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Spatial Distribution Patterns of the Hydro-Ecosystems' Quality Indicators in the Ukrainian Carpathians

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Abstract

This study is devoted to the two major hydro-ecosystems of the Carpathian region in Ukraine, the Dniester and Danube Rivers. For the first time, the patterns of changes in the ecosystems' quality parameters were established by means of developing functional dependences among the ecological standard values of the composite quality indicators of natural waters and the river length and terrain altitude. Using the statistical processing of the data, the quality monitoring of the upper reaches of Dniester and Danube ecosystems in the Ukrainian Carpathians was conducted for the period from 2001 to 2019. The data on the Composite Potential Quality Indicators standard values was gathered for the heights of the Carpathian region: at 50 m interval for the altitude up to 1,000 m, and at 100 m interval for more than 1,000 m altitude. The acquired dependencies can be used as the territorial background standard values of the ecological indicators of basin ecosystems. It will help to scientifically substantiate the ecologically safe values of the anthropogenic pressure.

Keywords

Hydro-ecosystems; Integrated water quality; Functional dependences

Introduction

According to the Ukrainian environmental legislation[1] (Law of 2017), environmental quality assessment, including water resources, is carried out to set the maximum permissible levels of various environmental indicators. It guarantees the environmental safety to the population and ensures natural resource management, genetic conservation and sustainable development.

The Ukrainian Carpathians comprise the basins of four major rivers (Mandryk *et al*., 2017) that are grouped into two regional hydro-ecosystems (Figure 1): Dniester (right-bank tributaries in the territories of Lviv and Ivano-Frankivsk oblasts) and the Danube rivers. Later includes the Prut river within the territories of Ivano-Frankivsk and Chernivtsi oblasts, together with the Siret tributary in Chernivtsi oblast and the Tysa tributary in Transcarpathian oblast. These waterways are of international importance, as their basins are located within several countries. The Prut and the Siret rivers flow through Ukraine, Romania and Moldova; the Tysa river crosses through Romania, Hungary and Slovakia; the Dnister river flows through Moldova (Kinash *et al*., 2019). For the reason of cross-boundary water flows, this investigation and modeling of the upstream quality of international water flows becomes an important task (Odnorih *et al*., 2020).

The watershed of the Ukrainian Carpathians covers about 28,000 watercourses, most of which are small ones with a total length of more than 50,000 km. The river network density averages 1-1.5 km per km^2 (Prykhodko *et al*., 2020). Due to the mountainous terrain of the Carpathian ranges, the basin areas are small. Small rivers (up to 10 km long) dominate and account for almost 98% of all watercourses (Khilchevskyi, Kurylo and Sherstyuk, 2018). There are 457 rivers over 10 km in length. In the Prut river basin, all rivers, except for the main river, are classified as small (Karpinski *et al*. 2018). There are seven rivers having100 to 300 km length in the basins of the Dniester, Tysa and Siret rivers. The total area of river surface basins in the Carpathians exceeds 37,500 km^2 (Mandryk *et al*., 2020).

The purpose of the study is to establish the background values of the qualitative parameters of the hydro-ecosystems of the Ukrainian Carpathians and to determine the ecological standards of the components of natural waters within the study area. To achieve this, the general and individual patterns of their spatial distribution based on statistical processing of data from the results of hydro-chemical observations has been studied, using data from the state network for monitoring the quality of water bodies for the period 2001-2019.

Methodology

To undertake the study, following research methods were used. First was an analysis of environmental information on hydro-ecosystems and its processing; and second was the statistical and mathematical analysis using Microsoft Excel and TableCurve 2D software (Stevens, Springer and Ledbetter, 2011).

One of the complex criteria used to assess water quality in Ukraine is the Water Pollution Index (WPI). The WPI is a composite quantitative assessment of water quality by a set of key indicators and types of water use (Singh, Yadav and Yadava, 2016). This integral index is calculated by the following formula:

$$WPI = \sum(C/MPC)/n, \tag{1}$$

where MPC is maximum permissible concentration (value) of the indicator;
C is actual concentration (value) of the indicator; and
n is number of indicators.

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[1] https://zakon.rada.gov.ua/laws/main/en/t1

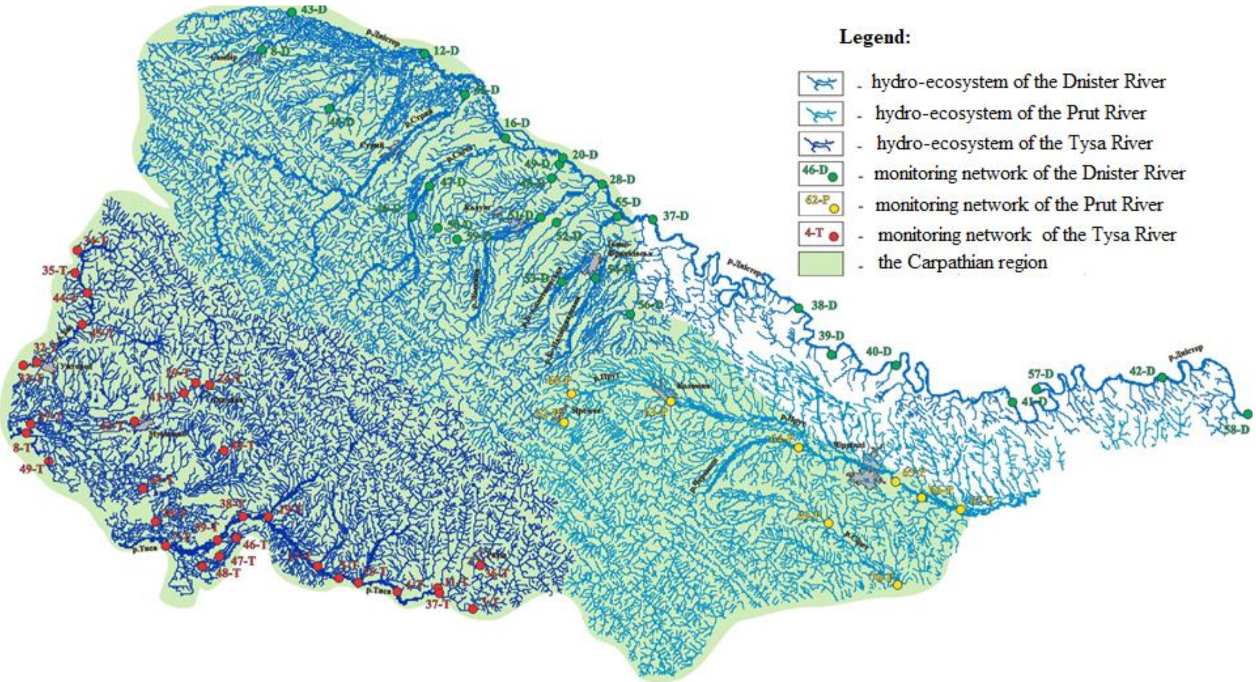


Figure 1: State monitoring network of water bodies of the Carpathian region of Ukraine

