MONITORING OF PHOSPHORUS CONTENT IN "WATER-PARTICULATE MATERIALS-BOTTOM SEDIMENTS SYSTEM" FOR RIVER PRUT

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ABSTRACT. – **Monitoring of phosphorus content in "water-particulate materials-bottom sediments system" for river Prut**. Seasonal and spatial dynamics of phosphorus forms in water, particulate materials and bottom sediments of river Prut was elucidated. The scheme for determination of phosphorus forms in water and particulate materials according to World Health Organization classification was evaluated. Additionally, this scheme was tested for estimation of phosphorus content in bottom sediments. The supplemented scheme allows the analysis of the phosphorus forms for the entirely system "water – particulate materials – bottom sediments", extending possibilities for interpretation of phosphorus dynamics in natural waters.

Keywords: phosphorus forms, particulate materials, bottom sediments.

1. INTRODUCTION

Phosphorus is one of key factor responsible for the eutrophication of freshwaters. Its concentration in rivers results from both external inputs and internal loading from the bottom sediments [1]. Phosphorus is introduced into the aquatic environment in a number of different chemical forms, and has been described in general as being in the aqueous phase as a small fraction of the total phosphorus and in the solid phase as a large fraction of the total phosphorus [2]. Each fraction is constituted of a large number of different components, most of which may change between their dissolved or particulate state. Phosphorus in bottom sediments as a result of abiotic and biotic processes is released into its interstitial water, and under certain conditions is mobilized in overlying water horizons [3]. According to World Health Organization (WHO), phosphorus compounds occurred in natural waters are classified into 12 phosphorus forms, by chemical type and by physical state [4]. The objectives of this paper were (i) to evaluate the scheme for determination of phosphorus forms in water and particulate materials according to WHO classification, (ii) to test this scheme for estimation of phosphorus content in bottom sediments, and (iii) to determinate level of quality and trophicity of water from river Prut.

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2. CASE STUDY

Samples of water, particulate materials and bottom sediments were collected during the spring and summer of 2004 and 2009 years along river Prut (sites Costesti, Cobani, Sculeni, Ungheni, Valea Mare, Stoianovca, Cahul, Caslita-Prut, Giurgiulesti, Fig. 1).

Figure 1. ***Geographical map of Republic of Moldova. Sampling sites (Costesti, Cobani, Sculeni, Ungheni, Valea Mare, Stoianovca, Cahul, Caslita-Prut, Giurgiulesti) where water, particulate materials and sediments were collected.***

Contents of phosphorus forms in water and particulate materials were determined using methods according to WHO classification [4]. Thus, it was determinate the total forms of phosphorus forms in filtered and unfiltered samples, e.g. the total content in water (P1, Fig. 2), the total dissolved (P5) and the total in particulate materials (P9). In each category the content of orthophosphates (P6 in filtered water, P10 in particulate materials and P2 in unfiltered water), poly- and pyrophosphates (P7 in filtered water, P11 in particulate materials and P3 in unfiltered water) and organic-phosphorus (P8 in filtered water, P12 in particulate materials and P4 in unfiltered water) were established. Analysis of phosphorus involves 2 steps: (i) digestion or conversion of the phosphorus to dissolved orthophosphate; (ii) colorimetric determination of dissolved orthophosphate [5].

Additionally, the scheme was tested for estimation of phosphorus content in sediments being determined (i) inorganic phosphorus, (ii) organic-phosphorus and (iii) the total amount of phosphorus [6]. In order to determine the total phosphorus in sediments (P13, Fig. 2) fresh (wet) samples were used, subjected to persulfate oxidation. Inorganic phosphorus (P14) was determined by acidic hydrolysis in moderate severely conditions. The amount of organic phosphorus (P15) was obtained by subtracting inorganic phosphorus (P14) from the amount of total phosphorus (P13).

