J. Elementol. 2010, 15(1): 161–170

SPECIATION ANALYSIS OF PHOSPHORUS IN BOTTOM SEDIMENTS – COMPARISON OF TWO METHODS

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Abstract

The purpose of this paper was to compare two methods of fractionation of reactive phosphorus forms (RP) in bottom sediments of polymictic water reservoirs located in rural areas. As a criterion for estimation, quantities RP extracted in analyzed fractions versus the general content of Al, Fe and Ca were used. The sediments were collected in springtime, from rural areas with different land use in the drainage basin (arable fields, uncultivated land, farmyards). The sediments were collected with a KC-Denmark core sampler for bottom sediments, which makes it possible to collect samples leaving the upper structure of 6 cm in thickness intact. After mineralization, each sample was analyzed for the general phosphorus content and a speciation analysis was performed by two methods. With the first method (M1), the RP bonded to Al (Al_RP), Fe (Fe_RP) and Ca (Ca_RP) was determined. The second method (M2) was applied to determine fractions of reactive phosphorus released from the sediments under reduced conditions, mainly from bonds with iron and manganese (BD_RP), adsorbed on aluminium oxides mainly Al_2O_3 and other surfaces (NaOH_RP) and apatite phosphorus and bonds with carbonates.

In almost all the sediments, most RP was determined in the phosphorus fractions with Ca extracted with acid solution. For the fractions obtained via the M1 method, more of the general RP, as well as phosphorus bonded to calcium and iron was found than for fractions obtained with the M2 method, and the differences might be attributed to translocation of phosphorus from organic to inorganic compounds during fractioning. The fraction of reactive phosphorus determined with the M1 method is correlated more strongly with the general content of the metal in the sediments than reactive phosphorus fractions determined with the M2 method. The strong correlation between the content of iron and the fraction of BD_RP in mineral sediments shows that it can be an indicator of the sensitivity of sediment to changes in the redox potential.

Key words: bottom sediments, kettle holes, phosphorus, fractionation, multivalent metals.

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ANALIZA SPECJACYJNA FOSFORU W OSADACH DENNYCH – PORÓWNANIE DWÓCH METOD

Abstrakt

Celem pracy by³o porównanie dwóch metod frakcjonowania reaktywnych form fosforu (RP) w osadach dennych polimiktycznych zbiorników wodnych zlokalizowanych na terenach wiejskich. Jako kryterium oceny przyjêto iloœæ RP wyekstrahowanego w badanych frakcjach w odniesieniu do zawartoœci ogólnej Al, Fe i Ca. Osady do badañ pobrano w sezonie wiosennym, z szeœciu oczek wodnych zlokalizowanych na terenach wiejskich o ró¿nym sposobie zagospodarowania zlewni (pola uprawne, od³óg, gospodarstwa rolne). Osady pobierano próbnikiem rdzeniowym osadu dennego KC-Denmark, który umo¿liwia pobór prób z nienaruszon¹ struktur¹ wierzchni¹ warstwy osadów o gruboœci 6 cm. W ka¿dym osadzie oznaczono, po mineralizacji, ogóln¹ zawartoœæ fosforu (TP), Fe, Ca, Al oraz przeprowadzono analizê specjacyjn¹ fosforu dwoma metodami. Metod¹ 1 (M1) oznaczono reaktywny fosfor (RP) zwi¹zany z: Al (Al_RP), Fe (Fe_RP) i Ca (Ca_RP). Metod¹ 2 (M2) oznaczono frakcje reaktywnego fosforu uwalnianego z osadów w warunkach zredukowanych g³ównie z po³¹czeñ z tlenkami ¿elaza i manganu (BD_RP), zaadsorbowanego na tlenkach metali g³ównie na Al_2O_3 i innych powierzchniach (NaOH_RP), fosfor apatytowy i zwi¹zany z wêglanami (HCl_RP). Prawie we wszystkich osadach najwiêcej RP oznaczono we frakcjach fosforu zwi¹zanego z Ca ekstrahowanego roztworem kwasu. We frakcjach otrzymanych metod¹ M1 oznaczono wiêksze iloœci ogólnego RP oraz fosforu zwi¹zanego z wapniem i z ¿elazem ni¿ w metodzie M2, a powsta³e ró¿nice mog¹ wynikaæ z przemieszczania siê fosforu ze zwi¹zków organicznych do nieorganicznych w trakcie frakcjonowania. Frakcje fosforu reaktywnego oznaczonego metod¹ M1 s¹ silniej skorelowane z ogóln¹ zawartoœci¹ tych metali w osadzie ni¿ frakcje fosforu reaktywnego oznaczonego metod¹ M2. Silna korelacja miêdzy zawartoœci¹ ¿elaza i frakcji BD_RP w osadach mineralnych wskazuje, ¿e mo¿e ona byæ wskaŸnikiem wra¿liwoœci osadu na zmianê potencja³u redoks.

