ECOLOGICAL ENGINEERING & ENVIRONMENTAL TECHNOLOGY

Ecological Engineering & Environmental Technology 2022, 23(4), 107–114
https://doi.org/10.12912/27197050/150311
ISSN 2719-7050, License CC-BY 4.0

Received: 2022.05.13
Accepted: 2022.05.25
Published: 2022.06.01

Surface Water Quality of the Prut River Basin in a Tourist Destination

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ABSTRACT

The aim of the article is to investigate the water quality in the Prut River, which tends to tourist destinations, and to establish the interdependence of the water pollution index with the number of tourists visited in the Yaremche Tourist Cluster. The article scientifically proves the indirect influence of tourist flow on water quality in the Prut River. Water samples from the Prut River were taken, such as pH, temperature, nitrates and nitrites, phosphates, ammonium and mineralization were analyzed. Using membrane tests Sensafe in water samples, we determined the content of the following metals: Ni, Co, Zn, Cd, Hg, Fe. Based on the results, we calculated the water pollution index, which is 0.52. It is established that the water is clean. IZV is determined at each point of water withdrawal in the dynamics during 2016–2020, the interdependence of water quality of the Prut River with the number of visitors to the tourist destination. The forecast of the index of water pollution and tourist flow for 2021–2025 is carried out using the data received in the operating system Exel. It is proved that with the growth of tourists the water quality deteriorates, although it fluctuates within the norm.

Keywords: Prut River, water quality, water pollution index, tourist flow, tourist destination.

INTRODUCTION

The main principle of the mountain tourist destination of the Carpathian region is ecological sustainability. The development of tourism should be correlated with the support of basic ecological processes, biological diversity and biological resources. Rivers are the waterways of the state, which form not only natural landscapes, their biogeocenoses and entire ecosystems, but also directly affect human life. There is also a feedback: the daily life of society, its production activities inevitably affect the waterways, their cleanliness or pollution, the ability to self-clean or, conversely, can lead to complete degradation and destruction. Unauthorized discharge of pollutants, such as heavy metals, slag, petroleum products and other toxic chemicals, reduces the quality of water in the river. In view of this, the development of effective measures and recommendations for solving these problems and scientific substantiation of rational water use and water protection of the largest tourist destination in Prykarpattia, Yaremche in the upper reaches of the Prut River basin is of great importance. Almost everywhere there is a steady trend of significant pollution of water bodies due to the disorderly discharge of wastewater from settlements, businesses and especially tourist accommodation.

MATERIALS AND METHODS

The methodological basis of the study of water bodies is their knowledge, which is based on a system-structural approach [Bezuhla et al., 2022], as well as the relevant categories and laws [Hydrologic Modeling, 2021]. According to this approach, the object of study is considered as a geosystem - a spatially ordered system formation within the geographical shell [Mandryk et al., 2020]. The system approach belongs to general scientific research methods, it is used for system analysis and system synthesis [Eigen and Schuster, 2012]. The goal of system analysis is to investigate the internal structure and organization of the river system, as well as its structure. [Arkhypova and Pernerovska, 2015]. Systemic synthesis aims to study the properties of the system of a water body as a whole, in particular its functions [Kravchynskyi et al., 2021]. This method distinguishes the following structural sections (structures) in the water body system.: territorial (elements and forms of location or manifestation of problems observed in the basin of this water body), functional (directions of pollution effects), sectoral (pollution sources), ingredient (pollutants), organizational and managerial (management system of water basin development) [Kravchynskyi et al., 2021].

