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CHANGES OF PHOSPHORUS COMPOUNDS CONCENTRATIONS IN WATERS OF LOWLAND CATCHMENTS WITH VARIOUS ANTHROPOPRESSION LEVELS

ZMIANY STĘŻEŃ ZWIĄZKÓW FOSFORU W WODZIE ZLEWNI NIZINNYCH O RÓŻNYM STOPNIU ANTROPOPRESJI

Abstract: Phosphorus compounds concentrations in surface and interstitial water as well as groundwater within river Krzemianka and river Jaroszowka catchments, that are characterized by various anthropopression levels, were analyzed in the study. These phosphorus compounds concentrations varied along with the increase of anthropopression within the catchment. In waters of river Jaroszowka catchment, only 15 % total phosphorus (TP) was made up by soluble reactive phosphorus (SRP), which indicated the supply of organic contaminants to surface water and groundwater in urban areas. Organic phosphorus form prevailed in all types of waters in studied catchments, and its mean concentrations amounted to: 198 μgP/dm^3 in groundwaters, 208 μgP/dm^3 in interstitial waters, and 139 μgP/dm^3 in surface waters. Higher concentrations of studied phosphorus forms were recorded in interstitial waters, which in the case of intensive river drainage, may contribute to considerable eutrophication of flowing waters.

Keywords: lowland river, interstitial water, SRP (soluble reactive phosphorus), total phosphorus

Phosphorous significantly affects the living organisms, because it is essential in physiological processes. In waters, it can originate from organic plant and animal remains decay, dissolving the minerals, remains of fertilizers, as well as industrial and municipal wastewaters pollution. Increasing phosphorus load in water reservoirs is a main cause of eutrophication process [1, 2].

In river water, bottom sediments and hydraulic connection between surface and groundwaters mainly affect the phosphorus compounds content [3, 4]. In rivers that drains groundwaters, biological processes occurring in sediments may have periodic influences on surface waters by considerable decreasing of their quality [5]. It is associated with intensified supply of interstitial waters to surface ones. That phenomenon is present after heavy rainfalls preceded by a drought. Quality of river waters is

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then significantly worsened, which is expressed as decreased oxygen concentration and elevated concentrations of some chemical parameters, mainly biogens [6].

The study aimed at analyzing the phosphorus compounds concentrations in surface, interstitial, and groundwaters within two lowland catchments with various anthropopression levels.

Material and methods

Determinations of phosphorus compounds were conducted in two catchments of Bialystok Height: afforested catchment of river Krzemianka localized within Knyszynska Forest and within urban catchment of river Jaroszowka near the city limits of Bialystok [7, 8]. Analysis of phosphorus compounds in surface waters was made in 5 hydrometric profiles of river Krzemianka (7.2 km of water course – Kopisk village, 6.0 km of water course – Bialystok–Augustow road, 3.0 km of water course – Rybniki village, 2.0 km of water course – below ponds in Rybniki village, 1 km of water course – afforested area) and in 5 profiles of river Jaroszowka (3.5 km of water course – below Raginis Street, 2.8 km of water course – near Skrzatow Street, 2.2 km of water course, 1.8 km of water course – at Saint Wanda track, final fragment of the river below fish ponds). Phosphorus compounds in shallow groundwaters near riverbeds and interstitial waters collected from 10, 30, 50, and 70 m depths of river bottoms, were analyzed in two hydrometric profiles of river Krzemianka (upper fragment – Bialystok–Augustow road and lower section – below ponds in Rybniki village) and single profile of river Jaroszowka (near Skrzatow Street) [6]. Water samples for hydrochemical analyses were collected every two months in 2003–2004. In total, 60 samples of surface water from river Krzemianka, 96 samples of interstitial water, and 24 samples of groundwater from river Krzemianka catchment were collected. Considering the river Jaroszowka, 60 samples of surface, 48 samples of interstitial, and 12 samples of groundwater were collected.