S³owa kluczowe: osady denne, oczka wodne, fosfor, frakcjonowanie, metale wielowartoœciowe.

INTRODUCTION

The influence of phosphorus on the trophic state of water depends not only on its concentration but also on the cycling of phosphorus compounds in an entire aquatic ecosystem. In the processes of transformation and accumulation of phosphorus in aquatic environments, bottom sediments play the main and unquestionable role, and depending on the physical and chemical conditions in a reservoir, they may either be a trap for phosphorus or a source of autochthonous phosphorus (Psenner et al. 1988, Kentzer 2001). As a result of sedimentation of organisms, absorption of insoluble phosphates on silty materials and precipitation of insoluble complexes, phosphorus translocates from oxygenated surface waters to bottom sediments. In the topmost bottom sediments, phosphorus occurs in its organic form and is chemically bonded to multivalent ions of metals, including Al, Fe and Ca, together forming hardly soluble salts and complex compounds. The basic processes which control translocation of phosphorus between water and sediments include sorption, desorption, dissolution and precipitation, which highly depend on physical and chemical qualities of the bottom water layer and sediments, e.g. oxygen conditions, redox potential, forms of phosphorus in both phases and the structure and hydration of sediments.

The quantitative and qualitative description of how phosphorus is incorporated in the bottom sediments is an important indicator which helps to predict and limit eutrophication. Therefore, many methods have been developed for speciation analysis of this element. Generally, all analyses are modifications of the methods used for fractioning and determination of phosphorus in soil and in biologic materials. The methods help to determine the total content of mineral and organic phosphorus (Go£achowska 1977), organic compounds of phosphorus (Shapiro et al. 1971, Go£achowska 1978, Golterman et al. 1998) and its mineral forms (Go£achowska 1978, Hietltjes, Lijklema 1980, Pssener et al. 1985). The latest methods for speciation analysis of phosphorus involve specific chelating agents – NTA lub EDTA (Golterman, Booman 1988, Ruttenberg 1992, Golterman 1996). The basic objective of speciation analysis of phosphorus in sediments is to characterize the sediment as a potential internal source of this element in an aquatic ecosystem. Therefore, the methods for fractioning of inorganic compounds of phosphorus, which are bio-assimilable and dissolve in water better than its organic compounds, play a more important role. This conclusion finds support in limnology, where inorganic phosphorus is defined as reactive and organic phosphorus as non-reactive (Psenner1988). Because the specificity of applied extractants, compared to the defined connections of phosphorus, depends on the type of sediments (e.g. content of organic matter and limestone), selection of an appropriate method requires their earlier comparison (Psenner1988). The purpose of this paper was to compare two methods for fractionation of reactive phosphorus forms (RP) in bottom sediments of polymictic water reservoirs located in rural areas. As a criterion for estimation, quantities of RP extracted in analyzed fractions versus the total content of chosen metals were used.

