Vertical and Horizontal Changeability of Chemical Features of Bottom Sediment in River and Lacustrine Sections in Lake-River System

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Abstract. Bottom sediment is regarded as an important element in water ecosystem, playing the role of a nutrient “trap” but also of the potential and practically inexhaustible source of nutrients. Various transformations of mineral and organic components (diagenesis, dehydration, recrystallization, cementation, chemical reactions) take place in sediment, leading to the migration of nutrients compounds from sediment to water. The bottom sediment is composed of mineral and organic substances removed from the water during the processes of precipitation, sorption and sedimentation. Bottom sediment, that fills river beds, is characterized by a completely different chemical composition comparing to lake sediment. This is caused by the constant flow of water in the river and its good oxygenation. The aim of study was analysis of chemical composition of riverine and lacustrine bottom sediment. Research of bottom sediment was carried in the lake - river system of upper Pasłęka. The upper Pasłęka basin is situated in the north-east of Poland. The river Pasłęka flows into Vistula Lagoon. The total area of the upper Pasłęka River basin is 246.7 km2, while the length of the upper part of the river is 40.5 km (total area of Pasłęka catchment is 2294.5 km2, total length of river is 211 km). The average fall of the upper course of Pasłęka is 1.70 ‰. Pasłęka River in upper course flows through the lakes with different morphometric properties: Pasłęka, Sarąg, Łęguty and Isąg. The surface of lakes ranges from 8.5 to 397.5 ha, and a maximum depth - 5.0 to 54.5 m. The research showed a clear spatial differentiation of the content of silica, organic matter and carbon dioxide in the bottom sediments of particular river and lakes sections. The percentage share of other bottom sediments components i.e. macroelements (Ca, Mg, Fe, Mn) and nutrients (P, N), was also various in river and lake sediment. The dominant component of river sediments was silica (56.9 to 96.7% d.w.). With the flow of the river, the share of silica in the sediment was higher. In lake sediment, silica was also predominant, but not in such a wide range as in the river (24.8 to 53.2% d.w.). The content of organic matter in river sediment did not exceed 27%. In the sediments of the lakes Pasłęka and Sarąg organic matter was the second component of sediments and ranged from 19.5 to 30.1%. In other lakes the content of organic components ranged from 12.3 to 20.3%. In lake sediment a high proportion of carbon dioxide was noted - between 14.4 and 24.2%, while in river sediment, this component did not exceed 6.3%.
1. Introduction

Bottom sediment is regarded as an important element in water ecosystem, playing the role of a nutrient “trap” but also of the potential and practically inexhaustible source of nutrients. Various transformations of mineral and organic components (diagenesis, dehydration, recrystallization, cementation, chemical reactions) take place in sediment, leading to the migration of nutrients compounds from sediment to water [1, 2, 3]. The bottom sediment is composed of mineral and organic substances removed from the water during the processes of precipitation, sorption and sedimentation. Binding of elements has a temporary character and in favourable conditions comprising aerobic conditions, redox potential, pH, temperature, sediment’s chemical composition, and the concentration gradient between the overlying and interstitial water, the elements can be released to the water [4]. The main components of water ecosystem sediments are the mineral particles of abiotic origin (produced by weathering and denudation), particles of biogenic origin (carbonates, silica, iron compounds) and auto- and allochthonous organic matter [5]. The formation of bottom sediments is also influenced by physical-chemical processes such as precipitation of insoluble calcium carbonate, iron (II) hydroxide, manganese (IV) and phosphate salts of these metals [6]. The autochthonous matter in the suspended particles dissolved in water (metabolites, enzymes) is characterized by high content of nitrogen and phosphorus compounds. In the rivers and lakes basin with the high share of forest, important sources of macro and microelements are plant remains and mineral-organic compounds of humus origin. In the aspect of water ecosystem functioning, the most important are the processes of accumulation of nitrogen and phosphorus compounds and the mechanisms of their release to the water.

Bottom sediment, that fills river beds, is characterized by a completely different chemical composition comparing to lake sediment. This is caused by the constant flow of water in the river and its good oxygenation.

The aim of study was analysis of chemical composition of riverine and lacustrine bottom sediment in lake-river system for example of upper Pasłęka system.