For surface waters, the number of indicators used to calculate the WPI should not be less than 5 regardless of whether they exceed the MPC or not. But they must include the dissolved oxygen (DO) and biological oxygen demand for 5 days (BOD_5) (Shmandiy *et al*., 2017). The advantages of this index are the ease of calculation, data accessibility and availability. That is why it is most often used in the State Water Resources Agency of Ukraine (the central executive body, which implements the state policy in the field of water management development) to assess river pollution.

Despite popular usage of WPI, the WPI does not sufficiently assess clean rivers. In the classification, there is quality class 1 (very clean water) having WPI < 0.2, and class 2 (clean water) having WPI from 0.2 to 1 (Government of Ukraine, 2018). It is believed that the Water Pollution Index is not flexible and sufficient to assess the degree of self-purification of rivers, the dynamics of changes in the ecological potential depending on the height and width of the terrain, water content of rivers, dynamics of changes in the anthropogenic load, and so on.

Considering the above-explained limitations of WPI, the Composite Potential Quality Indicator (CPQI) (Arkhypova *et al*., 2019) was used to determine natural regularities in this article. The CPQI is obtained by adding the coefficients of indicator reserves (relative reserve capacity) if the actual value is less than the permissible value, and by subtracting if the actual value is greater than the allowablepermissible value. The product is divided by the number of values used. The excess of the permissible value on the actual value shows the coefficient of stock (potential, reserve capacity) of the hydroecosystem. Moreover, the excess of the actual value over the permissible value shows the stock deficit ratio (relative reserve shortage).

The outcome is divided by the number of indicators used.

$$CPQI = \frac{1}{n}\sum_{i=1}^{n} x_i; \quad x_i = \begin{cases} \frac{QS_i}{C_i}, if \frac{QS_i}{C_i} > 1 \\ -\frac{C_i}{QS_i}, if \frac{QS_i}{C_i} < 1 \end{cases}, \qquad (2)$$

where QS_i is the water quality standard for the i^{th} indicator–limit values of water status indicators that meet the requirements of different types of water use;
C_i is actual value of water quality for the i^{th} indicator;
n is the number of indicators.

The water samples for physicochemical studies were taken at least 4 times a year (in different hydrological seasons) in accordance with the procedure prescribed by the normative document KND 211.1.1.106-2003 (Zasidko *et al*., 2019). The following indicators were used to calculate the WPI: NH_4^+ (MPC – 0.5 mg/dm^3), NO_2^- (MPC – 0.08 mg/dm^3), NO_3^- (MPC – 40.0 mg/dm^3), BOD_5 (MPC – not more than 3 mg/dm^3), dissolved oxygen (MPC – not less than 6 mg O/dm^3).

This research used a statistical model based on the mathematical processing of the statistical dataset. The data included hydro-chemical analyses of surface waters conducted by the certified laboratories of the Dniester Basin Authority and the Analytical Control Department of the Carpathian National Nature Park. Each numerical result, corresponding to a specific monitoring section, is an integrated value of over 50 values, as the samples were taken every year, four times a year. The existing hydro-chemical monitoring database was processed by the method of determining the geometric mean:

$$F(x) = \ln x, \qquad (3)$$

The geometric mean reflects the arithmetic mean of the logarithms of individual values. However, at the same time, the effect of the extreme values on the mean is greatly reduced, which is often observed in the variation series of monitoring the quality of natural waters (Singh, Yadav and Yadava, 2016).

TableCurve 2D was used to obtain linear functional dependences and regression equations for statistical series of observations. Functional dependence equation, equation coefficients, and calculated statistics parameters are represented in the description above the dependences curve. TableCurve 2D uses four goodness-of-fit statistics.

In the following descriptions, *SSM* is the sum of squares of the mean; *SSE* – the sum of squares of errors (residuals); n is the total number of data values; m is the number of coefficients in the model; *DOF* is the degree of freedom (Krešić and Stevanović, 2010).

$$DOF = n-m, \qquad (4)$$

where r^2 coefficient of determination (r squared):

$$r^2 = 1 - SSE/SSM. \qquad (5)$$

Degree-of-freedom adjusted coefficient of determination:

$$DOF\ r^2 = (1 - SSE*(n-1))/(SSM*(DOF-1)). \qquad (6)$$

Calculated standard errors:

$$StdErr = sqrt(SSE/DOF). \qquad (7)$$

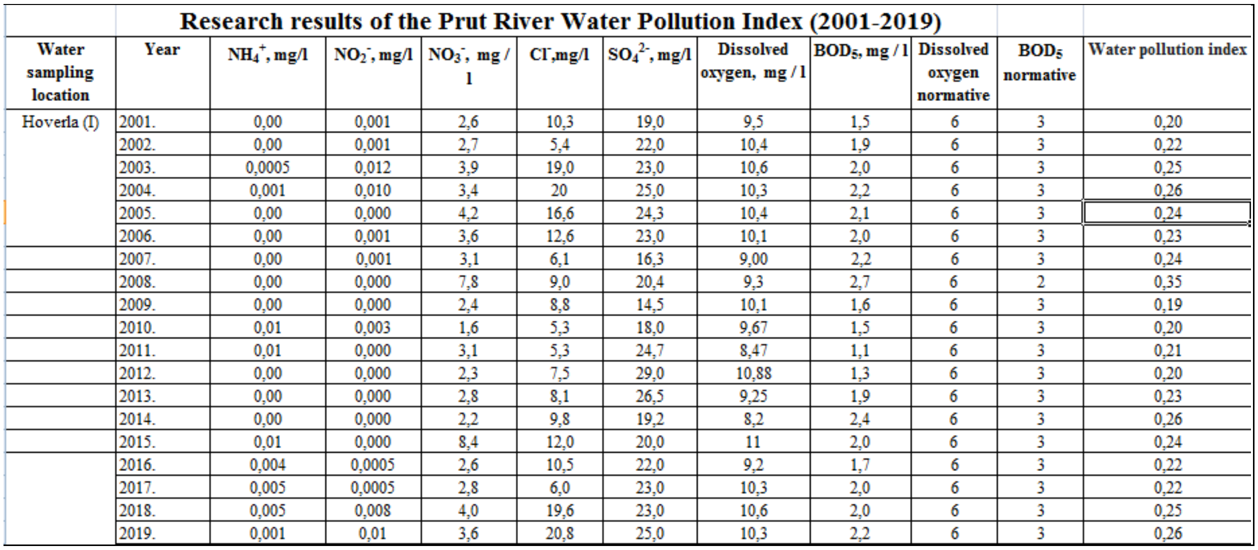
F-statistics:

$$F\text{-}stat = ((SSM-SSE)/(m-1))/(SSE/DOF). \qquad (8)$$

The dependence between data sets will be closer if the r^2 values approach 1.0 (0 is the total lack of correlation), the standard error decreases to zero, and the F-statistics goes to infinity. For the upper reaches of the tributaries of the Danube ecosystem, the ecological monitoring database was processed using formula (1). The WPI calculations gave long-term values sets of the composite quality indicator, which reveals certain patterns of spatial distribution. In hydrometeorological calculations, the concept of standard value (as the long-term annual average of the indicator value) is used. For the long-term annual average of WPI values (8 monitoring sections at different altitudes), dependence curves and functional linear regression equations were obtained that can be the basis for determining the WPI standard value.

Results

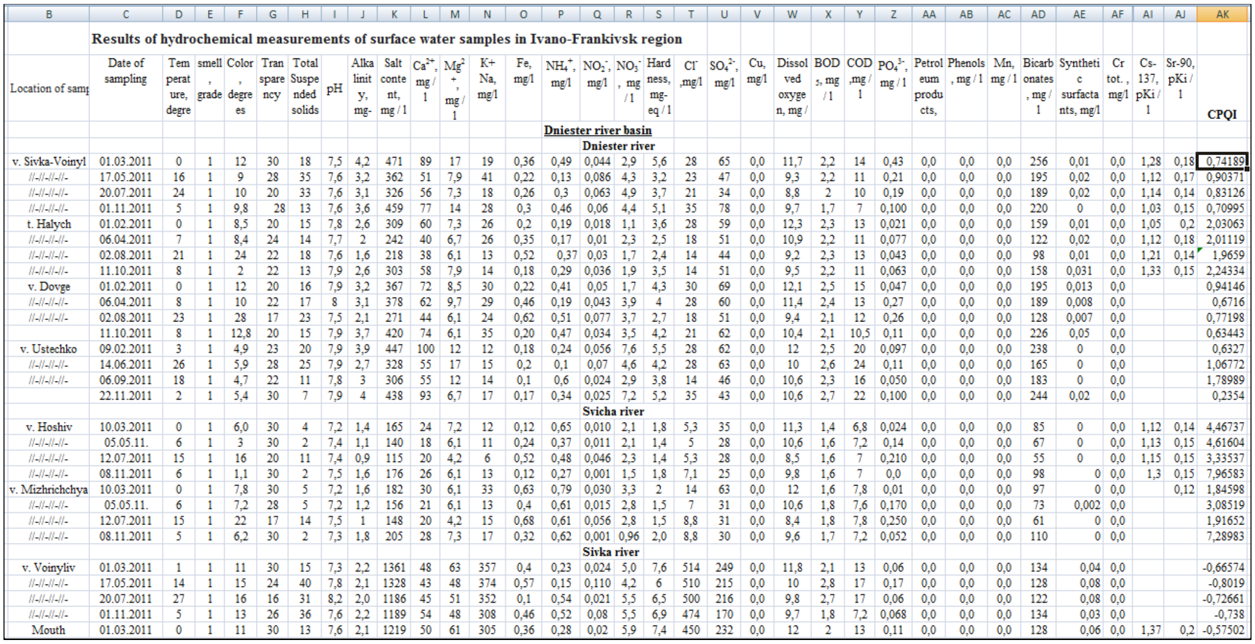
The general and individual regularities of spatial distribution of water quality indicators on the basis of statistical processing of data of readings of the hydro-chemical observations were analyzed, using data of the state network for monitoring of quality of water objects for the period 2001-2019 (Figure 2). An example of calculating the Water Pollution Index is shown in Figure 2, and an example of calculation of the CPQI is depicted in Figure 3.



Research results of the Prut River Water Pollution Index (2001-2019)

Water sampling location	Year	NH_4^+, mg/l	NO_2^-, mg/l	NO_3^-, mg / l	Cl^-,mg/l	SO_4^{2-}, mg/l	Dissolved oxygen, mg / l	BOD_5, mg / l	Dissolved oxygen normative	BOD_5 normative	Water pollution index
Hoverla (I)	2001.	0,00	0,001	2,6	10,3	19,0	9,5	1,5	6	3	0,20
	2002.	0,00	0,001	2,7	5,4	22,0	10,4	1,9	6	3	0,22
	2003.	0,0005	0,012	3,9	19,0	23,0	10,6	2,0	6	3	0,25
	2004.	0,001	0,010	3,4	20	25,0	10,3	2,2	6	3	0,26
	2005.	0,00	0,000	4,2	16,6	24,3	10,4	2,1	6	3	0,24
	2006.	0,00	0,001	3,6	12,6	23,0	10,1	2,0	6	3	0,23
	2007.	0,00	0,001	3,1	6,1	16,3	9,00	2,2	6	3	0,24
	2008.	0,00	0,000	7,8	9,0	20,4	9,3	2,7	6	2	0,35
	2009.	0,00	0,000	2,4	8,8	14,5	10,1	1,6	6	3	0,19
	2010.	0,01	0,003	1,6	5,3	18,0	9,67	1,5	6	3	0,20
	2011.	0,01	0,000	3,1	5,3	24,7	8,47	1,1	6	3	0,21
	2012.	0,00	0,000	2,3	7,5	29,0	10,88	1,3	6	3	0,20
	2013.	0,00	0,000	2,8	8,1	26,5	9,25	1,9	6	3	0,23
	2014.	0,00	0,000	2,2	9,8	19,2	8,2	2,4	6	3	0,26
	2015.	0,01	0,000	8,4	12,0	20,0	11	2,0	6	3	0,24
	2016.	0,004	0,0005	2,6	10,5	22,0	9,2	1,7	6	3	0,22
	2017.	0,005	0,0005	2,8	6,0	23,0	10,3	2,0	6	3	0,22
	2018.	0,005	0,008	4,0	19,6	23,0	10,6	2,0	6	3	0,25
	2019.	0,001	0,01	3,6	20,8	25,0	10,3	2,2	6	3	0,26

