SŁUPSKIE PRACE GEOGRAFICZNE

Nr 14 ss. 213-222 2017

ISSN 2083-4721

Przyjęto: **10.04.2017**
Zaakceptowano: **25.06.2017**

Alina Sliuta
Chernihiv National T.H. Shevchenko Pedagogical University, Ukraine
sliuta.alina@ukr.net
Ivan Kirvel
Pomeranian University in Słupsk
kirviel@yandex.ru

THE CHEMISM OF SMALL RIVERS WATERS OF THE EASTERN POLESIE OF UKRAINE (ON THE EXAMPLE OF THE UBED RIVER)

CHEMIZM WÓD MAŁYCH RZEK WSCHODNIEGO POLESIA UKRAINY (NA PRZYKŁADZIE RZEKI UBED)

***Abstract*:** The hydrochemical characteristics of small rivers waters of the Eastern Polesie and their changes during the spring-summer period in 2012-2015 have been investigated. The results of the research showed that the surface water resources of the region belong to the hydro-carbonate class, and the hydrochemical parameters have rather close relationship with the geochemistry of the rocks forming the catchment. It was determined that phosphates are isolated in high concentrations among nutrients. The fluctuation of soluble oxygen in the water of the Ubed River has been shown.

***Key words*:** water resources, the Ubed River, hydrochemical parameters, maximum allowable concentration
***Słowa kluczowe*:** rzeka zasoby wodne, rzeka Ubed, wskaźniki hydrochemiczne, maksymalnego dopuszczalne stężenie

Introduction

Natural ecosystems have different rates of evolutionary processes and the degree of the anthropogenic impact changing the pace and the direction of their development. The assessment of the dynamics and the directions of the changes occurring in the ecosystems, included into the structure of the river basin, caused by both natural

and anthropogenic factors, requires a comprehensive study based on the regional environmental monitoring data and aimed at studying the elements of eco- and geosystems of the river basin in their close relationship. It is a complex studying of holistic natural-territorial structures, such as river basins, allows to reveal the peculiarities of transformation of ecosystems, to optimize the parameters of natural resources (land use and forestry in particular) and improve the management systems at the expected complex of impacts on the ecosystems.

The Eastern Polesie has an extensive hydrological network. Small rivers due to their huge number are one of the most important elements of the hydrographic network and are of great importance in the society. They have a number of peculiarities that must be considered at the development of their rational use and protection measures. The first of them is the brightly expressed dependence of the water availability, the hydrological regime and the water quality of small rivers on the surface condition of the catchment, the value of which in some cases is more important than the climate and the weather factors. Therefore, the hydrological and hydrochemical parameters may differ significantly from the characteristic ones for the given zone or area. The second important peculiarity is that small rivers are the initial link of the river network, and any changes in their regime undoubtedly affect the whole hydrographic chain (Ximko 2005, Lisetskiy, Degtjar 1998, Sljuta 2015).

Materials and methods

The goal of the study is to assess the quality of water in the water regime of small rivers on the example of the Ubed River, during the time of the survey (2012-2015) in the time dynamics. To suggest the measures for improvement of small rivers in the Eastern Polesie as the essential elements of the hydrographic network. For the assessment of hydrochemical parameters of small rivers of the Eastern Polesie (on the example of the Ubed River) physico-chemical methods of the research for determining the water quality based on the physical and chemical methods of the research have been used. The data of the Desna Basin Department of Water Resources of the State Water Agency of Ukraine and the Ecological Passport of the Ubed River were also used.

The chemistry of the Ubed River was assessed using the standard landscape and hydrochemical methods (Alekseev 1996, Afanas'ev 2001). In the first phase of the study the landscape map of the territory of the river basin were made and the impact of major pollution sources were assessed. In the second phase the samples from various locations along the Ubed River marked on the map-scheme (fig. 1) were selected, followed by the physico-chemical water parameters assessment. In the third one the seasonal dynamics of the main chemical parameters of the Ubed River water was held. The chemical analysis of the water was carried out using common methods of hydrochemical analysis (Cuglenok 2014).