There are several methods of ecological assessment of river water quality. In particular, Hryb V.Y [Hryb, 2003] developed the concept of ecological classification of surface water quality. Based on this classification, a method of comprehensive assessment of the state of river basins from water management positions was created. Boyarin M.V [Boyarin, 2006] recommends calculating the water quality index using a collection of key indicators relevant to a certain sector of application (domestic, drinking, fisheries, etc.). In the scientific literature we come across several proposals to assess the water quality of small rivers using a graphical method [Kukurudza, 2009; Chizhevskaya, 2002]. It is based on drawing up a model-map of pollution of a certain section of the river and deriving the ecological coefficient of water quality. Very close to these studies are the results published by Khilchevskyi V.K., Zabokrytska M.R., Sherstyuk N.P [Khilchevskyi et al., 2018], which provides a detailed description of the water quality of several rivers in the Western Bug basin. The Snizhko S.I [Snizhko, 2001] monograph should be mentioned among the substantial review works on the topic of water quality evaluation and methodological developments Jacyk A.V, Romanenko V.D [Jacyk and Romanenko, 2008; Korchemlyuk et al., 2019], describing in detail the algorithms for calculating the numerical values of the relevant criteria. Some of the methods are official documents in Ukraine, so most environmental practitioners and scientists use them to describe and evaluate individual water bodies [Kirilyuk, 2013]. Many researchers have addressed this topic regarding the assessment of water quality in the upper part of the Prut River. Among their studies are [Klymchuk et al., 2022; Korchemlyuk and Arkhypova, 2016; Odnorih et al., 2020], which provide a detailed examination of the ecological state in the Prut River and its basin as a whole. Having made a brief analysis of monitoring observations of this region in previous years, it can be stated that a network of hospitals for the study of various natural components has been established in the park. Among them, one of the leading places is the control over the hydrochemical parameters of both the river itself and related objects. A significant contribution to the study of rivers of the Carpathian region was made by Kravchinsky R.L, Khilchevsky V.K, Korchemlyuk M.V, Stefurak O.M. However, previous studies on the Prut River and individual ecosystems on its banks conducted by relevant and related organizations are quite fragmented, indicating the need and relevance of further detailed study of their condition to assess and predict the impact of increasing tourist flows from year to year on the state of surface natural waters [Kopei et al., 2020; Gomelia et al., 2018; Mandryk et al., 2020].

Water is a complex and versatile component that is involved in all biological and physicochemical interactions with the natural environment. In our opinion, it is advisable to take into account as many evaluation criteria as possible during the study of water quality [Kneysler et al., 2020; Komlev et al., 2021; Hryniuk and Arkhypova, 2018]. Only a comprehensive analysis of all influencing factors allows us to analyze and develop recommendations for improving quality characteristics. The components of water quality cover such basic quality parameters as physicochemical and biological. Physico-chemical parameters are a comparison of permissible concentrations of chemicals with the corresponding limit values [Jacik, 2002]. MAC is determined by the criterion that has the lowest subthreshold and threshold concentrations relative to certain established chemical parameters (normative indicators). However, the study of exclusively chemical composition of water has certain limitations on the adequate reflection of the qualitative state of the aquatic ecosystem [Kolesnik et al., 2017]. The method's merits are in determining the chemical composition of pollutants, while its disadvantages are in the expressiveness of the results and material costs [Korchemlyuk and Arkhypova, 2016]. In the modern surface water monitoring system there is a trend of transition from exclusively chemical to biological control, which is based on the study of changes in the structure and functioning of groups of benthic aquatic organisms that reflect the overall effect of the environment on surface water quality [Jacyk and Romanenko, 2008]. Field research was carried out in order to independently analyze the impact of discharges from existing treatment facilities on the area of the Carpathian NNP during the spring floods (Figure 1). Indicators of the presence of wastewater in river waters were adopted: BOC5 (biochemical oxygen consumption for five days); COD (chemical oxygen demand, mainly dichromate method, other permanganate); NH4 + (total ammonium); NO2- (nitrites); NO3 + (nitrates); PO4 (phosphates). Indicators of electrical conductivity, pH, dissolved oxygen and water temperature were measured by special portable devices. Laboratory study of hydrochemical parameters of selected water samples was performed in accordance with generally accepted ND and methods, using measuring equipment (FTA), the list of which is given in (Table 1).