Figure 2: Example of the Water Pollution Index calculation with monitoring data processing



B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AI	AJ	AK
	Results of hydrochemical measurements of surface water samples in Ivano-Frankivsk region																																
Location of samp	Date of sampling	Temperature, degre	smell , grade	Color , degrees	Transparency	Total Suspended solids	pH	Alkalinity, mg-	Salt content, mg / l	Ca^{2+}, mg / l	Mg^{2+}, mg / l	K+ Na, mg/l	Fe, mg/l	NH_4^+, mg/l	NO_2^-, mg/l	NO_3^-, mg / l	Hardness, mg-eq / l	Cl^- ,mg/l	SO_4^{2-}, mg/l	Cu, mg/l	Dissolved oxygen, mg /	BOD_5, mg / l	COD ,mg / l	PO_4^{3-}, mg / l	Petroleum products,	Phenols , mg / l	Mn, mg / l	Bicarbonates , mg / l	Synthetic surfactants, mg/l	Cr tot. , mg/l	Cs-137, pKi / l	Sr-90, pKi / l	**CPQI**
														Dniester river basin																			
															Dniester river																		
v. Sivka-Voinyl	01.03.2011	0	1	12	30	18	7,5	4,2	471	89	17	19	0,36	0,49	0,044	2,9	5,6	28	65	0,0	11,7	2,2	14	0,43	0,0	0,0	0,0	256	0,01	0,0	1,28	0,18	0,74189
//-//-//-//-	17.05.2011	16	1	9	28	35	7,6	3,2	362	51	7,9	41	0,22	0,13	0,086	4,3	3,2	23	47	0,0	9,3	2,2	11	0,21	0,0	0,0	0,0	195	0,02	0,0	1,12	0,17	0,90371
//-//-//-//-	20.07.2011	24	1	10	20	33	7,6	3,1	326	56	7,3	18	0,26	0,3	0,063	4,9	3,7	21	34	0,0	8,8	2	10	0,19	0,0	0,0	0,0	189	0,02	0,0	1,14	0,14	0,83126
//-//-//-//-	01.11.2011	5	1	9,8	28	13	7,6	3,6	459	77	14	28	0,3	0,46	0,06	4,4	5,1	35	78	0,0	9,7	1,7	7	0,100	0,0	0,0	0,0	220	0	0,0	1,03	0,15	0,70995
t. Halych	01.02.2011	0	1	8,5	20	15	7,8	2,6	309	60	7,3	26	0,2	0,19	0,018	1,1	3,6	28	59	0,0	12,3	2,3	13	0,021	0,0	0,0	0,0	159	0,01	0,0	1,05	0,2	2,03063
//-//-//-//-	06.04.2011	7	1	8,4	24	14	7,7	2	242	40	6,7	26	0,35	0,17	0,01	2,3	2,5	18	51	0,0	10,9	2,2	11	0,077	0,0	0,0	0,0	122	0,02	0,0	1,12	0,18	2,01119
//-//-//-//-	02.08.2011	21	1	24	22	18	7,6	1,6	218	38	6,1	13	0,52	0,37	0,03	1,7	2,4	14	44	0,0	9,2	2,3	13	0,043	0,0	0,0	0,0	98	0,01	0,0	1,21	0,14	1,9659
//-//-//-//-	11.10.2011	8	1	2	22	13	7,9	2,6	303	58	7,9	14	0,18	0,29	0,036	1,9	3,5	14	51	0,0	9,5	2,2	11	0,063	0,0	0,0	0,0	158	0,031	0,0	1,33	0,15	2,24334
v. Dovge	01.02.2011	0	1	12	20	16	7,9	3,2	367	72	8,5	30	0,22	0,41	0,05	1,7	4,3	30	69	0,0	12,1	2,5	15	0,047	0,0	0,0	0,0	195	0,013	0,0			0,94146
//-//-//-//-	06.04.2011	8	1	10	22	17	8	3,1	378	62	9,7	29	0,46	0,19	0,043	3,9	4	28	60	0,0	11,4	2,4	13	0,27	0,0	0,0	0,0	189	0,008	0,0			0,6716
//-//-//-//-	02.08.2011	23	1	28	17	23	7,5	2,1	271	44	6,1	24	0,62	0,51	0,077	3,7	2,7	18	51	0,0	9,4	2,1	12	0,26	0,0	0,0	0,0	128	0,007	0,0			0,77198
	11.10.2011	8	1	12,8	20	15	7,9	3,7	420	74	6,1	35	0,20	0,47	0,034	3,5	4,2	21	62	0,0	10,4	2,1	10,5	0,11	0,0	0,0	0,0	226	0,05	0,0			0,63443
v. Ustechko	09.02.2011	3	1	4,9	23	20	7,9	3,9	447	100	12	12	0,18	0,24	0,056	7,6	5,5	28	62	0,0	12	2,5	20	0,097	0,0	0,0	0,0	238	0	0,0			0,6327
//-//-//-//-	14.06.2011	26	1	5,9	28	25	7,9	2,7	328	55	17	15	0,2	0,1	0,07	4,6	4,2	28	63	0,0	10	2,6	24	0,11	0,0	0,0	0,0	165	0	0,0			1,06772
//-//-//-//-	06.09.2011	18	1	4,7	22	11	7,8	3	306	55	12	14	0,1	0,6	0,024	2,9	3,8	14	46	0,0	10,6	2,3	16	0,050	0,0	0,0	0,0	183	0	0,0			1,78989
	22.11.2011	2	1	5,4	30	7	7,9	4	438	93	6,7	17	0,17	0,34	0,025	7,2	5,2	35	43	0,0	10,6	2,7	22	0,100	0,0	0,0	0,0	244	0,02	0,0			0,2354
															Svicha river																		
v. Hoshiv	10.03.2011	0	1	6,0	30	4	7,2	1,4	165	24	7,2	12	0,12	0,65	0,010	2,1	1,8	5,3	35	0,0	11,3	1,4	6,8	0,024	0,0	0,0	0,0	85	0	0,0	1,12	0,14	4,46737
//-//-//-//-	05.05.11.	6	1	3	30	2	7,4	1,1	140	18	6,1	11	0,24	0,37	0,011	2,1	1,4	5	28	0,0	10,6	1,6	7,2	0,14	0,0	0,0	0,0	67	0	0,0	1,13	0,15	4,61604
//-//-//-//-	12.07.2011	15	1	16	20	11	7,4	0,9	115	20	4,2	6	0,52	0,48	0,046	2,3	1,4	5,3	28	0,0	8,5	1,6	7	0,210	0,0	0,0	0,0	55	0	0,0	1,15	0,15	3,33537
//-//-//-//-	08.11.2011	6	1	1,1	30	2	7,5	1,6	176	26	6,1	13	0,12	0,27	0,001	1,5	1,8	7,1	25	0,0	9,8	1,6	7	0,0	0,0	0,0	0,0	98	0	0,0	1,3	0,15	7,96583
v. Mizhrichchya	10.03.2011	0	1	7,8	30	5	7,2	1,6	182	30	6,1	33	0,63	0,79	0,030	3,3	2	14	63	0,0	12	1,6	7,8	0,01	0,0	0,0	0,0	97	0	0,0		0,12	1,84598
//-//-//-//-	05.05.11.	6	1	7,2	28	5	7,2	1,2	156	21	6,1	13	0,4	0,61	0,015	2,8	1,5	7	31	0,0	10,6	1,8	7,6	0,170	0,0	0,0	0,0	73	0,002	0,0			3,08519
//-//-//-//-	12.07.2011	15	1	22	17	14	7,5	1	148	20	4,2	15	0,68	0,61	0,056	2,8	1,5	8,8	31	0,0	8,4	1,8	7,8	0,250	0,0	0,0	0,0	61	0	0,0			1,91652
//-//-//-//-	08.11.2011	5	1	6,2	30	2	7,3	1,8	205	28	7,3	17	0,32	0,62	0,001	0,96	2,0	8,8	30	0,0	9,6	1,7	7,2	0,052	0,0	0,0	0,0	110	0	0,0			7,28983
															Sivka river																		
v. Voinyliv	01.03.2011	1	1	11	30	15	7,3	2,2	1361	48	63	357	0,4	0,23	0,024	5,0	7,6	514	249	0,0	11,8	2,1	13	0,06	0,0	0,0	0,0	134	0,04	0,0			-0,66574
//-//-//-//-	17.05.2011	14	1	15	24	40	7,8	2,1	1328	43	48	374	0,57	0,15	0,110	4,2	6	510	215	0,0	10	2,8	17	0,17	0,0	0,0	0,0	128	0,08	0,0			-0,8019
//-//-//-//-	20.07.2011	27	1	16	16	31	8,2	2,0	1186	45	51	352	0,1	0,54	0,021	5,5	6,5	500	216	0,0	9,8	2,7	17	0,06	0,0	0,0	0,0	122	0,08	0,0			-0,72661
//-//-//-//-	01.11.2011	5	1	13	26	36	7,6	2,2	1189	54	48	308	0,46	0,52	0,08	5,5	6,9	474	170	0,0	9,7	1,8	7,2	0,068	0,0	0,0	0,0	134	0,03	0,0			-0,738
Mouth	01.03.2011	0	1	11	30	13	7,6	2,1	1219	50	61	305	0,36	0,28	0,02	5,9	7,4	450	232	0,0	12	2	13	0,11	0,0	0,0	0,0	128	0,06	0,0	1,37	0,2	-0,57502