When assessing the ecological status of the water the following parameters were being analyzed: the content of soluble oxygen (by Winkler) (Korostovenko 1998), oxidability (by Kubel method), pH, general mineralization, general hardness, general iron content (Cuglenok 2014), the amount of heavy metals, the concentration of

chloride-, nitrate-, nitrite-, and fluoride-ions (Murav'ev 1999, Novikov 1990), the organic substance content was determined by the indirect indicators – the chromaticity and the permanganate oxidizability (PO). The methods of the titrimetric and photoelectrocolorimetric analysis were used (Mitčel' 1995). All the figures obtained were compared with the MPC and the norms characteristic for the surface waters (Bespamjatkov 1985). The results obtained were statistically handled using the *Excel* program.

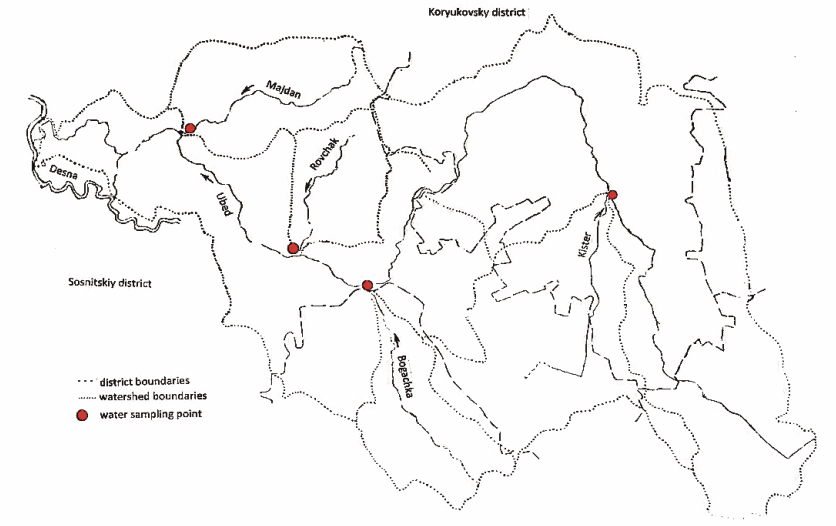

Fig. 1. The map-scheme of the sampling stations location
Rys. 1. Schematyczna mapa rozmieszczenia punktów poboru próbek

The Ubed River, a right-bank tributary of the Desna river, originates from the sources of the marshy beam near the village of Orlovka (Novgorod-Seversky). The river has 4 tributaries of more than 10 km in length (the Kister river, the Bohachka river, the Rovchak river, the Maidan river), the total length of which is 74.4 km. The river flow is regulated poorly. The total number of ponds and reservoirs regulating the local flow is 35, besides 12 floodgates were built.

The basin of the Ubed River is located within the Holmenskaya moreno-outwash plain, the Desna terraced plain, the Novgorod-Seversky height, the Dnieper-Donetsk artesian basin.

The conditions forming the surface flow of the river are generally favorable. The climate of the basin is temperate continental with warm, humid summers and drier winters. The average temperature is 5.8°C. The snow cover in the basin is observed in 100% of the cases. The average height of the snow cover is 25 cm, maximum – 63 cm. The river is powered with snows and rains, the total volume of annual drainage on the proportion of the snow cover is of about 50%, precipitation – 30%, groundwater – 20%.

The Ubed River has an extensive hydraulic system, so that the state of the environmental well-being of the whole basin depends on it. Taking into account the topography of the basin, we can assume that the surface drains have a large influence

on the chemical composition of the water, which are the sources of a large number of organic substances in the upper and middle flows of the river (table 1).