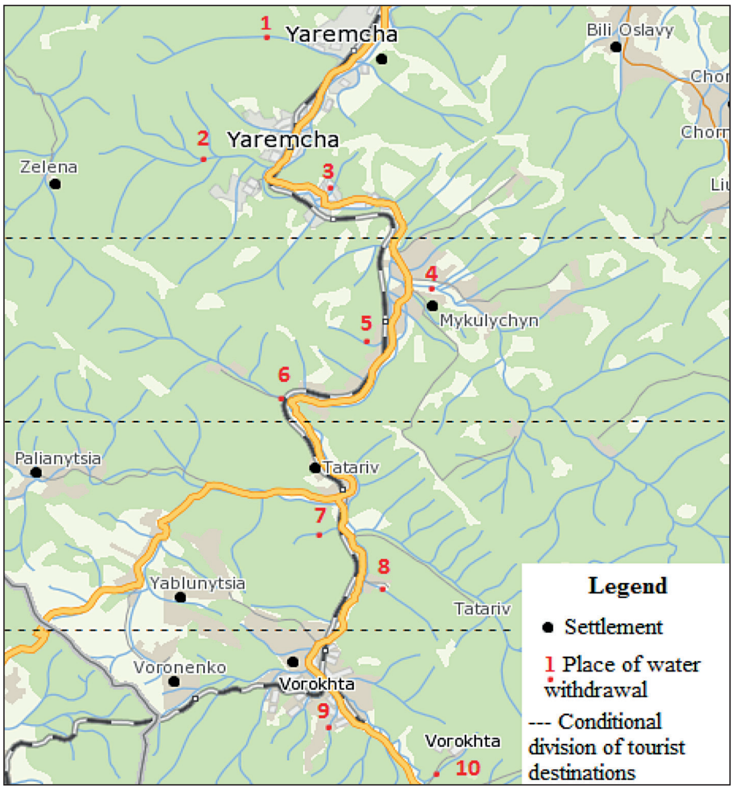

Figure 1. Scheme of the research area and location of observation points

Table 1. List of methods and ND used for laboratory study of hydrochemical parameters of water samples from the Prut River

No. groups of indicators	Indicator	Method of determination	Normative document
1	Sampling, temperature	Physical	GOST 17.1.5.05-85
2	Color, transparency, smell	Organoleptic	According to the instructions for the respective devices
3	Hydrogen index, mineralization	Potentiometric	According to the instructions for the respective devices
4	General and carbonate hardness, chloride content	Potentiometric	With the help of special test strips
5	Sulfate content	Titrometric	According to the instructions for the respective devices
6	Content of nitrites, nitrates, ammonium, phosphates, iron	Photometric	With the help of special test strips
7	BIA	Titrometric	KND 211.1.4.021 - 95

RESULTS

The evacuation of sewage from small hotels and rural estates in the Yaremche City Council remains an issue, as there are no centralized drainage systems in the great majority of tourist locations [Kinash et al., 2017; Ivashkiv et al., 2020]. The growth of the tourism industry leads to a high concentration of tourists and an increase in the relevant infrastructure [Nesterchuk et al., 2021]. Characterizing (Table 2), it is clear that the tourist flow increased rapidly until 2019 in 2020 decreased only due to the pandemic and quarantine restrictions. This has led to a deterioration in the development of the tourism business, a reduction in tourism revenues, but has relieved tourist destinations and reduced the negative impact on the environment, including a reduction in runoff from tourist estates and hotels.

It should also be noted that most industrial enterprises in the territory of Yaremche City Council do not have their own treatment facilities and discharge their untreated wastewater into the municipal city system and are considered secondary water users. This creates an additional burden on treatment systems and pollutes the rivers to which these effluents are discharged (Table 3).

After reviewing the scientific publications and production reports of enterprises studying the ecological status of water in the Prut River, it was found that the quality of its water upstream is significantly deteriorating. This fact is detrimental not only to the health of those who live on the river's banks and use water for domestic and industrial purposes, but it is also detrimental to the maintenance of the natural state of the entire region of the Prut River's upper reaches.In addition to being a nature reserve of national importance, this area is becoming an increasingly popular resort and important recreational facility.

Wastewater treatment plants in all settlements are point sources of pollution in the entire Prut basin. Visits to sampling points were preceded by analytical work to identify point sources of pollution, which are wastewater discharges from treatment plants in settlements and built treatment plants in some tourist facilities. In most situations, sewage treatment plants have depleted their resources and operate inefficiently. Their design and technology do not allow to provide wastewater treatment with modern pollutants.

At each of these observation points, river water samples were taken in accordance with current regulations (CR). Water parameters such as odor, temperature, acidity and mineralization (by salt content) were measured at the sampling site. The content of iron, nitrates, nitrites, and phosphates was also determined at the sampling site using test strips. The total mineralization of the samples was calculated later, after determining the content of all components of the sample. To determine the remaining indicators, the selected water samples were preserved in accordance with the established CR requirements, and delivered to the research laboratory in Yaremche.