2. Material and Methods

The upper Pasłęka basin is situated in the North-East of Poland. The river Pasłęka flows into Vistula Lagoon. The total area of the upper Pasłęka River basin is 246.7 km², while the length of the upper part of the river is 40.5 km (total area of Pasłęka catchment is 2294.5 km², total length of river is 211 km). The average fall of the upper course of Pasłęka is 1.70 ‰. The Pasłęka River flows through one voivodship, Warmia and Mazury. The sources of the river are located around 20 km from Olsztyn, near Gryźliny village. According to the physico-geographic division proposed by Kondracki [7], the Pasłęka basin area is situated in the following macroregions: Olsztyn Lake District, Masurian Lake District. Pasłęka River in upper course flows through the lakes at different morphometric properties: Pasłęka, Wymój, Sarąg, Łęguty and Isąg (figure 1, table 1). The surface of lakes ranges from 8.5 to 397.5 ha, and a maximum depths of 5.0 to 54.5 m.

Samples of bottom sediments were collected in November 2017. The sediments from the lakes were collected at their maximum depth (St. I, II, III, IV, V), and from the river on 10 sites located along the course of the river at its inflow and outflow from each lake (St. 1-10), figure 1.

These diments from lakes were collected using Kajak bottom sampler, and from river were collected using pipe bottom sampler. The undisturbed sediment cores were divided into two layers (0-5 cm and 6-10 cm). The sediment analysis included: organic matter as a LOI using weight analysis, carbonates - using weight analysis in sediment after preliminary pyrolysis and later addition of CO₂ saturated water, total nitrogen by Kjeldahl method, silica - using weight analysis after preliminary digestion of a sediment sample in a mixture of the strong mineral acids (H₂SO₄, HClO₄, HNO₃ 1:2:3) and filtering through No. 390 filter, iron, manganese and aluminium - in filtrate after mineralization using Merck spectrophotometer, calcium and magnesium – in filtrate using titration method.
3. Results
Research carried out in the lake-river system of the Upper Paslęka showed a clear difference in the chemical composition of river and lake sediments. The dominant component of river sediment, except for both layers (0-5 cm and 6-10 cm, 18.98% d.w. 44.66% d.w.) inflow and upper layer (0-5 cm, 18.31% d.w.) outflow from Paslęka lake was silica, which share was from 56.9 to 96.7% d.w. With the
flow of the river, the proportion of silica in the sediment was higher. The amount of silica also increased with depth of the sediment (figure 2).

In lakes’ sediment silica also was dominated, but not as wide as in the river - from 24.8 to 53.2% (‘figure’ 3). The Isąg lake sediment contained the most of silica, and the Wymój lake - the least. In sediment of all analyzed lakes, the silica content also increased with the depth of the sediment layer (‘figure’ 3). A high proportion of organic matter in river sediments was found only on the inflow of Pasłęka River to Lake Pasłęk (St. 1) - an average of 58.2% d.w. and in the upper layer at the outflow of the river from this lake - 63.83% d.w. (‘figure’ 2). In the other sites along the river, the maximum share of organic matter in the sediment did not exceed 27% d.w. In the sediment of Lake Pasłęk and in the upper layer of Sarąg lake sediment, the organic matter was the second largest component and ranged from 19.5 to 30.1% d.w. In other lakes the content of organic matter ranged from 12.3 to 20.3% d.w. The bottom sediment of Isąg lake contained minimal amount of organic matter - 12.5% d.w. on average (‘figure’ 3).

Figure 2. Chemical composition of Pasłęka River bottom sediment
In lakes’ sediment a high proportion of carbon dioxide was noted - between 14.4 and 24.2% d.w. while in river sediment, this component did not exceed 6.3% s.m. (figures 2, 3).

River sediment generally contained lower amounts of phosphorus and nitrogen compared to lake sediment. In the bottom sediment of the analyzed lake-river system, nitrogen constituted from 0.06 to 2.45% of their composition, and phosphorus - from 0.08 to 0.67% d.w. (figures 2, 3). Bottom sediment in the river contained from 0.07 to 7.0% of iron in dry weight, and lake sediment - from 1.46 to 18.36% d.w. (‘figures’ 2, 3). Both in the river and in lakes there was a very small proportion of manganese in the chemical structure of bottom sediment (figures 2, 3).

