Journal of Ecological Engineering

Journal of Ecological Engineering 2023, 24(6), 294–302
https://doi.org/10.12911/22998993/163166
ISSN 2299–8993, License CC-BY 4.0

Received: 2023.03.13
Accepted: 2023.04.17
Published: 2023.05.01

Evaluation of Water Quality of the Siret River by Zooperiphyton Organisms

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ABSTRACT

The extensive nature of natural resource use in the Siret River basin in recent years has led to a significant depletion of its water resources and deterioration of the ecological state of surface waters. The following paper presents the results of assessing the degree of water pollution of the Siret River. A number of biotic water quality indices were used for this purpose. In particular, the Trent Biotic Index (TBI) and the Biological Monitoring Working Party Index (BMWP), both of which use the density ratio of different macroinvertebrate taxa in the aquatic communities, and the Pantlé and Bucca saprobility index, which uses the absolute density and saprobility of indicator species of aquatic organisms. A comprehensive assessment of the aquatic ecosystem of the watercourse was carried out using the water pollution index (WPI). The biological indices were calculated on the basis of data on zooperiphyton communities formed on an artificial fibre media of the «VIYA» type. The VIYA fibre carrier was used for more accurate determination of the species composition and quantitative characteristics of zooperiphyton communities in the studied river sections. The TBI index ranged from 5 to 6 (which corresponds to a water quality assessment of 'satisfactory'). The BMWP index ranged from 8 (very poor) to 32 (good), and the saprobicity index from 1.52 to 1.95 (good water quality). The WPI index at the control sites in the Siret River ranged from 4.6 (which corresponds to a water quality assessment of 'polluted') to 8.1 (which corresponds to a water quality assessment of 'extremely polluted'). Significant differences in the results of the assessment by different biotic indices indicate that these indices cannot be used as indicators for an exhaustive assessment of water quality using zooperiphyton. They can only be used as relative indicators for comparing the state of water pollution at different locations. The values of hydrochemical indicators of water quality at two observation posts of the river were analysed. The maximum permissible concentrations of nitrite ions, ammonium ions and suspended solids in the control sections of the river were found to be exceeded.

Keywords: water quality, zooperiphyton, ecological value, biotic indexes.

INTRODUCTION

In the modern period of scientific and technological progress, the anthropogenic impact on the environment is increasing. At the same time, the forms and extent of this impact are very diverse. Therefore, improving the water quality of the hydrosphere through the introduction of cutting edge wastewater treatment technologies (Malovanyy et al., 2019; Kostenko et al., 2017; Malovanyy et al., 2020) is a key task. One of the issues that needs to be solved at the state level is the restoration of a favorable hydrological regime, sanitary condition and improvement of water quality of medium and small rivers of Ukraine, whose water resources are an integral component of the country's total water resources.

The river network of the middle Siret River basin belongs to the regions with a high degree of economic development of natural resources and their intensive and long-term exploitation, thus a comprehensive study of the water quality problems of this network is particularly relevant today. The basin of the Siret River, which is one of the largest tributaries of the Danube River, has a transboundary character. The total length of the river is 513 km, 100 km of which flows through the Chernivtsi region. Within the region, the river's catchment area is 2070 km^2 (the total catchment area is 47600 km^2). The density of the river network is 1.34 km/km^2. The upper part of the Siret River (up to the village of Berehomet) is a typical mountain river, while downstream it is a foothill-plain river with a wide valley. The Siret River flows into the Danube River near the city of Galati in Romania.

Evaluation of the quality of surface waters in the Siret River basin and the negative impact of economic activity on the ecological state of this watercourse are covered in the works of both domestic scientists (Karavan, 2011; Kuzmych et al., 2015; Masikevych et al., 2021) and foreign researchers. For example, (Zait et al., 2022; Mănescu et al., 2014) present material on water quality and monitoring of priority pollutants in the Siret River basin in Romania. The works of other authors (Zaharia, 2014; Gheorghe, 2012) provide information on the state of surface and groundwater in the Siret River basin under the influence of agricultural activities. In the framework of water resources management in Romania, a comprehensive water monitoring system for the Siret River was developed as an important mechanism for protecting water resources (Dăscăliţa, 2011).