Phosphorus forms were determined by means of spectrophotometry in accordance with ISO norms:

– orthophosphates (SRP) – molybdate method after sample filtration through GF/C filter;

– total phosphorus (TP) – molybdate method after acidification, UV digestion, and pH adjusting against phenolphthalein using diluted NaOH and H_2SO_4 solutions;

– organic phosphorus (OP) was calculated as a difference between TP and SRP.

Statistical processing was made with a help of Statgraphics 5.0 for Windows and Phreeqc Interactive 2.15 software. Statistical difference significance of chemical parameters in various water types was determined applying Duncan's multiple difference test.

Results and discussion

The SRP concentrations in river Krzemianka water amounted from 44 to 110 $\mu gP/dm^3$. The highest values were recorded in the section closing the catchment, where arable lands prevailed in adjacent areas [2]. In the forest part of the catchment, average SRP concentrations reached slightly above 70 μg/dm^3. Mean TP concentrations in river Krzemianka water also oscillated within wide range from 147 to 717 μgP/dm^3 (Fig. 1a).

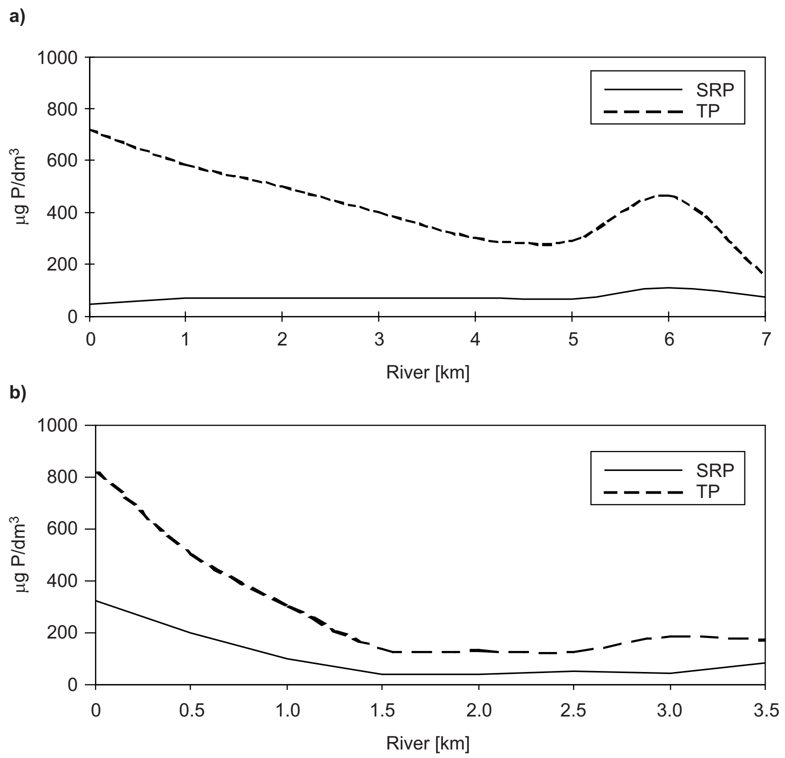

Fig. 1. Changes in concentrations of phosphorus along: a) the Krzemianka river, b) the Jaroszowka river
SRP – soluble reactive phosphorus; TP – total phosphorus

In urban fragment of the river, mean SRP concentrations were much higher than in forest-catchment river (39–325 μgP/dm^3). Particularly high mineral phosphorus concentrations were recorded in the section that drained the urban area. Average TP concentrations along the river Jaroszowka river changes in similar pattern as SRP: they varied from 125 to 819 μgP/dm^3 (Fig. 1b).