The bottom deposits of individual sections of the lake-river system of the Upper Pasłęka contained various amounts of calcium and magnesium. Lakes’ sediment was richer in calcium carbonates (4 - 11% d.w.) than the river sediment (0.6 - 4% p. M.) (‘figures’ 2, 3). In the case of magnesium, the opposite situation was found. River sediment contained larger amounts of this element (0.3 - 6% d.w.) than the lake ones (1.1-2.6% d.w.) (figures 2, 3).

Figure 3. Chemical composition of lakes’ sediment of Upper Pasłęka
4. Discussion

The chemical composition of bottom sediment in both rivers and lakes is determined by various local and regional factors [9]. In sediment of Pasłęka River and analyzed lakes the dominant component was silica, which amount increased along the course of the river and also with the depth of the sediment layer. A statistically significant correlation was found between the silica content and the rate of water flow ($\text{SiO}_2 = 42,195Q_{sr} + 49,95$, $R^2 = 0,398$, $R = 0,631$, $n=10$, $\alpha=0,05$). The rapid stream of water is conducive to revealing the silicate elements of the geological bedrock substrate and moving the lighter parts in down of the river. In the analysed lakes of Upper Pasłęka, the highest proportion of silica in the sediment composition was also found; however, these values were quite low compared to other eutrophic reservoirs [10, 11]. In river sediment, silica showed a highly significant negative correlation with the content of organic matter ($\text{SiO}_2 = -1,1033\text{MO} + 90,575$, $R^2 = 0,935$, $R = -0,967$, $n=10$). The highest content of organic matter in river sediment was found on the inflow and outflow of the river from Lake Pasłęk.

In this section, the river flows through marshy meadows and peat bogs, which are the source of allochthonous organic matter. The main components forming peats are humified plant debris and peat humus [12, 13]. In further sections of the river, organic matter occurred in negligible quantities, and only episodically its share increased where the river flowed through forest areas. In the bottom sediment of lakes, the organic matter share was in the range from 12.3 to 30.1% d.w. It is assumed that the main source of organic matter of bottom sediment is detritus from both: the decomposition of aquatic plants and those inhabiting the area around the lake and surface inflow of water. The organic material undergoes modifications during transport to the lake, during sedimentation to the bottom and after deposition on the bottom. The pace and nature of the changes depends on the chemical properties of the organic material and the conditions prevailing in the lakes. For example, the mineralization of algae organic matter proceeds very quickly, because it is made of material with a low C/N ratio [14], and macrophytes or vascular terrestrial plants, which are rich in cellulose, characterize much higher values of this ratio and less susceptibility to decay [15].

In shallow reservoirs, the organic material is deposited faster in the bottom sediment and thus for a shorter time exposed to the oxidation processes occurring in the water. In deep lakes, the situation is reversed. This is confirmed by the results obtained during the study of the lake-river system of Upper Pasłęka. The highest content of organic matter in the sediments was found in the shallowest Pasłęk lake, the lowest in the deepest - Isąg. The processes of organic matter decomposition led to depletion of oxygen from the bottom water. The share of calcium in river sediment was small and did not exceed 4% d.w., and in lakes its content reached 11% d. w. In comparison with data from other lakes, it can be considered that these are average values [11]. As is known, this metal gets into bottom sediment from the basin or is accumulated as a result of physico-chemical and biological processes [5]. The occurrence of the calcium associated with the presence of carbonate, as in the form of common chemical bonds (calcium carbonate), or combinations of sorption both components are deposited in the bottom sediment. Statistical analysis showed a highly significant correlation between the content of calcium and carbon dioxide. The regression equation was $y = 0.2799x + 1.259$, $R^2 = 0.734$, $R = 0.857$, $n = 30$, $\alpha = 0.05$). Such a result confirms the genetic connections of both these components.