Table 2. Visiting KNNP by tourists

Year	2016	2017	2018	2019	2020
Number of tourists	81099	69222	79840	93184	65404

Table 3. Information on discharges into the surface water bodies of pollutants in the composition return (wastewater), for 2020

Water user code	Return water volume without standard clean (million cubic meters)	The amount of pollutants discharged together with the return (wastewater)							
		Ammonium nitrogen T	BSC5 T	Suspended solids T	Nitrates T	Nitrites T	Sulfates T	Dry residue T	Phosphates kg
260469	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.80
260574	0.002	0.00	0.00	0.00	0.00	0.00	0.10	0.00	1.60
260611	0.441	0.50	1.10	3.00	2.60	0.10	28.70	128.9	111.40
260759	0.017	0.20	0.20	0.50	0.00	0.00	1.10	5.50	34.70
260997	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.30	2.00
260999	0.002	0.00	0.00	0.00	0.00	0.00	0.10	0.60	5.00
261070	0.005	0.00	0.00	0.10	0.00	0.00	0.30	1.30	9.50

The content of such heavy metals as: Cu, Ni, Co, Zn, Cd, Hg, Fe in water samples was determined by visual membrane tests for Sensafe drinking water [Klymchuk et al., 2022]. The following portable devices and reagents were used for operational monitoring according to the instructions:

- Ph meter, conductometer, salt meter, oximeter - AZ-86031;
- GPS tracker - GPSmap 60Cx;
- visual tests of nitrates and nitrites, phosphates and ammonium - Ptero;
- visual membrane tests to determine the content of heavy metals - Sensafe.

Based on the laboratory study of water samples from the Prut River, it was established that the water is quite clean; exceedances of the maximum concentration limit are not observed. The only exception may be a water sample within the city of Yaremche, where elevated concentrations of phosphates were detected (Table 4). There are 2 methods for assessing the quality of water resources: physico-chemical and biological, we used the first method [Boyarin, 2003]. There are such advantages of physicochemical methods as accurate assessment of water pollution of a particular pollutant; accounting for the combined effects of pollutants; possibility of water quality classification; relative simplicity of the method compared to others. To assess water quality, we used the method of WPI - water pollution index. WPI is calculated by six indicators [Klymchyk et al., 2022] (NH4 +, NO2 -, NP, phenols, dissolved O2, BSC5) according to the formula WPI = (1/6) Σ (Si / MACi), (1) where Si is the arithmetic mean water quality indicator; MAC - maximum allowable concentration. In formula (1) for O2, the MAC is divided by the average value of its concentration. Assessment of water quality is performed according to the following classes: I - very clean (WPI≤0,3); II - pure (0.310). We calculate the WPI for the Prut River (Table 5).

The value of the index of water pollution WPI, the calculation of which is given in table will be equal to: WPI = 3.12 / 6 = 0.52. Water with such WPI has class 2 (pure) (Figure 2). To determine the most polluted area of the NNP, we need to determine the WPI for each line in which water was taken for 5 years, for this we use the data of 2016–2020 taken from the laboratory of Yaremche KNNP (Table 6). In order to determine the interdependence of the number of tourists with the index of water

Table 5. Calculation index of water pollution for the river Prut

No.	Indicator	HDKi	Si	Si/HDKi
1	Dissolved oxygen	6.0	9.82	0.61
2	BSK	3.0	2.8	0.93
3	Ammonium ion	0.5	0.25	0.50
4	Nitrites	0.08	0.087	1.08
5	Petroleum products	0.05	0.00	0.00
6	Phenols	0.001	0.00	0.00
-	Σ	-	-	3.12

Table 4. The results of studies of the physico-chemical composition of river waters KNNP (Prut river basin)