Figure 3: Example of calculation of CPQI by the monitoring data processing

The pollution level and state of the hydro-ecosystem are assessed based on the value of the Water Pollution Index or the Composite Potential Quality Indicator (Table 1).

Table 1: Numerical criteria for the aquatic ecosystem state assessment based on the values of composite quality indicators

Water pollution level	*WPI value*	*Water quality class*	*Aquatic ecosystem state*	*CPQI value*
Very clean	<0.2	1	buffer state (ecological balance area)	>5
Clean	0.2-0.1	2	optimal state	3-5
Low pollution	1.0-2.0	3	adaptation tension	1-3
Medium pollution	2.0-4.0	4	pessimum zone	-1<CPQI<1
High pollution	4.0-6.0	5	critical state	-3<CPQI<-1
Very high pollution	6.0-10.0	6	crisis state	-3 <CPQI<-5
Extreme pollution	>10.0	7	catastrophic state (ecological disaster area)	<-5

On the basis of the results shown in Table 1, the analysis was performed for different hydrological seasons and monitoring sections. The average annual values were calculated, and the data obtained for the period of 2001-2019 were summarized. It is observed that the water quality at altitudes above 500 m in the Ukrainian Carpathians generally meets the reference conditions.

The long-term monitoring results of surface waters in mountain areas, the beds of which are located at altitudes above 500 m, show that the water belongs to the quality classes “clean”, “fairly clean”, “good” or “very good”. The discharge of sewage water from mountain settlements diffuses pollution in 99% of the cases.

For the upper reaches of the tributaries of the Danube ecosystem, the functional dependences among the changes in the composite quality indicator of surface water ecosystems and the river length and terrain altitude were obtained (Figures 4, 5). The obtained curve (Figure 4) of the dependence between the Water Pollution Index standard value and the terrain altitude for the Prut river passes through the centre of the cluster of observation points, the curves describing the 95% confidence interval are nearby. Thus, there is a close functional dependence between these properties. The coefficient of determination ($D=r^2=0.82$) shows that 90% of the variance in Y is due to the variance in X. The actual quality state of the Danube ecosystem in Ukraine to the altitude of 700 m is the optimal state, and below this level is the state of adaptation tension.