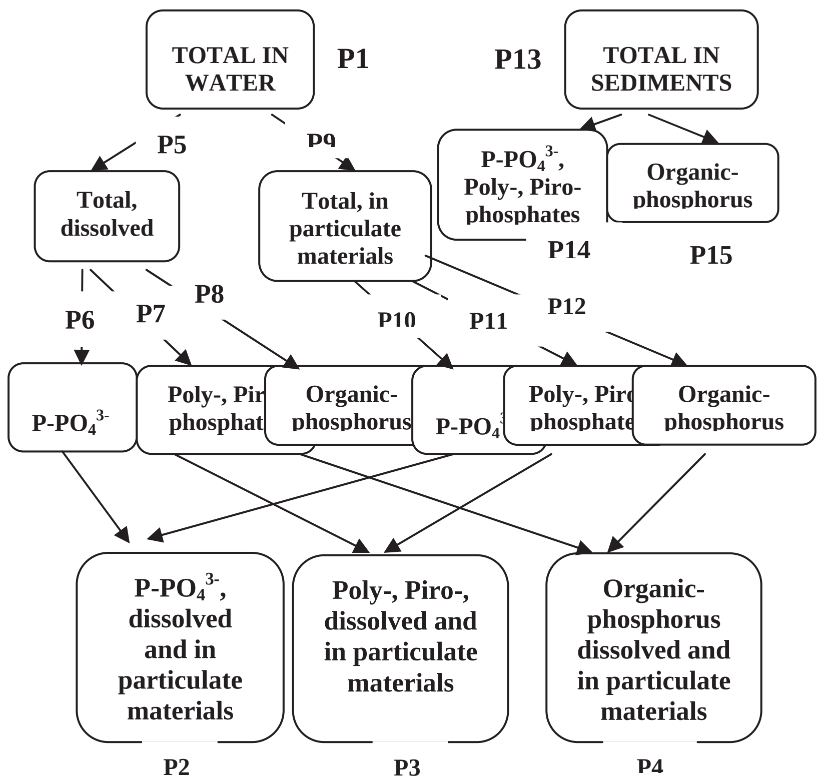

Figure 2. ***Phosphorus forms in natural waters for the entirely system "water-particulate materials-bottom sediments". Supplemented scheme for analysis of the phosphorus forms in water and particulate materials according to World Health Organization classification (forms 1-12) and in sediments (forms 13-15).***

3. RESULTS AND DISCUSSION

The spatial dynamics of researched phosphorus forms during spring of 2009 year recorded a slight decrease for the most forms of phosphorus, namely the total phosphorus in water (P1), the total in filtered water (P5) and total in particulate materials (P9), the organic-phosphorus in water (P8) and in particulate materials (P12), registered the highest values of their content in the middle sector

Prut River (station Sculeni) (Fig. 3). Only for condensed dissolved form of phosphorus (P7) an increase was founded along the river, its content being greater in the lower sector of the river (station Caslita-Prut).

The spatial dynamics established in the summer of 2009, in general, has the same trend, maximal for the content of the total phosphorus in water (P1), of all forms in filtered water (P6, P7, P8, P5), of particulate orthophosphates-phosphorus (P10) and those organic in particulate materials (P12), being recorded in the middle sector (stations Ungheni - Valea Mare). Content of total particulate phosphorus (P9) didn't change along river.

