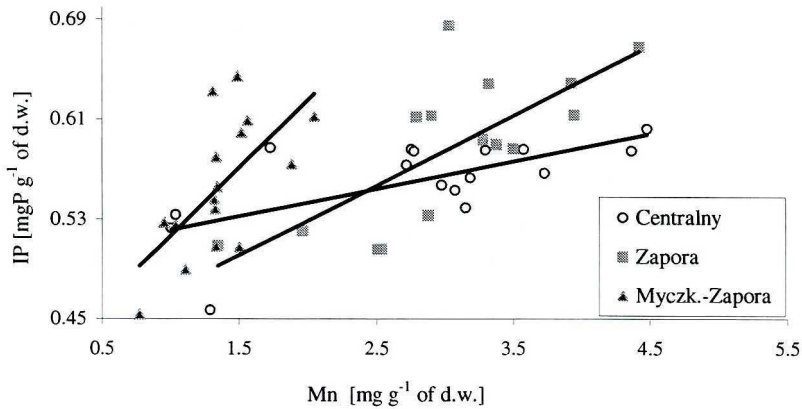


Fig. 4. Relationships between IP [mgP g^{-1} of d.w.] and manganese [mg g^{-1} of d.w.] in bottom sediments at the Centralny ($r=0.66$, $n=16$, $p<0.01$), Zapora ($r=0.74$, $n=15$, $p<0.01$) and Myczkowce-Zapora ($r=0.64$, $n=16$, $p<0.01$) sampling stations.

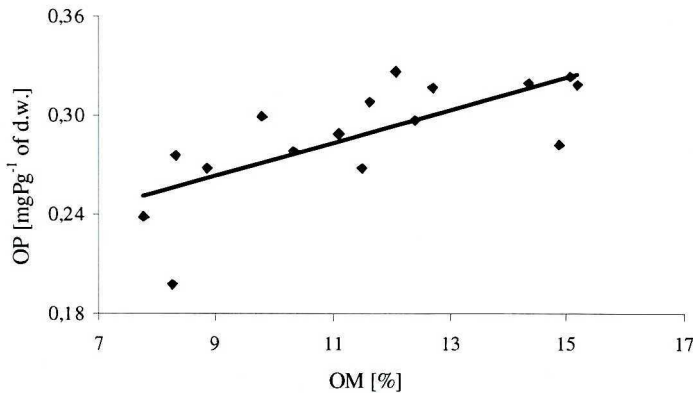


Fig. 5. Relationship between OP [mgPg^{-1} of d.w.] and organic matter (OM) [%] in bottom sediments at the Myczkowce - Zapora ($r=0.72$, $n=16$, $p<0.01$) sampling station

There was a significant positive correlation between total phosphorus and manganese in the sediments collected at the Zapora and Myczkowce-Zapora stations ($r=0.79$, $p<0.001$; $r=0.68$, $p<0.01$ respectively), as well as between the IP fraction and manganese in the sediments at the Centralny, Zapora and Myczkowce-Zapora stations (Fig. 4). The correlation with iron and manganese in the sediments at only some of the stations shows how different the contributions to total content of phosphorus in bottom sediments made by Fe-P and Mn-P compounds can be, in various parts of reservoirs. Iron seems to have greater influence on phosphorus distribution where the shallower parts of the two reservoirs are concerned, manganese in the case of the deeper parts.

Results from the Solina Reservoir revealed a positive correlation between total phosphorus and organic matter in the sediments from the stations Centralny ($r=0.52$, $p<0.05$), Zapora ($r=0.65$, $p<0.01$) and Brama ($r=0.51$, $p<0.05$).

In the Myczkowce Reservoir, such a correlation arose only for the sediments at the Zapora station ($r=0.71$, $p<0.01$), additional confirmation was provided by a positive correlation between the OP fraction and organic matter (Fig. 5). The occurrence of the correlation with organic matter shows the rather significant influence this has on the deposition and release of phosphorus from bottom sediments at these stations (especially in the deeper parts of reservoirs).

A positive dependence of total phosphorus upon calcium in sediments was only found for the Zapora station (Fig. 6), at which there was also a positive dependence of AP and IP fractions upon calcium ($r=0.58$, $p<0.05$; $r=0.69$, $p<0.01$ respectively). The low content of calcium in sediments probably limits formation of the apatite fraction in this part of the Reservoir.

Depth changes along the longitudinal axes of the reservoirs are reflected in bottom sediments of varying character. The varieties of chemical compounds in which phosphorus occurs in sediments can differ slightly in dam reservoirs of different depths, or in the same reservoir in relation to depth. The release of phosphorus can therefore take place via various mechanisms, often with no influence of the resuspension of sediment particles (Bartoszek 2007). The high content of aluminium in the sediments of reservoirs can have a very significant influence on the retention of phosphorus. Were there to be any increase of the trophic status of the reservoirs due to excessive loading with pollutants (especially organic), the Ca-P compounds would seem to offer better protection against internal feeding than would compounds comprising manganese and iron (NAIP), which are not resistant to oxidation-reduction conditions in the above-bottom zone.

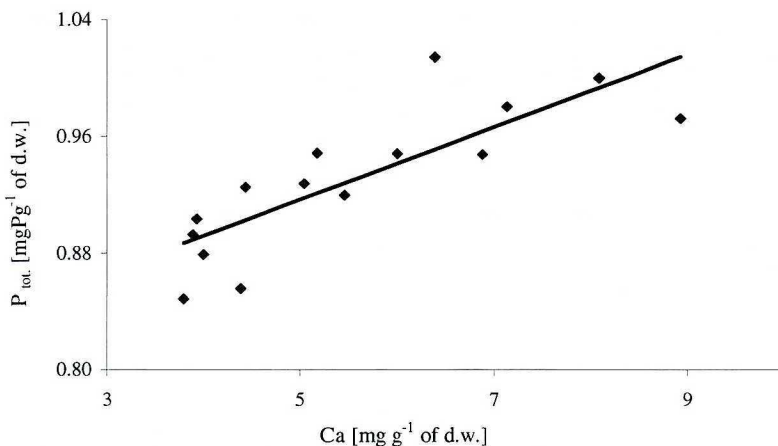


Fig. 6. Relationship between total phosphorus (P_{tot}) [mgP g^{-1} of d.w.] and calcium [mg g^{-1} of d.w.] in bottom sediments at the Zapora ($r=0.81$, $n=15$, $p<0.001$) sampling station.

CONCLUSIONS

1. In the shallower parts of both reservoirs, iron seems to have the major influence on phosphorus distribution in sediments. The same is true of manganese in the deeper parts. Aluminium exerts a very strong influence on phosphorus retention in the sediments throughout the Solina Reservoir, forming permanent compounds with this element.

2. The considerable contribution of the apatite fraction to total phosphorus in the bottom sediments suggests that calcium may have a significant influence on phosphorus retention in the sediments of both reservoirs.
3. The seemingly greater resistance to degradation processes displayed by the Solina Reservoir reflects both advantageous morphometric parameters and higher contents of iron, aluminium and manganese in bottom sediments – as compared with the Myczkowie Reservoir.
4. In the case of possible trophy increase of both reservoirs due to receiving appreciable loads of pollutants, especially organic ones, less soluble Ca-P compounds seem to be better protection of the reservoirs against internal feeding than compounds with manganese and iron (NAIP) which are not resistant to oxidation – reduction conditions in the above - bottom zone.

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