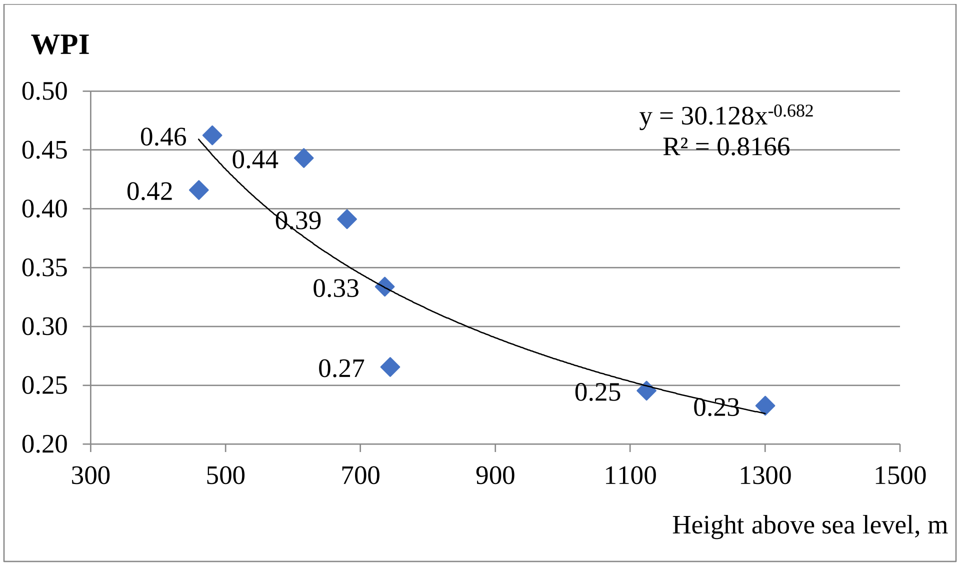


Figure 4: Functional dependence between the change in the Water Pollution Index of the Danube ecosystem and the terrain altitude in the Ukrainian Carpathians

The significance of the coefficient ($r^2=0.82$) was estimated using the F-distribution quantiles tables and the tables of coefficient significance. The latter have two entries – the number of degrees of freedom, which is equal to the number of observations minus 2; the significance level is accepted at 5%. The critical coefficient value was found after determining the significance level and the number of degrees of freedom. In this case, the value of the coefficient $r^2=0.82$ was greater than the table critical value $r^2=0.707$ (for sample volume 11 and significance level p=0.05) (Mandryk *et al*., 2020). That is, the null hypothesis of no correlation between the properties was rejected. The hypothesis that there is a significant correlation between the properties was accepted.

Therefore, for the first time, the functional dependence between the change in the long-term annual average of the Water Pollution Index in the Danube ecosystem in the Ukrainian Carpathians and the altitude is represented. It is expressed by the following significant regression equation:

$$WPI = 30.128 \cdot H^{0,682}, \quad (9)$$

where H is the absolute height of the terrain, m

Despite the continuous diffusion of pollution, which was observed in the Danube ecosystem (even with the values of WPI<1), a close relationship between the composite Water Pollution Index and the length of the river from its source is evident (Figure 5).

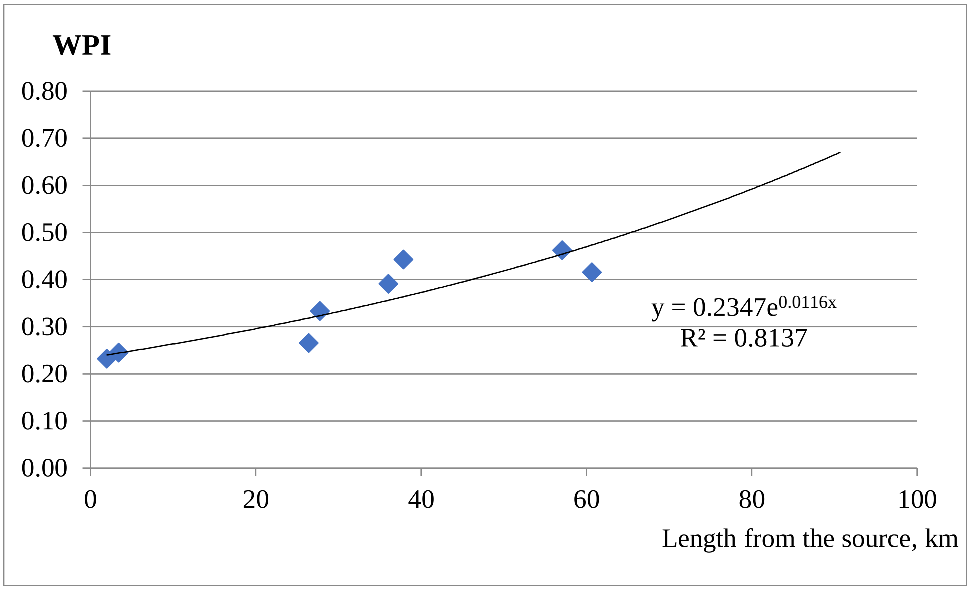


Figure 5: Functional dependence between the quality standard value of the water bodies of the Prut ecosystem and their length from the source

F-test or F-statistics is calculated using the software. The information on the distribution of this value allows to check the statistical significance of the regression model based on the value of the coefficient of determination. In fact, these tests test the hypothesis that the true coefficient of determination is equal to zero. The critical values of F-test were looked up in standard tables. The proposed hypothesis (on the existence of close dependence) is rejected if the table value of *Fstat* is greater than the calculated one and it is accepted as true if *Fstat* is less than the calculated one. In all the cases considered, the proposed hypothesis was accepted as true if the significance level was assumed to be 1%. In this case, *Fstat=56.88 (calculated)>Fstat=5.99* (table value) (Toms and Lesperance, 2003). Thus, the correlation between the properties is not accidental, it is significant.

Therefore, as a result, for the first time the linear functional dependence between the change in the Water Pollution Index of the Danube ecosystem and the length of the river in the Carpathian National Nature Park was found. It is described by the following significant regression equation:

$$WPI=0.235\cdot e^{0.0116L}, \tag{10}$$

where L is the length of the watercourse from its source to the monitoring section, km.