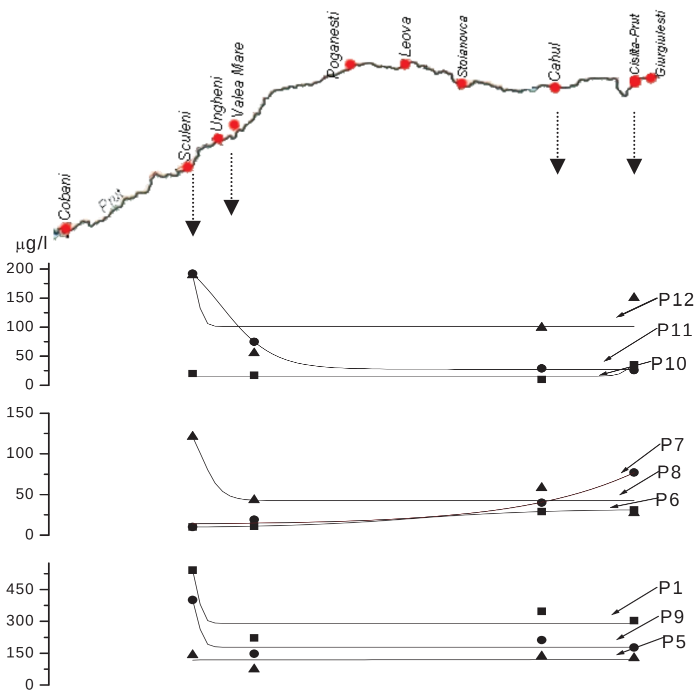

Figure 3. ***Spatial dynamics of phosphorus forms for river Prut during spring of 2009. Dissolved forms P6, P7, P8 –orthophosphate, condensed forms (poly- and pyrophosphates) and organic-phosphorus, respectively. Phosphorus forms in particulate materials P10, P11, P12 -orthophosphates, condensed forms and organic-phosphorus, respectively. Total phosphorus forms P1, P9, and P5 – total phosphorus, total in particulate materials and total dissolved, respectively.***

Dynamics of the content of phosphorus forms is different during the year. Thus, the content of dissolved orthophosphate-phosphorus (P6, Fig. 2) increases from spring to summer (mostly in Valea Mare station). For other stations, the content of this form practically isn't changed during the research period. Content of poly- and pyrophosphates dissolved (P7) increases from spring to summer, while the content of dissolved organic phosphorus decreases during this period (Fig. 3, 4). During the studied period it was established a decrease of phosphorus-orthophosphate content in particulate materials (P10), as well as content of other phosphorus forms in particulate materials (poly- and pyrophosphates (P11) and ones organic (P12). In general, this seasonal dynamics during of 2009 is similar with the dynamics of phosphorus forms established during 2004 [6].

Distribution of phosphorus forms in water was different during 2004 year (Fig. 5). On the spring the content of total phosphorus in particulate materials (P9) was higher. During the summer, however, dissolved phosphorus prevails, varying within limits of 75-80%. The same trend was recorded during of 2009. Thus, during the spring dissolved phosphorus (P5) percentage varied within 25-45%, while during the summer being in the limits of 55-75%.

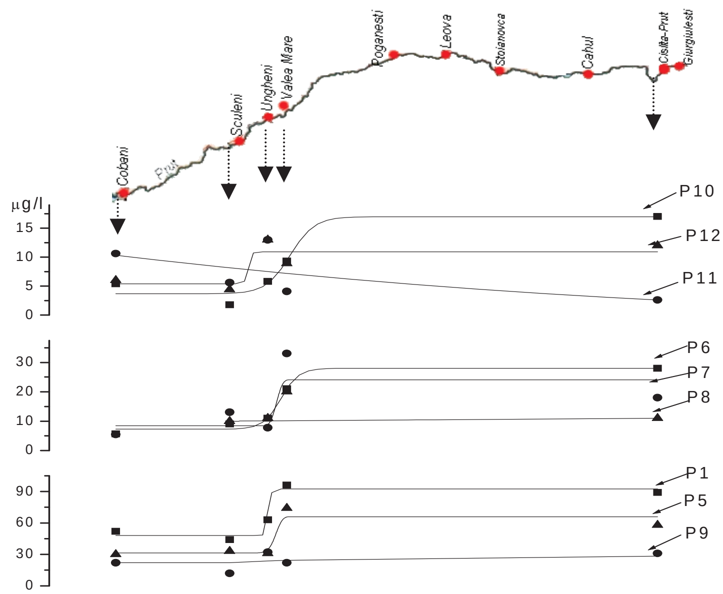

Figure 4. ***Spatial dynamics of phosphorus forms for river Prut during summer of 2009.***

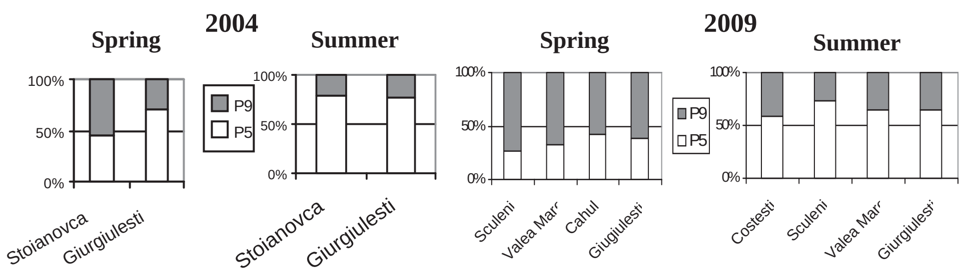

Figure 5. ***Distribution of phosphorus forms in water during 2004 and 2009 years. The total dissolved (P5) phosphorus and total phosphorus in particulate materials (P9).***

Distribution of dissolved organic (P8) and inorganic (P6+P7) phosphorus forms in water (filtered samples) was similar during 2004 and 2009 years (Fig. 6), being registered the tendency of increasing of the percentage of inorganic phosphorus from spring to summer.