In environmental issues, especially in solving the problem of water pollution and its purity, an independent monitoring system is needed, in particular for hydrobiological indicators. It will allow promptly receiving signals of emergency situations regarding exceeding the level of pollution from the most problematic places along with identified potential sources of danger (Zapolskyi, 2005). Indicators of water pollution are important characteristics of environmental conditions in aquatic ecosystems. One of the ways to assess them is to use various biotic indices of water quality. Such indices are very commonly used in studies of anthropogenic pressure on aquatic ecosystems, but since the diversity of aquatic life communities depends not only on water quality, their use requires caution. Macrozoobenthos and zooperiphyton are the most indicative for assessing water pollution, as they are the fixed communities that most objectively reflect the quality of their habitat. Zooperiphyton, as an ecological group of aquatic organisms, is highly sensitive to pollution. As habitat conditions deteriorate, changes occur in the structure of zooperiphyton communities: rare species disappear, species diversity decreases, the evenness of abundance decreases, and the percentage of dominant species increases. This allows the use of the zooperiphyton community as a biological indicator of the quality of natural waters. River pollution has a stronger effect on the zooperiphyton of riparian vegetation than submerged vegetation, and turbellaria, mossflies, springtails, may fly larvae, stoneflies, stoneflies and midges are used as indicators of pure water (Protasov, 1994).

Assessment of environmental risks arising in water bodies under the influence of anthropogenic and natural factors is a reliable method of research and assessment of the state and sustainability of aquatic ecosystems. Systematic, scientifically based bioindicative studies of water quality in the Siret River basin and adjacent areas according to well-known European indices have not been conducted to date.

Separate studies concerning the use of hydrobiological flora as an indicator of anthropogenic water pollution and the ecological status of transboundary rivers in the Chernivtsi region are available (Sinchenko, 2017). The study (Karavan, 2012; Karavan, 2013) presents the results of studying the phytoperiphyton to determine the anthropogenic regression of aquatic ecosystems in the Siret River basin.

Therefore, the aim of this study was to use a number of biotic indices (TBI, BMWP and the Pantlé-Bucque saprobility index) to determine the water quality of the transboundary Siret River using data on the taxonomic composition and density ratio of zooperiphyton.

MATERIALS AND METHODS

Hydrobiological material was collected in the summer period (June-July) of 2022. Samples of macrozoobenthos and zooperiphyton were collected from the coastal areas of the channel on a silt-sand substrate at four observation stations of the Siret River. The first station (station 1) is located near the village of Berehomet, the second (station 2) – near the town of Storozhynets, the third (station 3) – below the town of Storozhynets and the fourth (station 4) – in the area of the confluence of its right tributary Malyi Siret River into the Siret River (near the village of Hlyboka), see Figure 1.

Samples of macrozoobenthos were collected with a hydrobiological scraper net (inlet diameter 20 cm) from an area of 0.1 m^2 with subsequent recalculation of the density and biomass of organisms per 1 m^2. The top layer of bottom sediments (up to 5 cm deep) was sampled for the study. The collected samples of benthic invertebrates were thoroughly washed through a sieve with a mesh size of 1 mm, removing small stones, plant remains and coarse detritus, the presence of which in the sample leads to damage to the hydrobiological material. All material was fixed with a 90% ethanol solution and transported to the laboratory for further analysis. For a denser concentration of zooperiphyton organisms, a fiber carrier of the VIYA type, which is used to immobilize microbiota in biological wastewater treatment, was installed at the observation stations (Dombrovkiy et al., 2020). Samples of zooperiphyton were taken according to the methodology tested in similar studies (Dombrovskiy et al., 2018). The density of organisms of the fouling biocenosis was determined from a fiber carrier VIYA with an area of 250 cm^2 and then recalculated per 1 m^2. In some cases, the concept of «lower identification taxon» (LIT) was used to identify hydrobionts.