Interstitial water from river Krzemianka catchment contained the highest concentrations of SRP, OP, and TP in relation to adjacent aqueous environments (Fig. 2a, b). In afforested part of river Krzemianka catchment, TP and OP concentrations in interstitial water were much higher than in waters adjacent to hyporheic zone. The highest SRP concentration was recorded in catchment of river Jaroszowka, in interstitial water, but differences in particular water types of that phosphorus form were not statistically significant (Fig. 2c). The highest TP and OP concentrations in that section

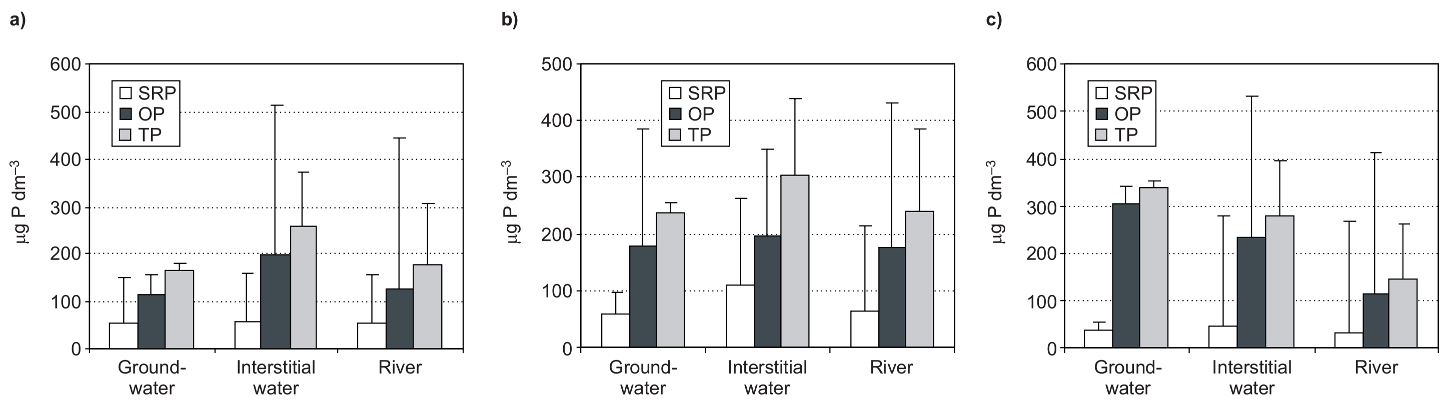

Fig. 2. a) The average (+standard deviation) concentration of phosphorus in groundwaters, interstitial waters and Upper Krzemianka river; b) The average (+standard deviation) concentration of phosphorus in groundwaters, interstitial waters and Lower Krzemianka river; c) The average (+standard deviation) concentration of phosphorus in groundwaters, interstitial waters and Jaroszówka river

SRP – soluble reactive phosphorus; OP – organic phosphorus; TP – total phosphorus were found in groundwater. High SRP concentrations in river Jaroszowka water originated from leaky cesspits or poorly purified wastewaters. Performed study revealed that interstitial or groundwaters could be a source of phosphorus in small rivers. Vallett et al [9] claimed that phosphorus compounds in interstitial waters enrich surface water. Examinations made by Hendricks and White [10] revealed much higher inorganic phosphorus concentration in groundwaters than surface waters in various hydrological seasons.

Surface, interstitial, and groundwaters of studied catchments contained mineral phosphorus in forms of $H_2PO_4^-$ and HPO_4^{-2}, ions, and also $CaHPO_4$ adn $MgHPO_4$ in lower Krzemianka river catchment. The groundwaters of upper Krzemianka and Jaroszowka rivers were characterized by considerable ability to dissolve the hydroxy-apatite (calculated saturation indexes – SI – reached values of –4.13 and –5.57, respectively), which could increase the amounts of mineral phosphorus dissolved in water of the spring fragments of rivers (Fig. 1a, b). In interstitial and surface waters of those profiles, SI indexes in relation to $Ca_5(PO_4)_3OH$ reached values close to 0. In waters of river Krzemianka catchment, SI values in relation to hydroxyapatite were much lower (from –1.66 in groundwaters to –1.06 in surface waters). SI relating to vivianite – $Fe_3(PO_4)_2 \cdot 8H_2O$ – showed similar tendencies in all profiles: its highest values exceeding –5 were recorded in surface waters.