In the conservation areas located in the upper reaches of the Danube ecosystem in the Ukrainian Carpathians, the Carpathian National Nature Park and the Carpathian Biosphere Reserve, the maximum permissible load on the Danube ecosystem should be the one when the WPI does not exceed the natural background value (long-term annual average standard), calculated in accordance with the dependences described above. These functional models for the monitoring assessment of the anthropogenic load on conservation areas should be used.

To process the monitoring base of the second large Dniester hydro-ecosystem, the Composite Potential Quality Indicator (2) was used, and the close regression functional dependence between the hydro-ecosystem quality standard (long-term annual average) of the whole Dniester basin in the Carpathian region and the terrain altitude was obtained (Figure 6).

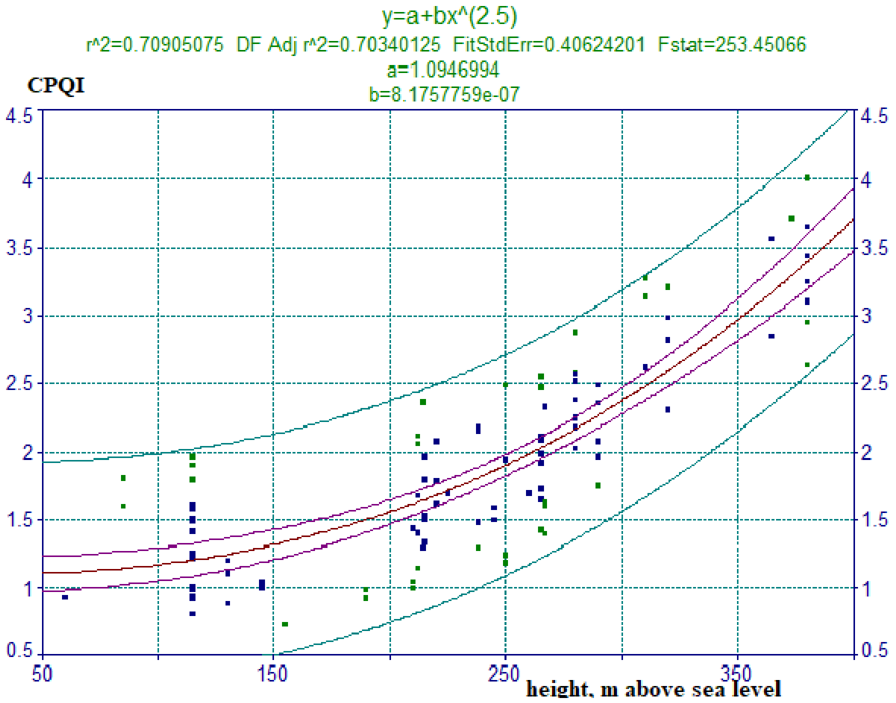


Figure 6: Functional dependence between the water quality standard of the Dniester ecosystem and terrain altitude

The calculated CPQI is a relative value that depends on the level of anthropogenic load. Even though the Dniester ecosystem is constantly polluted at most observation points (even with positive CPQI values), the close dependence between the Composite Potential Quality Indicator and the altitude is evident and is described by the curvilinear regression equation:

$$CPQI=1.095+8.18H^{2.5} \tag{11}$$

In this case, *Fstat=253.4 (calculated)>Fstat=3.94* (table value). Thus, the correlation between the properties is not accidental, it is significant.

The functional dependence obtained for the Dniester ecosystem in the Ukrainian Carpathians by interpolation, i.e., by means of the mathematical justification for the unknown values of the dynamic series of phenomena based on the established relationship between the CPQI standard and the altitude, was approximated by a continuous linear function (Figure 7):

$$CPQI = 1.002 + 2.705H^{2.5} \qquad (12)$$

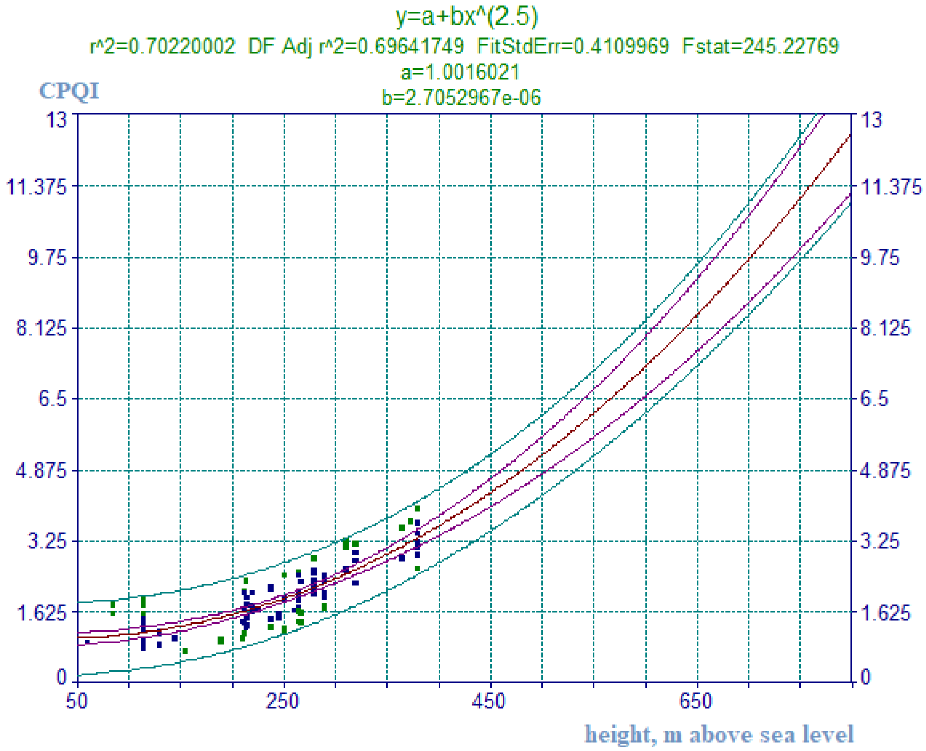


Figure 7: Approximated functional dependence between the quality standard value of the water bodies of the Dniester ecosystem in the Carpathian region and the terrain altitude

Thus, based on the acquired dependence, it is proposed to define the Composite Potential Quality Indicator standard value as a property of natural and technogenic safety at any point of the Dniester river ecosystem in the Carpathian region.