Sample number	Place of sampling	Altitude n.r.m., geogr.	Temp., C	pH	Ammonium ion, mg/dm^3	Nitrite ion, mg/dm^3	Nitrate ion, mg/dm^3	Phosphates, mg/dm^3	Mineralization, mg/dm^3	A mixture of metals	Dissolved oxygen, mgO	Cu, mg/dm^3	BSK5, mg/dm^3
1	Prut River, adj. Dora	447 m.r.m. N48028’28.5” E024035'12.8"	3.40	8.30	0.15	0.100	0.60	0.000	162.00	100.00	9.60	0.02	2.40
2	Zhonka River, Yaremche	521 m.r.m. N48026’43.0” E024032'13.7"	4.30	8.50	0.25	0.100	15.90	0.000	46.00	100.00	10.00	0.03	2.86
3	Prut River, Suv. Market	514 m.r.m.N48026’30.3” E024032'55.3"	3.40	8.14	0.00	0.150	15.90	0.020	108.00	20.00	10.80	0.03	3.82
4	Prut River, Vorotishchi	607 m.r.m. N48028’19.5” E024035'0.9"	3.30	7.60	0.05	0.080	12.50	0.150	125.00	20.00	10.60	0.02	2.75
5	Prut River, Tatariv	680 m.r.m.	3.30	7.26	0.25	0.080	12.80	0.020	106.00	50.00	9.40	0.02	2.71
6	Prutets Yablunytskyi,	686 m.r.m.N48020'21.0"	3.20	7.59	0.25	0.150	9.40	0.050	147.00	50.00	10.40	0.04	3.30
7	Kamyanytsia River (Tatariv village)	687 m.r.m. N48019’39.8” E024034,5’51.3"	3.00	7.76	0.25	0.050	8.60	0.020	68.00	20.00	9.40	0.02	2.50
8	Prut River, (Vorokhta town)	722 m.r.m.N48017’52.5" E024034'08.3"	3.00	7.44	0.25	0.080	0.80	0.020	155.00	10.00	9.30	0.02	3.49
9	Prutets River (Mykulychyn village)	584 m.r.m. N48024’16” E024036'58"	3.00	7.55	0.25	0.80	1.9	0.020	97.00	20	10.00	0.02	2.14
10	Prut River (Hoverlyanske PONDV)	1300 m.r.m.N4809’52.4” E024032'10.8"	2.80	7.90	0	0	0.3	0.05	43.00	10	8.79	0.02	2.19

pollution, we calculated the IPR for each year during 2016–2020, using the data of KNNP (Table 7). A trend line was also constructed using the Exel operating system and the acquired data, indicating that as the number of tourists increases, so does water pollution (Figure 3, 4). Using pre-calculated data and the Excel operating system, we made a forecast of the interdependence of the water pollution index and the volume of tourist flow for 2021–2025 (Table 8). The prognosis shows that as tourism grows, so does the index of water pollution (Figure 5), necessitating the establishment of a maximum permitted recreational load.

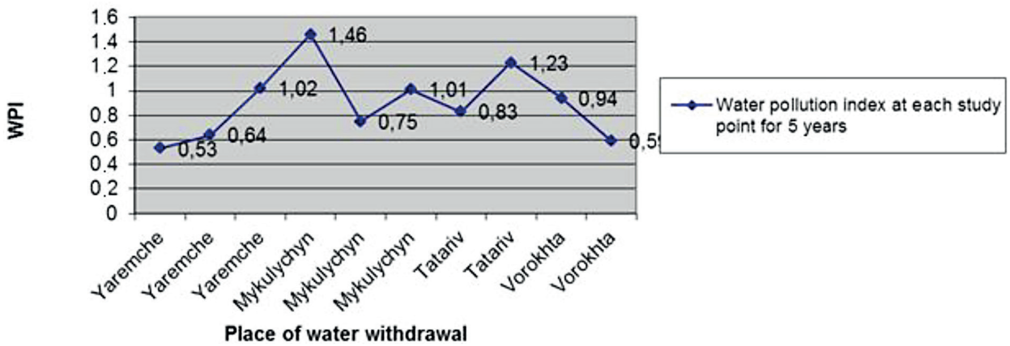

Figure 2. Index of water pollution in KNNP for 5 years

Table 6. Calculation of WPI in each water collection point for 5 years

Sample number	Place of selection	WPI	Water class
1	Prut River, Dora	0.53	Clean
2	Zhonka River, Yaremche	0.64	Clean
3	Prut River, near Suv. market	1.02	Moderately polluted
4	Prut River, "Vorotishche"	1.46	Moderately polluted
5	Prut river, Tatariv village	0.75	Clean
6	Prutets Yablunytskyi, village	1.01	Moderately polluted
7	Kamyanytsia River, Tatariv village	0.83	Clean
8	Prut River, Vorokhta	1.23	Moderately polluted
9	Prutets Chemyhivskyi, Mykulychyn village	0.94	Clean
10	Prut River (Hoverlyanske PONDV, above the farm "Zaroslyak")	0.59	Clean

Table 7. Index of water pollution for 2016–2020

Year	2016	2017	2018	2019	2020
Number of tourists	81099	69222	79840	93184	65404
WPI	0.96	0.48	0.64	0.79	0.58