MATERIAL AND METHODS

Sediments for the research were sampled in springtime from water ponds near the golf course in Binowo (O1, O2), from kettle holes in Ko³owo (O3 – located near some farms and O4 – in the middle of a field), from Lake Rusa³ka, a barrier lake in Kasprowicza Park in Szczecin (O5), and from a field kettle hole near Stobno (O6). The samples were collected from bottom sediments with a KC-Denmark core sampler, which enables collection of samples from the topmost layer. Thus, the upper layer of sediments, 6 cm thick, was examined. Each sample underwent speciation analysis of phosphorus with two methods: one suggested by GOŁACHOWSKA (M1) (1977) and the other one elaborated by PSENNER et al. (M2) (1984). With the first method, the following fractions of reactive phosphorus were determined: loosely bonded or absorbed in sediments – extracted with a 1 M solution of NH_4Cl; bonded to aluminum (Al_RP) – extracted with a 0.5 M solution of NH_4F; bonded to iron (Fe_RP) – extracted with a 0.1 M solution of NaOH and bonded to calcium (Ca_RP) – extracted with a 1 M solution of H_2SO_4. With the other method (M2), the following fractions of reactive phosphorus were determined: loosely bonded or adsorbed in the sediment – extracted with a 1 M solution of NH_4Cl; released from sediments under reduced conditions mainly from bonds with iron and manganese oxides – extracted with a mixture $NaHCO_3$ and $Na_2S_2O_4$ (RP_BD); adsorbed on metal oxides, mainly on Al_2O_3 and other surfaces, interchangeable with OH^- – extracted with a solution of NaOH (NaOH_RP); apatite and bonded to carbonates – extracted with a solution of HCl (HCl_RP). Having completed speciation analysis, in each of the sediment samples, hardly releasable phosphorus (RES_P) was determined so as to account for fractions of phosphorus which are practically insoluble, containing mainly fluorapatite and some forms of organic matter. Such fractions of phosphorus were determined after wet mineralization in a mixture of acids H_2SO_4 i $HClO_4$ (GOŁACHOWSKA 1977). Likewise, the total content of phosphorus in sediments before extraction was determined (TP). The content of phosphorus dissolved in individual extraction solutions was determined by spectrophotometry on a spectrophotometer UV/VIS 8500 (Techcomp). Based on the results, the total content of extracted reactive and non-reactive phosphorus was calculated for each of the methods. For each sediment sample, after mineralization with concentrated nitric acid (V) in a microwave oven, the total concentrations of Fe, Ca and Al were determined using the atomic absorption method (AAS) with a flame spectrophotometer Solaar S (ThermoElemental).

RESULTS AND DISCUSSION

The results of assays of the content of inorganic phosphorus fractions in sediment samples are shown in Table 1. With both the methods, the first fraction of phosphorus, loosely bonded with the sediment, was below the minimum determination limit and thus it was neglected. In each of the fractions tested, most reactive phosphorus (RP) was found in sample O5 with method M1 and in sample O3 with method M2. For method M1, fraction Fe_RP was an exception in that that a higher content of RP was determined in sample O1 than O5 (22.64 and 12.03% RP in the total TP phosphorus content, respectively). For method M2, fraction HCl_RP an exception was, as higher content of RP was found in sediments O2 and O5 than in sediment O3 (18.07, 15.91 and 13.56% RP in TP, respectively). In the ana-

Table 1

The content of phosphorus in tested sediments

Sediment	TP (mg P·g^{-1} d.m.)	Part of RP fraction in the total content of phosphorus (%)					
		method M1			method M2		
		Al_RP	Fe_RP	Ca_RP	BD_RP	NaOH_RP	HCl_RP
O1	1.11	2.52	22.64	9.44	0.91	4.02	3.04
O2	0.62	2.45	11.86	34.51	14.27	7.78	18.07
O3	1.47	3.00	3.73	13.04	23.18	12.48	13.56
O4	0.93	2.27	9.59	18.70	7.77	6.05	9.40
O5	0.95	9.64	12.03	33.65	5.19	10.06	15.91
O6	0.69	5.38	10.58	15.14	7.50	9.76	3.64
Average	0.963	4.21	11.74	20.75	9.80	8.36	10.60

lyzed sediments, most RP was determined with method M1 in a fraction extracted with a solution of acid, which is usually the largest fraction extracted with all methods for speciation analysis of reactive phosphorus (GOŁACHOWSKA 1977, HIELTJAS, LIJKLEMA 1980, GOLTERMAN, BOOMAN 1988). An exception was sediment O1, where most RP was determined with method M1 in fraction Fe_RP (22.64%), and sediment O3, where most RP was determined with method M2 in a fraction of phosphorus released from sediments under reduced conditions BD_RP (23.18%). The differences may have resulted from different content of organic matter in the examined sediments, related to Ca, as most of the tested samples were mineral ones (containing 2-3% of organic matter), expect mineral-humic sediment O3 (containing 3.7% of organic matter) and organic O1 (containing 30.31% of organic matter). The results confirm that the specificity of applied extractants towards the determined bonds of phosphorus depend on the type of sediment (PSENNER et al. 1988).