Taxonomic identification of the material was performed according to (Bauernfeind et al., 2012; De Moor et al. 2003). The authors (Kriska et al., 2013; Wallace et al., 2010) identified 14 representatives of the zooperiphyton out of 19 recorded taxa with species accuracy, which is 74%.

The authors used three approaches to assess the ecological status of aquatic ecosystems and surface water pollution. These are ecological evaluation using hydrochemical indicators, bioindication of saprobility by indicator species, and bioindication of pollution, which is based on the fact that with increasing pollution, indicator groups of aquatic organisms disappear from the aquatic ecosystem.

For the ecological evaluation of the water quality of the Siret River, the Woodiwiss index or the Trent River Index (TBI) was used, which is one of the most common indices used in the EU and other countries, except for some changes in the worksheets for calculating the index (Lyashenko and Zorina-Sakharova, 2012). The TBI assessment is based on a working scale that uses the sequence of disappearance of widespread macroinvertebrate benthic communities in accordance with water and sediment pollution, i.e. the ratio of taxa that are sensitive and insensitive to external factors. The results of the assessment are given in points from 0 to 10 (Afanasyev, Grodzynskyi, 2004). We also used the Biological Monitoring Working Party Index (BMWP), which was developed by the Institute of Freshwater Ecology

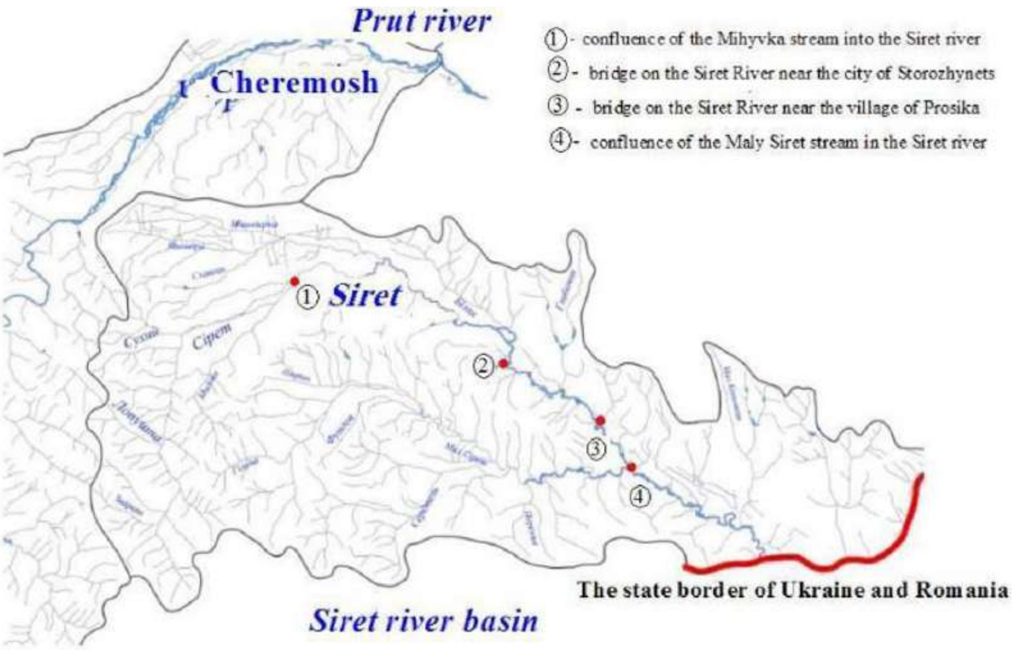

Figure 1. Map of sampling on the Siret River

(UK) as part of the RIVPACS system, which is the basis for assessing the state of surface waters in the UK and Australia (Armitage et al., 1983). It is also widely used in the EU countries. The correspondence of TBI to saprobility zones and the correspondence of BMWP to water quality classes are given in (Lyashenko et al., 2012).