Table 1

The main hydrological characteristics of the Ubed River

Tabela 1

Podstawowe właściwości hydrologiczne rzeki Ubed

The characteristics	Measurability	Value
The length	km	156.00
Mark: 1) the source 2) the mouth	m. asl	 175.00 121.50
The fall	$m \cdot km^{-1}$	0.34
The catchment area	km^2	1011.00
The average height of the catchment area	m. asl	169.90
The average slope of the catchment area	$m \cdot km^{-1}$	11.50
The marshiness	%	0.50
The woodiness	%	32.60
The district of lakes	%	0.20
The plowed territory	%	42.60
The urbanization	%	6.90
The length of the river network	km	180.40
The density ratio of the river network	km	407.50
	$km \cdot km^{-2}$	0.31
The tortuosity	$km \cdot km^{-2}$	1.55

The use of the basin is quite intense. There are 3 towns and 50 villages within it. Approximately 38.03 thousand people live on the territory of the basin. The agricultural land of the basin is 77.399 thousand ha or 59.1% of the total area. The arable land is 55.574 thousand ha, or 42.4% of all the agricultural land. Agricultural enterprises fixed 104,098 hectares of land, or 79.5% of the area of the basin.

The negative change in the properties of soils mostly appear in the middle of the Ubed River basin, as well as in its right-side tributaries, the Bohachka river and the Rovchak river, where water erosion with the formation of ravines and beams is observed.

The analysis of the results

The most informative for the chemical analysis of water is the lower flow of the Ubed River because it is situated within the boundaries of the populated area and therefore experiences not only the impact of chemical pollutants in the upper and middle flows of the river, but also the additional impact of man-made pollutants (there is an enterprise near – Sosnitsky cheese plant). Therefore, when conducting chemical analysis of water the effect of the potential sources of pollutants was taken into account. The analysis of the obtained results shows that in most samples the pH was shifted towards the alkaline environment, which indicates a moderate amount of

carbonates. The greatest activity of the hydrochemical processes falls in the spring and summer periods, so monitoring of the main chemical parameters of the water was carried out during this season. Most of the indicators fluctuated around the norm, in the period from 2012 to 2015 such parameters as total mineralization, the content of chloride ions, etc. corresponded to the norm (table 2).

Table 2

The main hydrochemical characteristics of the Ubed River water quality in the time dynamics (2012-2015)

Tabela 2

Podstawowe właściwości hydrochemiczne wody rzeki Ubed w latach 2012-2015

The characteristics of water quality	**The units of measurement**	**MPC (norm)**	**The Ubed River (the average values)**			
			2012	**2013**	**2014**	**2015**
t	degrees Celsius	–	+13.1	+12.6	+13.8	+13.6
pH	units	8.5	7.25	7.35	7.61	7.75
HCO_3^-	$mg \cdot dm^{-3}$	400	305.10	256.20	244.10	360.00
SO_4^{2-}	$mg \cdot dm^{-3}$	100	34.00	38.58	30.20	42.00
Cl^-	$mg \cdot dm^{-3}$	300	14.00	13.30	14.00	15.07
Ca^{2+}	$mg \cdot dm^{-3}$	180	40.08	44.09	46.10	48.09
Mg^{2+}	$mg \cdot dm^{-3}$	180	21.90	20.70	19.50	24.30
Na^+ ,K^+	$mg \cdot dm^{-3}$	20	5.30	7.80	14.80	16.20
Mn^{2+}	$mg \cdot dm^{-3}$	0.01	0.029	0,034	0.035	0.03
Suspended solids	$mg \cdot dm^{-3}$	–	12.1	14.6	14.4	12.70
Biogenic components: ammonium nitrogen (NH_4^+)	$mg \cdot dm^{-3}$	0.5	0.78	1.2	1.70	1.86
Nitrite nitrogen (NO_2^-)	$mg \cdot dm^{-3}$	0.08	0.08	0.34	0.18	0.44
Nitrate nitrogen (NO_3^-)	$mg \cdot dm^{-3}$	40	0.78	0.71	0.72	1.31
Total iron	$mg \cdot dm^{-3}$	0.10	0.68	0.25	0.52	0.22
Phosphates (PO_4^{3-})	$mg \cdot dm^{-3}$	0.20	1.10	1.07	1.70	1.50
Total phosphorus	$mg \cdot dm^{-3}$	0.17	0.68	0.69	0.58	0.67
Organic indicators: BOD_5	mg $O_2 \cdot dm^{-3}$	2.00	2.60	2.20	2.80	2.90
Chemical oxygen demand (COD)	mg $O_2 \cdot dm^{-3}$	–	52.50	49.00	48.70	41.30
O_2	mg $O_2 \cdot l$	6.00	8.40	9.40	9.20	10.60
Alkalinity	mg –eq$\cdot dm^{-3}$	–	2.20	2.00	2.50	2.60
Total hardness	mg –eq$\cdot dm^{-3}$	–	5.80	5.60	4.40	7.00
Chromaticity	degrees Pt-Co	–	50.00	46.00	96.00	78.00