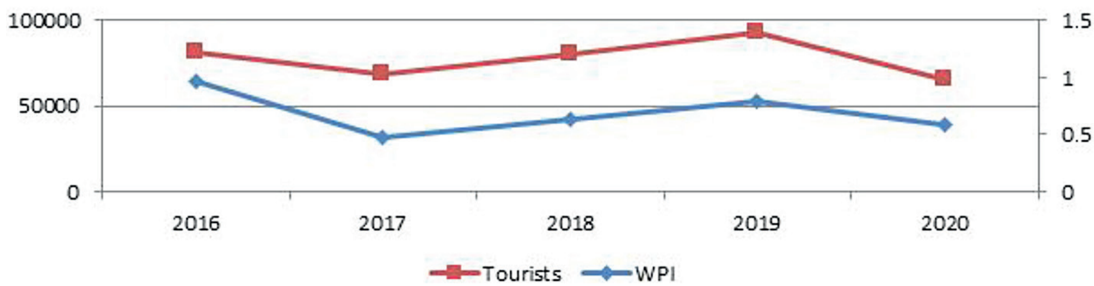

Figure 3. Graph of the relationship of the WPI with the number of tourists

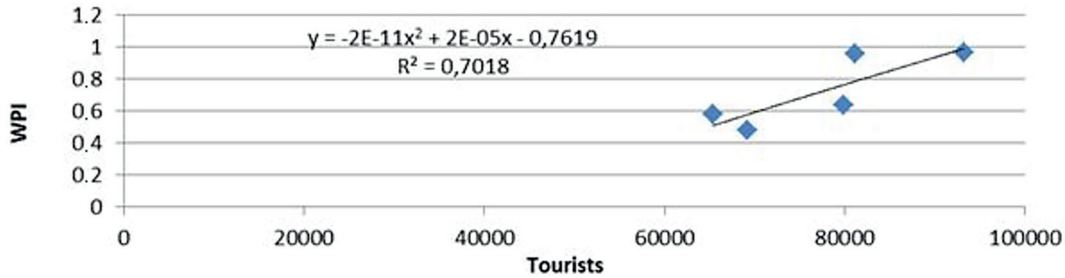

Figure 4. Trend line

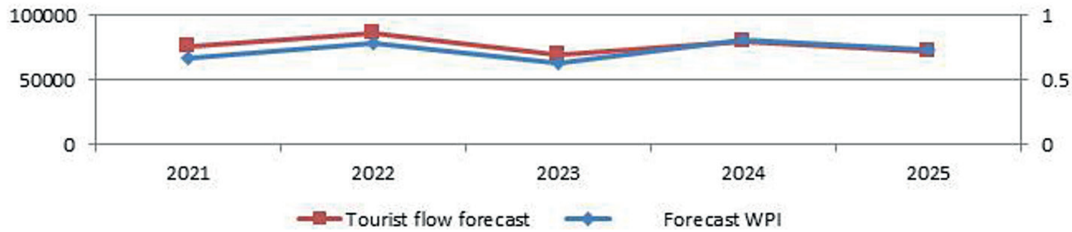

Figure 5. Graph-forecast of the connection of WPI with the number of tourists in 2021–2025

Table 8. Forecast of the interdependence of WPI and the volume of tourist flow in 2021–2025

Year	Forecast WPI	Tourist flow forecast
2021	0.67	75521
2022	0.79	85943
2023	0.63	69567
2024	0.81	79623
2025	0.74	72546

CONCLUSIONS

Thus, we evaluated the water quality in the Prut River, which flows through Yaremche, a popular tourist site, and established the interdependence of the WPI with the number of tourists visited in the largest tourist destination in the Carpathians. Based on the selected water samples in the Prut River, the water pollution index in 2021 (spring flood period) was calculated and the water was determined to be clean.

Significant exceedances of the WPI were not detected at each sampling point during 2016–2020, but at points located in Yaremche and Tatariv, the water is significantly contaminated. With the help of the Exel operating system, we forecast the water pollution index and the tourist flow for 2021–2025, which allowed us to see that as the number of tourists increases, the water quality deteriorates, though it swings within the mean. The study's findings imply that the maximum permitted recreational load in the Yaremche tourist attraction should be established and the necessity for wastewater discharge management by owners of tourist estates and hotels, as well as the feasibility of modifying sewerage and drainage systems in private areas.

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