The SRP to TP ratios in different types of waters in river Krzemianka catchment were similar (Table 1). The SRP made up to about 30 % of TP in both sections of that catchment, which proves the neutrality of the Puszcza Knyszynska aqueous environment [1]. In groundwaters of Jaroszowka, SRP to TP ratio was twice as low as in surface ones. The SRP to OP ratio in river Jaroszowka river was also over twice as high as in groundwaters. Interstitial waters of lower Krzemianka river contained SRP to organic phosphorus ratio even up to 0.55, which was the highest among all recorded ones. It indicates considerable mineral phosphorus load delivered to the waters and originating from the surface areas from cultivated fields.

Table 1

The relationship between forms of phosphorus in waters

Type of water	$\frac{SRP}{TP}$			$\frac{SRP}{OP}$		
	Upper K*	Lower K	J	Upper K	Lower K	J
Groundwaters	0.31	0.25	0.10	0.46	0.32	0.12
Interstitial waters	0.22	0.34	0.16	0.29	0.55	0.19
Rivers	0.30	0.27	0.22	0.42	0.36	0.29

* K – Krzemianka river, J – Jaroszowka river.

Besides the influence of a man's activity, the phosphorus concentration changes may result from phosphate ions adsorbed on silt or organic particles. Such situation could be present in spring fragment of river Jaroszowka, where average SRP concentrations exceeded 300 μgP/dm^3. The SRP sorption can occur at high inorganic phosphorus levels, while its low concentrations favor desorption. Under aerobic conditions, dissolved phosphorus can form complexes with metal oxides and hydroxides giving insoluble sediments. High SI indexes relating to $Fe_3(PO_4)_2 \cdot 8H_2O$ and calculated for river water indicate quite great possibility to migrate by mineral phosphorus forms in waters of Bialystok Height rivers.

Conclusions

1. Concentrations of phosphorus forms varied along the river course with the change of anthropopression intensity within the catchment.
2. OP prevailed in all water types within studied catchments, and its mean concentrations amounted to 198 μgP/dm^3 in groundwaters, 208 μgP/dm^3 in interstitial, and 139 μgP/dm^3 in surface waters.
3. SRP made up only 15% of TP in river Jaroszowka catchment, which indicates the supply of organic contaminants to surface and groundwaters in urban areas.
4. Higher phosphorus concentrations were recorded in interstitial rather than surface water, which during the intensive river drainage may contribute to significant eutrophication of flowing waters.

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ZMIANY STĘŻEŃ ZWIĄZKÓW FOSFORU W WODZIE ZLEWNI NIZINNYCH O RÓŻNYM STOPNIU ANTROPOPRESJI

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Abstrakt: W pracy przedstawiono zmiany stężeń związków fosforu w rzekach pierwszego rzędu cechujących się różnym nasileniem antropopresji w zlewni (Krzemianka – zlewnia leśna, Jaroszówka – zlewnia w strefie podmiejskiej). Stężenia związków fosforu zmieniały się wzdłuż biegu rzek wraz ze wzrostem antropopresji w zlewni. W wodzie zlewni Jaroszówka zaledwie 15 % TP stanowił SRP, co wskazuje na dopływ zanieczyszczeń organicznych do wód powierzchniowych i podziemnych na terenie miejskim. We wszystkich typach wody w badanych zlewniach przeważał fosfor organiczny, a jego średnie stężenia wynosiły: 198 μgP/dm^3 w wodach podziemnych, 208 μgP/dm^3 w interstycjalnych i 139 μgP/dm^3 w wodach powierzchniowych. W wodzie interstycjalnej stwierdzono większe stężenia badanych form fosforu, co w przypadku intensywnego drenażu rzecznego może przyczynić do znacznej eutrofizacji wód płynących.

Słowa kluczowe: rzeki nizinne, wody interstycjalne, SRP (rozpuszczalny fosfor reaktywny), fosfor całkowity