Figure 1 shows the percentage share of RP, non-reactive (NRP) and general phosphorus in all fractions (FTP), in the total content of phosphorus in the sediment (TP). The percentage of RP fractions determined with method M1 varied within the range of 19.4 to 54.27% and in almost all the cases was higher than determined with method M2, where it fluctuated between 8.0 and 51%. An exception was sediment O3, where this percentage was 19.9% as determined with method M1, and 51% – with method M2. This difference was due to a big quantity of RP extracted under reduced conditions, making up for 23% (Table 1). This sediment was the only one which was sampled from a pond surrounded by farms, which are the main source of pollution. With the two methods being compared, different amounts of general RP and NRP were extracted from individual samples, whereas the amounts of extracted TP were similar (Figure 1). The percentage of NRP

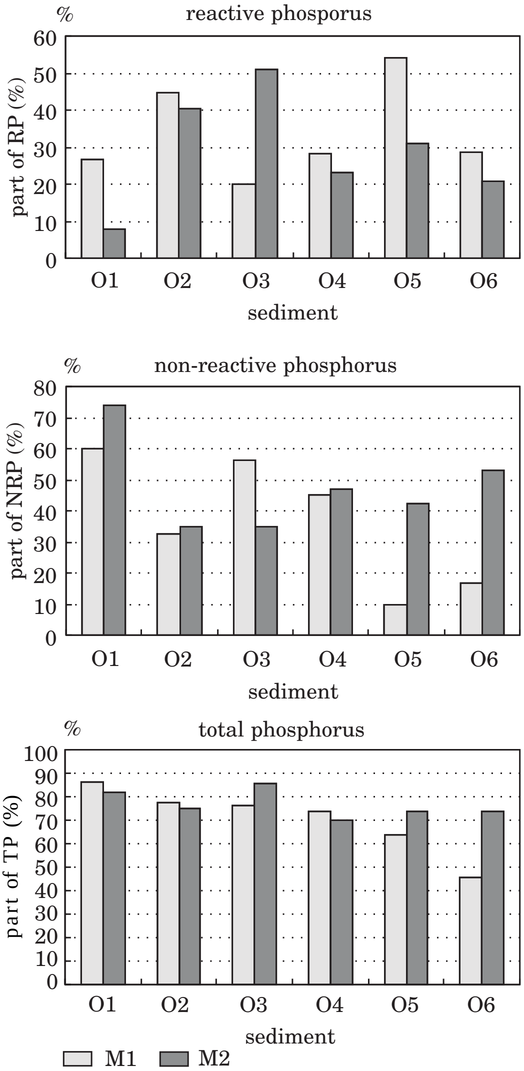

Fig. 1. Total sum of phosphorus in the fractions extracted by methods M1 and M2

fractions marked with method M1 ranged from 9.7 to 70.9%, while determined with method M2 – from 34.8 to 74.0%. According to M1 and M2 methods, the difference between the total extracted FTP varied from 1.0 to 10.0%, reaching as much as 28.0% only for sediment O6. This indicates the changes which may take place during fractionation, which are accompanied by migration of phosphorus between the organic and inorganic fraction of sediment. Because for the fractions obtained with method M1, higher amounts of the general RP and phosphorus bonded to Ca and Fe were determined, the differences might have resulted from translocation of phosphorus from organic to inorganic compounds. An exception was sample O3, where the amount of extracted phosphorus under reduced conditions and with application of NaOH was several-fold higher than in the Fe_RP fraction obtained with method M1. In the same sediment, in fractions extracted with acids, comparable amounts of RP bonded to Ca were determined, reaching 0.192 mg $P \cdot g^{-1}$ d.m. (13.04%) with method M1 and 0.200 mg $P \cdot g^{-1}$ d.m (13.56%) with method M2 Table 1). The process of extraction may cause dramatic changes in the sediment structure, e.g. NaOH may dissolve organic compounds of phosphorus, which cover the sediment particles and form a barrier to the release of inorganic fractions of phosphorus (GUNATILAKA et al. 1988). Extraction with a solution of NH_4F and NaOH may lead to the formation of fluorapatites or hydroxiapatites (GOLTERMAN, BOOMAN 1988), which are extracted in the last fraction. Excessively prolonged extraction in NaOH may increase the amount of phosphorus in fractions of reactive phosphorus by hydrolysis of organic compounds of phosphorus in the sediment, or may reduce the amount of extracted phosphorus by its adsorption to $CaCO_3$ (ROMERO-GONZALEZ et al. 2001).