To evaluate the level of organic pollution in the Siret River, the saprobility index was calculated using the Pantlé-Bukka methodology and absolute values of the density of indicator species (Klapwijk, 1988). We used the names of the saprobic water quality classes in accordance with the national methodological guidelines (by Romanenko and others). Taking into account that the selected indices have inconsistent scoring scales, a five-level scale was used to unify the presentation of the results, which was developed (Lyashenko and Lukashov, 2019) in accordance with the format of the EU Water Framework Directive 2000/60 [Directive 2000/60/EC]. The determination of water quality classes and their correspondence to biotic index values was in line with European standards (Wright et al., 1993) (Table 1).

The similarity of the zooperiphyton species composition was estimated by the Jaccard index. To calculate the TBI, BMWP, and Pantlé-Boucq indices, the hydrobiological data processing software BiotMetrics and Saprogram-ZB were used.

The water pollution index (WPI) was used to assess the water quality of the Siret River (Khilchevskyi, et al., 2021). The WPI was calculated based on six to seven mandatory hydrochemical indicators: dissolved oxygen, biochemical oxygen demand, suspended solids, ammonium nitrogen, nitrite nitrogen, phosphates, and oil products. WPI was calculated using the following formula:

$$\mathrm{WPI} = \frac{1}{n}\sum_{i=1}^{n}\frac{C_i}{\mathrm{MPC}_i} \quad (1)$$

where: WPI – water pollution index;
C_i – average concentration of the i-th water quality indicator;
MPC_i – maximum permissible concentration of the i-th water quality indicator.

Unlike other indicators, the ratio of standard/actual concentration is taken for dissolved oxygen in the WPI calculations.

The values of the calculated WPI were used to assess the water quality of the watercourse. In accordance with the methodology for assessing water quality based on the water pollution index, the following criteria and classes of water quality are distinguished:

- I class – very clean water (*WPI* value ≤0.3);
- II class – clean water (*WPI* value 0.3−1.0);
- III class – moderately polluted water (*WPI* value 1.0−2.5);
- IV class – polluted water (*WPI* value 2.5−4.0);
- V class – dirty water (*WPI* value 4.0−6.0);
- VI class – very dirty water (*WPI* value 6.0−10.0);
- VII class – extremely dirty water (*WPI* value >10.0).

The initial data for the calculation of the WPI were based on the materials of the basin water and soil monitoring laboratory of the Prut and Siret Water Resources Management Basin. Data of hydrochemical indicators for June 2022 from two observation posts was used. Observation site № A. Full name of the observation site: Siret River, 448 km, Storozhynets, w/o. Observation post № B. Full name of the observation post: Siret River, 418 km, Cherepkivtsi village, bridge, Romania border area.

RESULTS AND DISCUSSION

Three species of benthic invertebrates were found in the macrozoobenthos of the Siret River. Macrozoobenthos organisms were found only at two stations, one species was recorded at station 1 and two species of hydrobionts at station 3. *Oligochaeta* of the family *Tubificidae, Diptera* of the family *Ptychopteridae* and aquatic spiders (*Aranei*) were found here. The density of

Table 1. Evaluation of water quality according to the calculated index values

Indices	Quality class				
	excellent	good	satisfactory	low	extremely low
* TBI	9−10	7−8	5−6	3−4	0−2
* BMWP	> 51	31−50	21−30	11−20	0−10
** Pantlé and Bukka	< 1.0	1.0−2.0	2.1−3.0	3.1−3.5	> 3.5

Note: * Classification by Lyashenko A., Lukashov D.; ** Classification by Romanenko V., Zhukinskiy V., Oksiyuk O.

macrozoobenthos ranged from 20−70 specimens/m^2 (mainly due to oligochaetes), and the biomass was 6−9 mg/m^2. At other observation stations (Stations 2 and 4), where bottom sediments are represented by gray silt with impurities of silted sand and particles of detritus of plant origin, no macrozoobenthos organisms were found.

In the zooperiphyton of the VIYA-type fiber carrier, 19 LITs belonging to 10 taxonomic groups were found (Table 1).