The increase in the content of Fe^{2+} and the excess of it depends on the high content of this element in the rocks, which the river drains, and the exit of the crystalline rocks to the surface in the form of the Ukrainian shield. Due to the total mineralization of the surface waters (Alekseev 1996, Kirvel' 2005), they belong to the hydrocarbonate class.

Changing the salinity of the river water during the 2012-2015 biennium. It determines analogical change in water content of the hydrocarbonate ion (HCO^{3-}) and calcium ion (Ca^{2+}).

Between contents in the river water Eastern Polesie HCO^{3-} ions on the one hand, and total mineralization of water, on the other, there is a close relationship (fig. 2), which is somewhat disturbed for the Ca^{2+} ion and sulfate ion SO_4^{2-}.

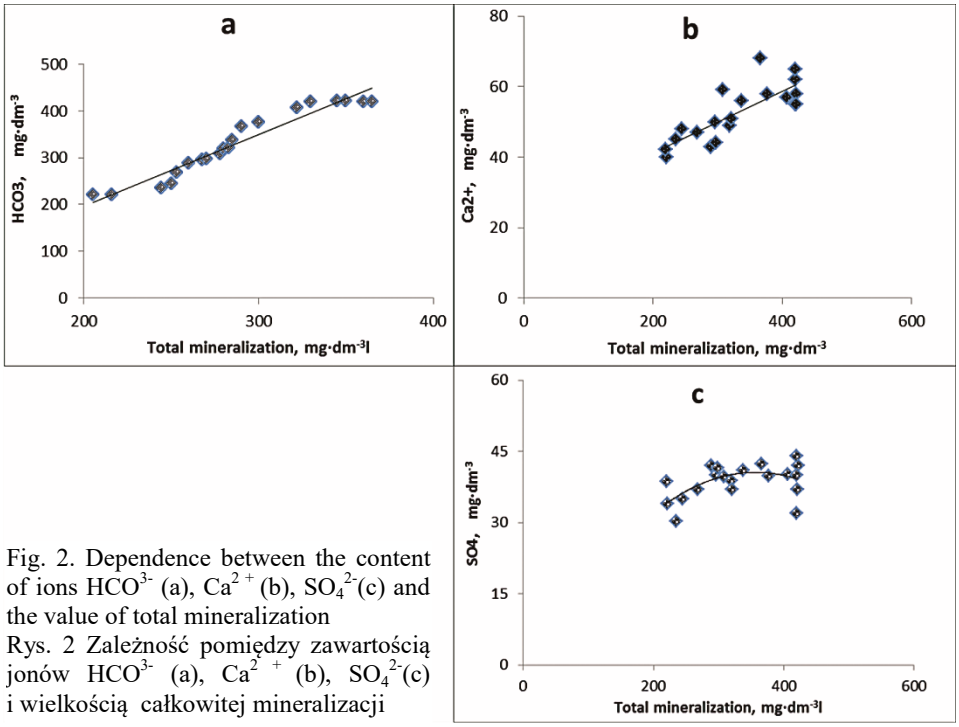

Fig. 2. Dependence between the content of ions HCO^{3-} (a), Ca^{2+} (b), SO_4^{2-}(c) and the value of total mineralization
Rys. 2 Zależność pomiędzy zawartością jonów HCO^{3-} (a), Ca^{2+} (b), SO_4^{2-}(c) i wielkością całkowitej mineralizacji

In 2015 one-time samples were taken for determination of heavy metals in them. In the whole hydrographic network it was found that Cr at 2 times exceeds at the rate of 0.05 mg·dm^{-3}, Ni – 3.5 times at a rate of 0.1 mg·dm^{3}, Cu and Zn – 2.5 and 3 times when the standard is 1.0 mg·dm^{-3}. Their increased content in the bottom sediments creates conditions for the secondary water pollution in ecosystems.