Ratio of inorganic: organic phosphorus in particulate materials was not homogeneous along the Prut River during 2004 and 2009 years (Fig. 7), although more frequently the percentage of inorganic phosphorus (P10+P11) prevailed over organic (P12) phosphorus.

The dynamics of phosphorus forms in bottom sediments differs from that reported for the forms in particulate materials. The content of inorganic phosphorus (P14, Fig. 2) in sediments decreased and organic phosphorus (P15) increased from spring to summer during 2009 (Fig. 8). Higher amounts of these forms of phosphorus were recorded on the Valea Mare - Cahul sector. Both during of 2004 and during of 2009, the inorganic phosphorus (P14) prevailed in sediments and constituted 65-95% (Fig. 9).

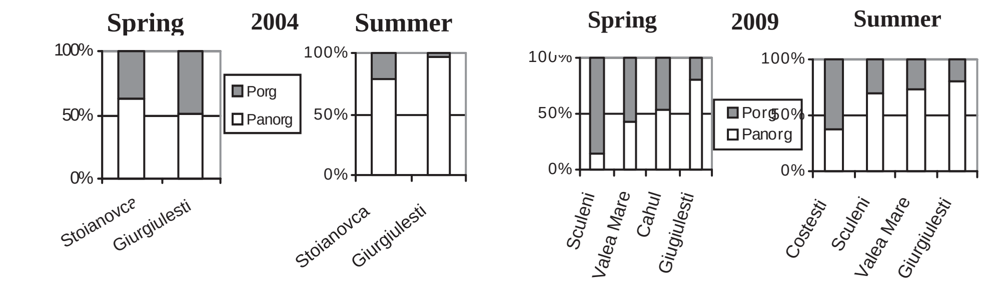

Figure 6. ***Distribution of dissolved (filtered samples) inorganic (P6+P7) and organic (P8) phosphorus in water during 2004 and 2009 years.***

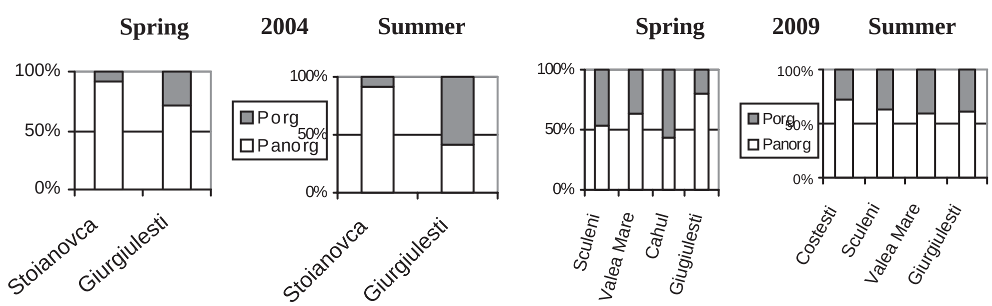

Figure 7. ***Distribution of inorganic (P10+P11) and organic (P12) phosphorus in particulate materials during 2004 and 2009 years.***

Currently, as quality standards, in Republic of Moldova there are applied maximum allowable concentrations of pollutants used since the former Soviet Union period and have not yet been adjusted according to European Union Directives [7]. The quality of surface waters in Romania is regulated by Order 1146/2002 - The Standard for surface water quality classification, which includes five-quality classes [8]. Limit values specified for each class in table correspond to the maximum allowable for respective quality class. On the basis of presented data in this work, water of Prut River should be attributed to the class I of quality according to orthophosphate-phosphorus content (P6), and to classes I-II of quality according to the content of total dissolved phosphorus (P5).