In order to evaluate the speciation methods used, significance of the correlations between the content of RP determined in fractions and the content of metals in the sediments was examined. Significant correlations between Fe and RP content determined with method M1 in Fe_RP fraction (excluding the fraction extracted from sediment O2) and with method M2 in BD_RP fraction (excluding the fraction from sediment O3) were calculated; the determination coefficient was 0.996 and 0.823, respectively. Linear regression functions which illustrate these relationships are shown in Figure 2. The strong correlation between Fe content and BD_RP fraction in mineral sediments suggests that it can be an indicator of the sediment sensitivity to changes in the redox potential. The content of compounds of phosphorus with iron is regulated mainly by the oxidative-reductive potential. Under oxidized conditions, they tend to form hardly dissolvable but easily sedimenting compounds, and when the redox potential reaches 200-300 mV, they are mostly dissolved and phosphorus may migrate to the solution. Significant positive correlations between the content of Ca in sediments and the content of RP as determined with method M1 in fraction Ca_RP and with method M2 in fraction HCl_RP were calculated. Here, the determination coefficient was 0.865 and 0.464, respectively. Linear regression functions which illustrate these relationships are shown in Figure 2. The strong correlation between the content of Al and the content of RP was calculated for the Fe_RP fraction only, and an exception was sediment O3, where the lowest level of Al was determined. The lack of significant correlations between the content of Al and the Al_RP fraction might be related to the low percentage of this fraction in the general content of TP, which on average was 4.2% (Table 1), and that confirms that, unlike in soils, in bottom sedi-

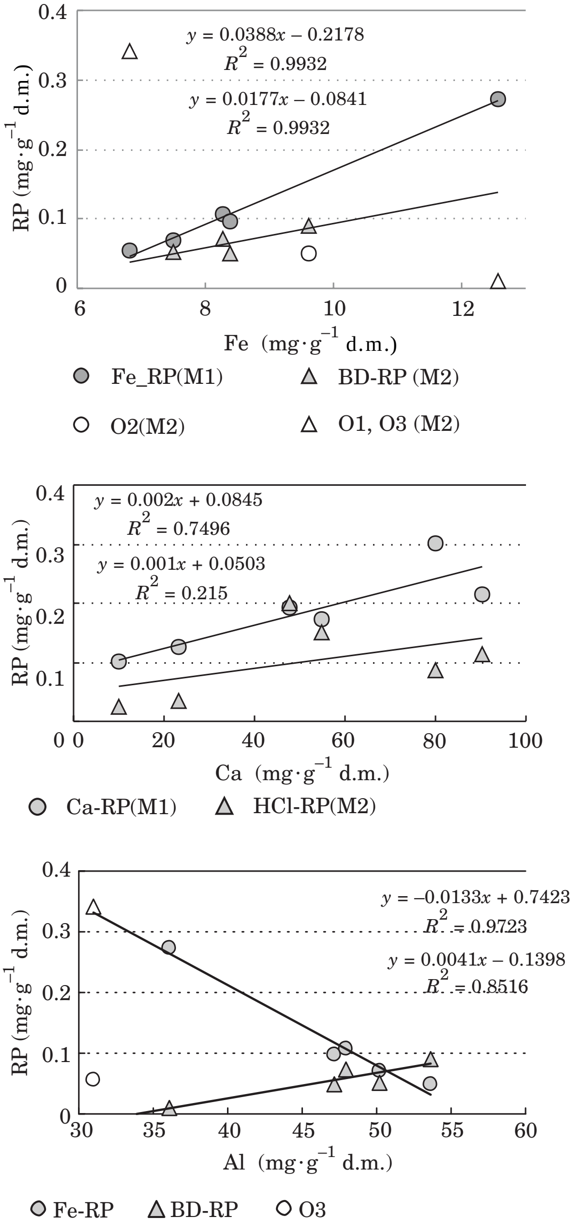

Fig. 2. Relationships between content of the metals and reactive phosphorus in selected fractions

ments aluminum does not play an important role in processes of binding RP and may be important only in extremely acidic waters (ULRICH 1997).

CONCLUSIONS

1. In sediment samples, most reactive phosphorus (RP) was determined in the phosphorus fractions with Ca extracted with acid solution. For the fractions obtained with the M1 method, more of general RP as well as phosphorus bonded to calcium and iron was found than with the M2 method, and the differences might be attributed to translocation of phosphorus from organic to inorganic compounds during fractionation.

2. The fraction of reactive phosphorus determined with the M1 method is correlated with the general content of the metal in the sediments more strongly than the reactive phosphorus fractions determined with the M2 method. The strong correlation between the content of iron and the fraction of BD_RP in mineral sediments shows that it can be an indicator of the sensitivity of sediments to changes in the redox potential

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