The main hydrochemical parameters have the expressions HCO_3^{-}>Ca^{2+}> SO_4^{2-} >Mg^{2+}> Cl^{-}>Na^{+}+K^{+}.

The source of ammonium compounds in the water is nitrogen-containing substances entering the surface and drainage waters in different ways: from the accumulated solid wastes of unauthorized dumps, the accumulated organic farm animals' wastes, the remnants of the warehouses of mineral fertilizers and pesticides, the mineralization of bottom sediments of the channels. The formation of nitrites and nitrates (nitrification) is caused by the following oxidation of the ammonium compounds.

The quantitative content of such a pollutant as nitrite nitrogen, in comparison with 2012 (0.08 mg·dm^{-3}) increased in 2013 (0.34 mg·dm^{-3}) and in 2015 is

0.44 mg·dm^{-3} (MPC ≤ 0.08 mg·dm^{-3}), which 5.5 times exceeds PDK in 2015 and 4.25 times in 2013. In most cases, the increase was at the beginning of the vegetation period. Such content of nitrite nitrogen indicates the adverse conditions for the oxidation of the organic substances and low self-cleaning ability of these rivers (fig. 3, 4). The content of such a pollutant as ammonia nitrogen in comparison with 2012 (0.78 mg·dm^{-3}) 1.6-3.7 times increased in 2015 in almost all sampling points and it is 0.78-1.86 mg·dm^{-3} (MPC < 0.5 mg·dm^{-3}). A significant decrease in nitrate nitrogen in the middle of the vegetation period should be noted.

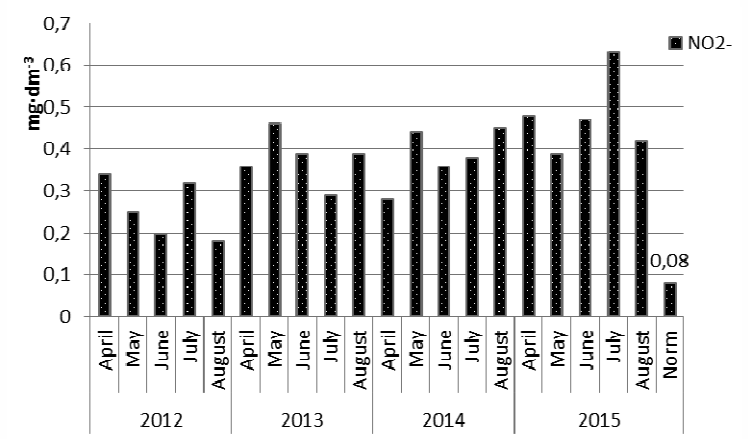

Fig. 3. The content NO_2^- of the Ubed River water
Rys. 3. Zawartość NO_2^- w wodzie rzeki Ubed

The highest content of ammonium nitrogen was observed during the spring flood, the jump of the ammonium nitrogen concentrations to 2.89 mg·dm^{-3} was observed in 2014-2015. The indicators 2-5 times exceeded the MPC which is connected with the seasonal characteristics of the flow of the process of ammonification and the consumption of ammonium by vegetation during the vegetation period.