In the macrozooperiphyton of the Siret River, 13 species and LITs of fouling were found. Among the 6 recorded taxonomic groups, *Ephemeroptera* (6 species) and *Chironomidae* (3 species) prevailed in terms of species diversity. Other taxes – *Diptera, Trichoptera, Hemiptera* and *Odonata* – were represented by only one species each.

As a result of using the artificial carrier VIYA as an immobilisation system, a larger pool of aquatic organisms was identified. In general, the species diversity of the zooperiphyton of the Siret River during the period of study was mainly determined by the larvae of amphibious insects, among which the *Ephemeroptera* group prevailed in terms of the number of species and density. A similar species composition of the zooperiphyton of the fibrous carrier VIYA was found during the study of the Stebnyk tributary of the Siret River in the National Nature Park 'Vizhnitsky' in 2016. Out of 12 species and subspecies of zooperiphyton hydrobionts, 6 taxa belonged to larvae of amphibious insects, 4 taxa – to rotifers and infusoria. Other systematic groups (*Turbellaria, Nematoda*) were represented by one species each (Masikevych et al., 2018).

To assess the structure of the zooperiphyton, the Jaccard similarity index was calculated. According to the results of its calculation, station 2 had the highest similarity of species composition in comparison to other stations (Jaccard index values from 0.22 to 0.30), the average value of the index was 0.26. The remaining observation stations (Stations 1, 3 and 4) were characterised by low values of species similarity (the average value of the Jaccard index ranged from 0.13 to 0.16).

The zoocoenosis of the zooperiphyton *Ephemerella ignita Poda + Xenopelopia falcigera* (Kieffer) was formed in the studied section of the Siret River near the village of Beregomet (station 1). The density of the zoocoenosis was 1240 ex/m^2 (mainly due to one-day-olds), biomass was 2.17 g/m^2. The saprobicity index according to the Pantlé and Bucca methodology reached 1.95, which corresponds to the assessment of water quality in this watercourse zone as «good».

In the lower areas (stations 2, 3), zooperiphyton communities were formed mainly by ostracod *Limnocythera inopinata* (Baird), which represented up to 46−50% of the fouling density. The density and biomass of zooperiphyton in these watercourse sections were lower and ranged from 400−440 specimens/m^2 and 0.09−0.26 g/m^2, respectively. It should be noted that these sections of the river are located in settlements where, due to the deterioration and lack of sewage treatment facilities, household wastewater enters the Siret River untreated. As a consequence of the increased concentrations of soluble and suspended organic matter entering the river, the species

Table 2. Characterization of invertebrate zooperiphyton of the Siret River fiber carrier in 2022

Taxonomic groups	Number of LIT			
	st. 1	st. 2	st. 3	st. 4
Macrozooperiphyton				
Chironomidae	1	1	0	1
Ephemeroptera	2	2	1	4
Trichoptera	1	0	0	0
Odonata	0	0	0	1
Hemiptera	0	0	1	0
Diptera (except *Chironomidae*)	1	0	0	0
Mejozozooperiphyton				
Ostracoda	0	1	1	0
Nematoda	1	1	1	1
Rotatoria	1	1	0	0
Protistoperiphyton				
Ciliophore	0	0	1	2
Total	7	6	5	9

composition of the zooperiphyton in these areas is becoming more simplified. Species with low indicator value and resistant to pollution (larvae of *Chironomidae, Ostracoda, Nematoda, Hemiptera* and bdeloid rotifers) predominate here.

The lower section of the Siret River (station 4) is located 20 km downstream of Storozhynets. In this area, the river merges with its tributary Malyi Siret. The zooperiphyton of this section differs from the above-mentioned communities in terms of qualitative and quantitative indicators. The zooperiphyton organisms were characterised by high density and biomass, which amounted to 960 specimens/m^2 and 12.97 g/m^2, respectively. The densest taxonomic groups at this station were *Ephemeroptera* and *Chironomidae*, which together accounted for 75% of the total zooperiphyton density (Fig. 2). The results of calculating the saprobility index using the Pantlé and Bucca methodology – 1.52 indicate an insignificant level of organic water pollution, which corresponds to the water quality assessment of the watercourse as «good».