Undoubtedly, the CPQI standard values at absolute altitudes below 300 m were influenced by the existing technogenic load on the ecosystem. The surface water quality monitoring point on the Tysmenytsia river is located in the town of Drohobych and is aimed to control the influence of sewage water from the towns of Truskavets and Boryslav. In Rozvadiv village, water quality of the Dniester ecosystem is monitored due to the impact of industrial wastewater from the town of Drohobych, and in Zhuravno village it was due to the impact of the sewage waters from the town of Khodoriv (Malovanyy *et al*., 2019).

To determine the standard of the qualitative component of ecological safety of hydro-ecosystems of the Ukrainian Carpathians, it is proposed to use the Table 2. In the table, the norm of CPQI (for the natural state of hydro-ecosystems) could be estimated using the value of the height sample location. Up to an altitude of 1,000 m above sea level, water quality can be determined at every 50 m distance, and at an altitude above 1000 m it should be measured at every 100 m distance.

Table 2: Standard values of the Composite Potential Quality Indicator for different absolute heights of the hydro-ecosystems of the Dniester, Prut, Siret and Tysa rivers

Absolute height, m	*Hydro-ecosystem*		
	Dnister	*Prut and Siret*	*Tysa*
1	2	3	4
50	1.03	-	2.50
100	1.13	0.21	4.24
150	1.31	0.52	4.91
200	1.57	0.84	5.34
250	1.94	1.18	5.64
300	2.39	1.53	5.84
350	2.94	1.89	6.02
400	3.60	2.26	6.14
450	4.35	2.63	6.25
500	5.21	3.01	6.34
550	6.17	3.40	6.43
600	7.23	3.79	6.50
650	8.41	4.18	6.57
700	9.69	4.58	6.64
750	11.08	4.98	6.68
800	12.58	5.38	6.73
850	14.19	5.79	6.76
900	-	6.21	6.81
950	-	6.62	6.85
1000	-	7.04	6.90
1100	-	7.88	-
1200	-	8.73	-
1300	-	9.59	-
1500	-	11.34	-
1600	-	12.23	-
1700	-	13.12	-
1800	-	14.01	-
1900	-	14.92	-
2000	-	15.82	-

Discussion

Water quality assessment is a time-consuming process because it is based on the comparison of the average concentrations observed at the water quality monitoring points keeping in view the standards for each ingredient (Staśko and Buczyński, 2018).

Following the principle of natural water unity, formulated by (Eigen and Schuster, 2012), the current system of water quality (drinking, waste, surface and underground waters) should be based on the classification built upon the indicators and the composition and properties (physical, chemical, biological) of water. It can be collectively used to solve a wide range of problems associated with different types of management, utilization and protection of water resources. The system should meet simultaneously the ecological, hygienic and technological requirements (Zubaidah, Karnaningroem and Slamet, 2019). At present, there exists no such system. Hence, it was a complex multidisciplinary task (Water Framework Directive 2000/60/EC[2]).

Difficulties arise when it becomes inevitable to analyze the trend of water quality over several years, in different parts of a water body, or to compare the water quality of different water bodies contaminated by variety of pollutants, or to identify the trend of water quality over time (Strzelczyk and Steinhoff-Wrześniewska, 2020). Thus, a need to develop a methodology for integrated water quality assessment arises (European Union, 2017).

This study focusing two major hydro-ecosystems of the Carpathian region, the Dniester and Danube rivers, used a methodology of integrating natural water quality assessment with the functional dependencies between quality indicators and altitudes. It is established that the relation is logical: with the increasing altitude, the level of anthropogenic load decreases, and the quality of natural waters improves. It has been observed that the Ukrainian Carpathians are low mountains, quite populated. In small settlements, there is no centralized water supply and sewage treatment. As a tourist region, the Ivano-Frankivsk oblast has the population of 1.4 million and is visited by more than 2 million tourists annually. A big ski resort, “Bukovel”, is situated in the area (Kinash *et al.*, 2019). Both the high-density population and the influx of tourists add to the pollution load of watercourses in the region.

Based on the above findings, it can be inferred that the self-purification of natural waters eliminates diffused pollution in the waters flowing through mountainous part of the Ukrainian Carpathians. The comparison of method (2) with the method (1) leads to the following conclusions. The methodology (2) is more flexible, which evaluates the buffering capacity and allows the use of a simple prioritization method; that is, certain regions or areas of ecosystems that meet certain environmental quality standards can be considered as reference having no further anthropogenic pressure, while other areas of hydro-ecosystems can be ranked and evaluated using the mathematical symbols and values of CPQI.

Finally, this method is proved to be effective in assessing the level of anthropogenic load on water bodies. The obtained dependencies can be used as territorial background standards for the ecological assessment of the basin ecosystems. This study proves to be important to justify and improve the Ukrainian water monitoring methodologies that are required to be adapted to EU laws.

Conclusions

For the first time, the patterns of changes in the ecosystems’ quality parameters established by means of developing functional dependences among the ecological standard values of the composite quality indicators of natural waters and the river length and terrain altitude. It is performed by using the statistical processing of the data of quality monitoring of the upper reaches of Dniester and Danube ecosystems in the Ukrainian Carpathians for the period from 2001 to 2019. The obtained dependencies can be used in the form of the territorial background standard values of ecological indicators of basin ecosystems. It will help substantiate scientifically the permissible levels of the anthropogenic pressure e.g., pollution load.

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Authors' Declarations and Essential Ethical Compliances

Authors' Contributions (in accordance with ICMJE criteria for authorship)

Contribution	Author 1	Author 2	Author 3	Author 4	Author 5
Conceived and designed the research or analysis	Yes	Yes	No	No	No
Collected the data	Yes	Yes	Yes	Yes	No
Contributed to data analysis & interpretation	Yes	Yes	No	No	Yes
Wrote the article/paper	Yes	Yes	Yes	Yes	Yes
Critical revision of the article/paper	Yes	Yes	Yes	No	Yes
Editing of the article/paper	Yes	Yes	No	No	Yes
Supervision	Yes	No	Yes	Yes	No
Project Administration	No	No	Yes	Yes	No
Funding Acquisition	No	Yes	No	No	No
Overall Contribution Proportion (%)	30	30	20	10	10

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The research did not involve plants or animal species. No

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