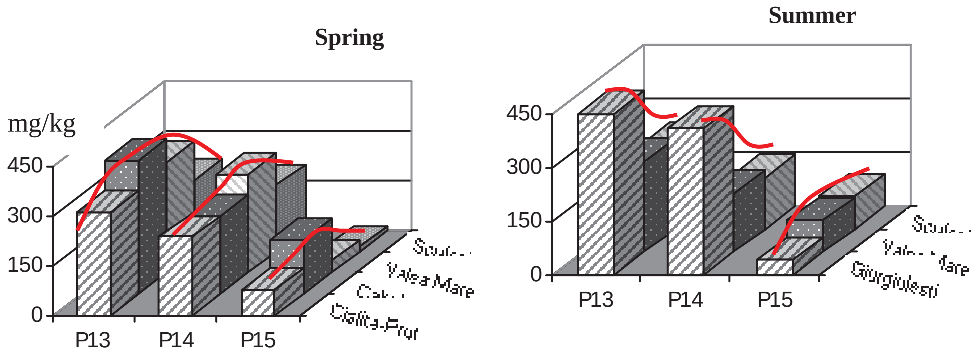

Figure 8. ***Spatial dynamics of phosphorus forms in the bottom sediments along river Prut (2009). P13, P14, P15 –total phosphorus in sediments, inorganic phosphorus in sediments (orthophosphate plus condensed forms) and organic-phosphorus in sediments, respectively.***

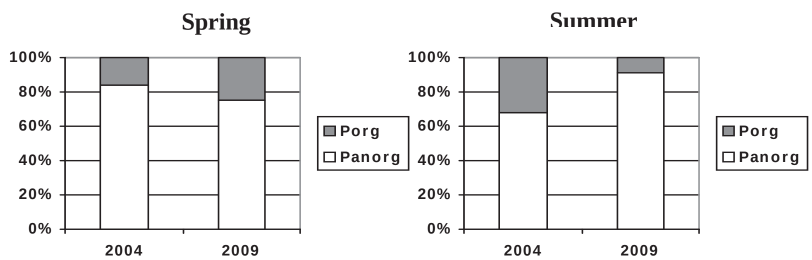

Figure 9. ***Distribution of inorganic (P14) and organic (P15) phosphorus in bottom sediments during 2004 and 2009 years.***

Quality grade of phosphorus forms in bottom sediments there isn't yet established, consequently at present is questionable to discuss its influence onto eutrophication level of water bodies.

Table [8]. ***Quality classification of surface waters by phosphorus content***

Limit value for classes	Class of quality, mgP/l				
	I	II	III	IV	V
Orthophosphates (P6)	0,05	0,1	0,2	0,5	>0,5
Total phosphorus (P5)	0,1	0,2	0,4	1	>1

The large amounts of phosphorus compounds in aquatic ecosystems have the fertilizing effect that affects eutrophication degree. The European Community Directive 91/676/EEC recommends that the level of eutrophication in rivers should be determined on the basis of quality parameters, such as nitrate, phosphorus compounds, chlorophyll, oxygen, etc. In accordance with the recommendations [9] eutrophication level is estimated according to the total phosphorus content (P1), while according to further recommendations [10] the level of eutrophication in rivers is estimated on the basis of soluble reactive phosphorus (P6, Fig. 2).

As whole, according to the classification mentioned in [9] and presented data in this work for total phosphorus content (form P1), the eutrophication level of Prut River should be attributed to class II-III, namely the oligotrophic-mesotrophic level

(P1 0,2 – 0,5 mgP/l). On the basis of the content of soluble reactive phosphorus (P6), the eutrophication level of Prut River should be attributed to oligotrophic-mesotrophic level of eutrophication (0,02 – 0,1 mgP/l).

CONCLUSIONS

The scheme for determination of phosphorus forms in water and particulate materials according to World Health Organization classification was evaluated. Additionally, this scheme was tested for estimation of phosphorus content in bottom sediments. The supplemented scheme allows the analysis of the phosphorus forms for the entirely system "water – particulate materials – bottom sediments", and considerably extends possibilities for interpretation of phosphorus dynamics in natural waters. On the basis of obtained data, water of Prut River should be attributed to classes I-II of quality according to Romanian standards. The eutrophication level of Prut River should be attributed to oligotrophic-mesotrophic level of eutrophication according to UE directives.

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