The analysis of the species composition of the zooperiphyton of all sections of the Siret River revealed that the organisms they consist of differ significantly in terms of their feeding type. Thus, in the relatively «clean» section of the river (station 4), collectors (larvae of mayflies and chironomids) dominate, consuming benthic algae and detritus. The trophic structure of zooperiphyton communities in the «polluted» sections of the Siret River is dominated by ostracods (soil consumers) with a small proportion of mayflies, stoneflies and chironomids (filter gatherers).

The overall evaluation of water quality according to the selected biotic indices is presented in Table 3.

The value of the TBI index ranged from 5 (stations 1–3) to 6 (lower river section, station 4), which corresponds to a water quality assessment of «satisfactory».

The results of calculating the saprobility index using the Pantlé and Bucca methodology indicate a low level of organic pollution in the Siret River at the studied observation stations. The saprobicity index for all observation stations varies within a very small range – from 1.52 to 1.95. The water masses of the Siret River at all studied sites are characterised by α-oligosaprobic

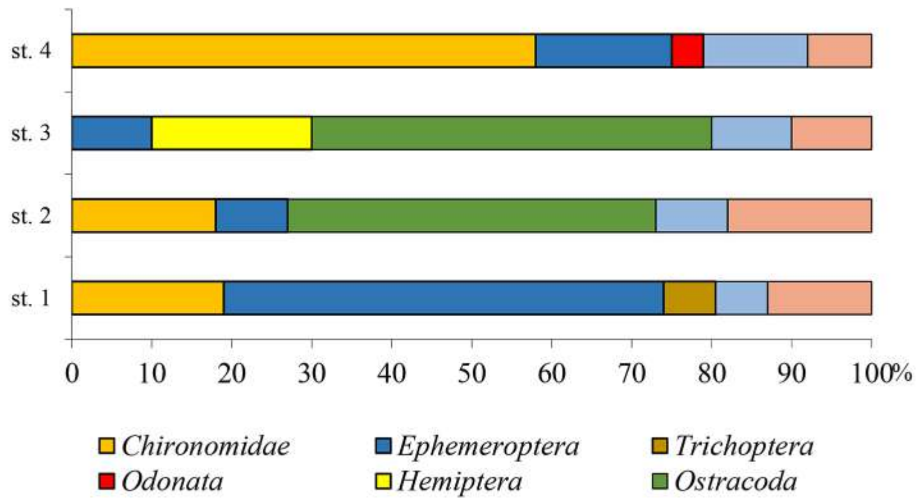

Figure 2. Relative density of taxonomic groups of zooperiphyton in the studied areas of the Siret River

Table 3. Water quality assessent of the Siret River by biotic indices

Stations	Evaluation by indicators		
	Saprobility by Pantlé and Bukka	TBI	BMWP
St. 1	1.95 / good	5 / satisfactory	23 / satisfactory
St. 2	1.75 / good	5 / satisfactory	8 / extremaly bad
St. 3	1.73 / good	5 / satisfactory	12 / bad
St. 4	1.52 / good	6 / satisfactory	32 / good

Note: St. 1 = Beregomet village, st. 2 = town Storozhynets, st. 3 = below the town of Storozhynets, st. 4 = Hlyboka village.