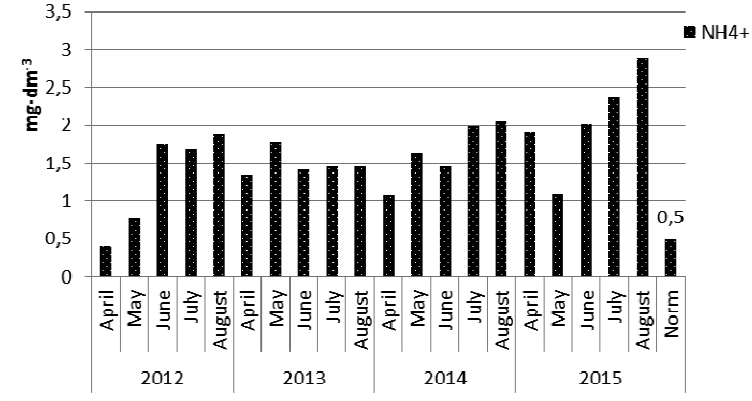

Fig. 4. The content NH_4^+ of the Ubed River water
Rys. 4. Zawartość NH_4^+ w wodzie rzeki Ubed

The content of nutrients in water depends on many factors and is largely determined by the vital activity of the aquatic organisms coming with the surface drain from the catchment. The removal of phosphorus and the formation of its load depends on the size of the catchment area, its structure (woodiness), the soil cover, the marshiness of the bedrock. The phosphate concentration in unpolluted surface waters typically corresponds to the hundredths and thousandths values. The phosphate concentration in the Ubed River is much higher and the dynamics of their content fluctuates from 1.07 to 2.49 during the entire studying period.

The phosphate concentration was on average 1.09 $mg \cdot dm^{-3}$ in spring of 2012 and 1.48 $mg \cdot dm^{-3}$ in summer; 1.895 $mg \cdot dm^{-3}$ in spring of 2013 and 1.6 $mg \cdot dm^{-3}$ in summer; 1.84 $mg \cdot dm^{-3}$ in spring of 2014 and 1.69 $mg \cdot dm^{-3}$ in summer; 1.69 $mg \cdot dm^{-3}$ in spring of 2015 and 2.31 $mg \cdot dm^{-3}$ in summer (fig. 5).

The organic substance in river waters is found as the substances of the humic origin washed from soils and marshes and as the breakdown products of various organic substances, mainly of the plant origin.

The chromaticity analysis showed that its values are 5-26° Pt-Co scale. The value of the chromaticity increases in the period of spring floods, which is connected with the increase in income of organic substances from the catchment. The maximum chromaticity was recorded in May, 2014 (120°). The character of the seasonal dynamics of the PO is of the same colour dynamics. The value of the PO is 1.5 to 12.7 $mg \cdot dm^{-3}$. The highest value of the PO is characteristic for the river in May, 2015.

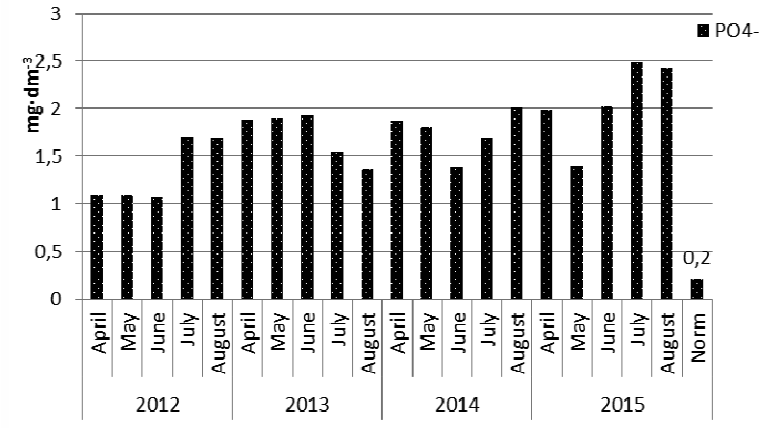

Fig. 5. The content PO_4^- of the Ubed River water
Rys. 5. Zawartość PO_4^- w wodzie rzeki Ubed