The amount of magnesium in the bottom sediments of the river was generally higher and in lakes it was lower than calcium. In river sediments a close relation of magnesium with the content of carbon dioxide carbon dioxide ($y = 1.0743x + 0.1305$, $R^2 = 0.738$, $R = 0.859$, $n = 30$, $\alpha = 0.05$) was observed, which indicates that it is deposited in sediment, mainly in the form of magnesium carbonate. There were no such dependencies in lake sediment. Bottom sediment of the whole system was characterized by a very low manganese content, only in the deeper layer of Łęguty lake sediment was found 1.62% d.w. of that metal. This is a known regularity [11, 16]. River sediments contained several times less iron than lakes. Comparing the obtained results with the values obtained by other researchers [17,18], the share of iron in the sediments of the analyzed lakes should be considered very high.
It was expected to obtain a statistically significant relationship between iron and organic matter content, due to the fact that besides the Wymój lake, which is probably supplied underground with iron-rich waters, higher content of this metal in sediments was recorded on river sections draining bog and forest areas and in a lake with forest catchment (Sarąg). But found no established relationship. Gawrońska [11] is of the opinion that retention of iron and manganese in bottom sediments is favored by the reduction character of the bottom, in particular by the presence of hydrogen sulphide arising from the biochemical reduction of sulphates during anaerobic decomposition of organic matter. Hydrogen sulphide reacting with iron or manganese can form sparingly soluble sulphides [19]. In addition, in such conditions, in the presence of: a large amount of organic matter, excess carbon dioxide and oxygen deficiency, both iron and manganese can be precipitated into the sediments in the form of carbonates. These dependencies also explain high concentrations of iron in Lake Łęguty.

The content of total phosphorus in river sediments was small, and its share in lake sediments as compared to other eutrophic lakes can be considered as average [11, 20]. Due to the fact that phosphorus is precipitated to bottom sediment, both in the form of a suspension, detritus and in connection with metals such as iron, manganese or calcium, a statistical analysis was performed to determine the correlation between phosphorus present in bottom sediment and the mentioned components. The analysis showed a highly significant relationship between phosphorus and organic matter in river sediment ($y = 147.53x - 10.779$, $R^2 = 0.513$, $R = 0.716$, $n = 20$, $\alpha = 0.05$), indicating that it is deposited there in organic form. In lakes there was no such relationship. Both in river and lake sediments, the relationship between phosphorus and iron was found ($y = 20.821x + 0.1936$, $R^2 = 0.396$, $R = 0.629$, $n = 20$; $y = 21.387x + 4.2148$, $R^2 = 0.181$, $R = 0.425$, $n = 10$). In the case of river sediments, there was also a correlation between the content of phosphorus, manganese and calcium, the equations were as follows: $y = 0.227x - 0.009$, $R^2 = 0.430$, $R = 0.656$, $n = 20$; $y = 5.6441x + 0.942$, $R^2 = 0.369$, $R = 0.608$, $n = 20$). There was no relationship with magnesium. In lake sediments the presence of phosphorus in the sediment did not correlate with the content of manganese, calcium or magnesium.

In bottom deposits of river, the proportion of nitrogen in the dry mass was higher than in the lakes of the Upper Pasłęka. In relation to other eutrophic lakes, the amount of nitrogen obtained in the analyzed sediment should be considered as low [11, 21]. Statistical analysis showed a highly significant relationship between the nitrogen content in sediment (both river and lake) and the amount of organic matter. The regression equations for the above compounds were: in the river $y = 24.773x = 2.5213$, $R = 0.743$, $n = 20$; in lakes $y = 32.353x - 12.689$, $R = 0.919$, $n = 10$. Such a result indicates the main source and form of this component.

5. Conclusion
In sediment of Pasłęka River and analyzed lakes the dominant component was silica, which amount increased along the course of the river and also with the depth of the sediment layer. A statistically significant correlation was found between the silica content and the rate of water flow. In river sediment, silica showed a highly significant negative correlation with the content of organic matter. The highest content of organic matter in river sediment was found in this section, the river flows through marshy meadows and peat bogs, which are the source of allochthonous organic matter.

In shallow reservoirs, the organic material is deposited faster in the bottom sediments and thus for a shorter time exposed to the oxidation processes occurring in the water. In deep lakes, the situation is reversed. This is confirmed by the results obtained during the study of the lake-river system of Upper Pasłęka. The highest content of organic matter in the sediment was found in the shallowest Pasłęk lake, the lowest in the deepest - Isąg.

The share of calcium in river sediment was small and did not exceed 4% d.w., and in lakes its content reached 11% d.w. The amount of magnesium in the bottom sediment of the river was generally higher and in lakes it was lower than calcium. River sediments contained several times less iron than lakes. Bottom sediment of the whole system was characterized by very low manganese content. The content of total phosphorus in river sediments was small, and its share in lake sediments as compared to other eutrophic lakes can be considered as average.
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