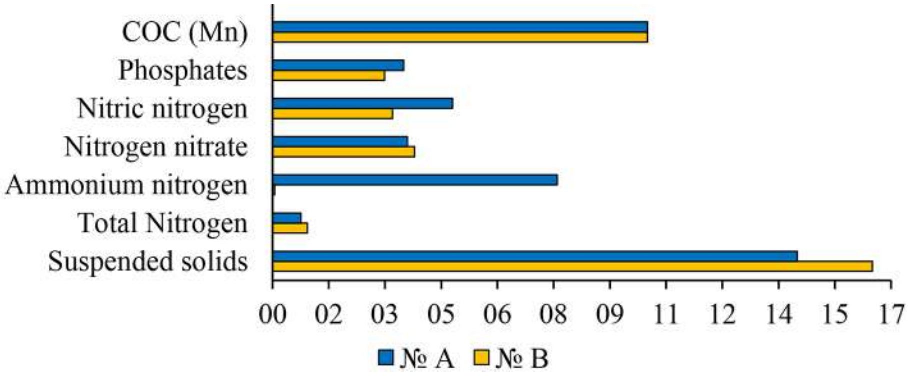

Figure 3. Hydrochemical parameters (mg/dm³) from the Siret River observation stations in June 2022, where A = Siret River observation station, 448 km, Storozhynets, inlet, B = Siret River observation station, 418 km, Cherepkivtsi village, bridge, border area with Romania

and β-mesosaprobic waters, corresponding to the second class of water quality.

The BMWP index for all observation stations recorded worse quality indicators compared to the TBI and saprobility indices, which may indicate a greater sensitivity of the BMWP index in this case. The BMWP index ranged from 8 (extremely bad water quality) to 32 (good water quality). Low values of the index (corresponding to low water quality assessments) were recorded at two observation stations (pp. 2–3).

Thus, these three indices showed rather different results. This is due to the specificity of the studied communities and the peculiarities of their taxonomic composition and density ratios of individual taxa compared to typical macrozoobenthos communities. Therefore, they cannot be used to draw exhaustive conclusions about the water quality of the study area. However, they can be used as a relative indicator for comparing water pollution indicators at different observation sites.

For the ecological analysis of the Siret River, a comprehensive assessment of the state of aquatic ecosystems was carried out based on the main hydrochemical indicators (Fig. 3).

Data from observation post № A (Storozhynets) indicate that the following indicators exceed *MPC* values for fishery water bodies: nitrite ions by 60 times, ammonium ions by 15.2 times. At the observation post № B (Cherepkivtsi village), the *MPC* values were exceeded for two indicators: suspended solids by 1.1 times and nitrite ions by 40 times. Other hydrochemical parameters were within normal limits.

In the control watercourse near Storozhynets, the water pollution index in June and July was 8.1. According to the determined *WPI* values, the water quality class of the Siret River corresponded to Class VI – 'very dirty'. The control station located in the village of Cherepkivtsi is characterised by a decrease in the water pollution index (4.6) compared to the upstream control station. The water of the watercourse corresponded to the V quality class – 'dirty'.

In general, the assessment of water quality by biotic indices and hydrochemical indicators indicates anthropogenic pollution of the studied sections of the Siret River. Due to the absence of centralised treatment facilities in Berehomet and Storozhynets, the river is directly discharged by the municipal wastewater of these large settlements, which is accompanied by a decrease in dissolved oxygen and an increase in the content of suspended solids.

CONCLUSIONS

The considered biotic indices of water quality, where data on the structural organisation of zooperiphyton communities were used for its calculation, can be used only as relative indicators for comparing different points of the study area, but not for an exhaustive assessment of the state of water pollution. The TBI index and the saprobility index using the Pantlé and Bucca methodology showed an increase in water quality at the studied observation stations, which corresponds to the assessment of water quality as «satisfactory» and «good», respectively. The calculation of the BMWP index yielded rather diverse indicators of the quality of natural waters of the Siret River, which corresponds to the assessment of water quality from 'very dirty' to 'good'.

The results of the Siret River water quality study revealed that the *MPC* (*ASEL*) value for fishery water bodies was exceeded for the following indicators: nitrite nitrogen, ammonium nitrogen, and suspended solids. The content of BOD_5, COD, dissolved oxygen, total nitrogen, phosphate and nitrate nitrogen was within the *MPC* standard.

Using the water pollution index, it was established that the ecological state of the Siret River is characterised as unsatisfactory, and the water quality of the watercourse corresponds to the following classes: 'dirty' (class V) – 'extremely dirty' (class VI).

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