The content of soluble oxygen in the water dramatically varied during all the years. So, in June, 2012, the amount of oxygen dissolved in a liter of water made up to 1.2 ml, and 2.3 ml in July, in August the oxygen content 5.2 times increased compared to the starting figure, and was 6.2, it corresponds to the lower limit of the norm (fig. 6). The indicators of O_2 with the lowest value were recorded in June – 0.9 $mg \cdot dm^{-3}$ and 3.6 in August, 2015, which does not meet the lower limit of the

norm. In the flood period (during 2012-2015), the dissolved oxygen content in water was almost 2 times below the norm, which does not satisfy the needs of aerobic aquatic organisms. There are a lot of objects such as gardens, pastures, houses, roads along the banks of the river, especially in the middle flow. In this period the Ubed River is out of the banks, and as a result the organic compounds, petroleum products, mechanical debris are constantly washed away from the surface into the river, and all this leads to strengthening the processes of oxidation and decreasing the oxygen content in water.

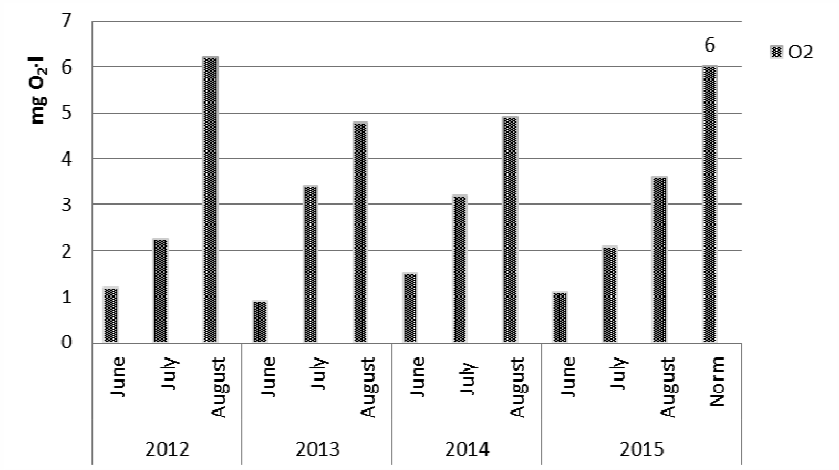

Fig. 6. The content of soluble oxygen in the Ubed River water in summer months during 2012-2015

Rys. 6. Zawartość tlenu rozpuszczonego w wodzie rzeki Ubed w miesiącach letnich w latach 2012-2015

Sharp fluctuations in the oxygen concentration may negatively affect the life of aquatic organisms as to support the normal functioning of aerobic aquatic organisms oxygen from 5 to 10 ml per 1 l of water is required (Kirvel' 2015).

When comparing the chemical parameters of oxidation and the dissolved oxygen the calculated correlation coefficient showed that they have a strong inverse relationship (k_{xy}= -0.89). It means that with increasing content of oxygen reduced the level of regenerative processes in water.

Such regularity is justified, as the Ubed River water regime is constantly changing, especially in the spring-summer period. Thus, we have the low oxygen concentration and a high level of reducing agents at the end of spring and at the beginning of summer, and these indicators get the optimal values only in August.

Conclusions

Thus, the state of the Ubed River can be assessed as extremely tense, as the increase of some hydrochemical parameters on the basis of the MPC is observed, as well as the fluctuation of the values of such a key indicator as soluble oxygen. The

content of biogenic and organic substances is determined by the characteristics of the surface drain from the catchment. Among the nutrients, high concentrations of phosphates are allocated, which is probably due to the geochemical conditions. According to the complex assessment of quality the Ubed River water quality corresponds to the 3rd class, moderately polluted, and in general the water of the river belongs to the hydro-carbonate class. The development of environmental activities in preserving the ecosystem of the river basin is an urgent task.

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Summary

The content of biogenic and organic substances the Ubed River is determined by the characteristics of the drain surface from the catchment basin. Among the nutrients, high concentrations of nitrates and phosphates are singled out, that is connected with geochemical conditions. Environmental activities in preserving the ecosystem of the river must be developed, because small rivers of the Eastern Polesie are ones of the most important elements of the hydrographic net and have great importance in the life of society.