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Formation of the chemical composition of water in the upper reaches of the transboundary Tisza River (Ukrainian Carpathians)

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SUMMARY

The transboundary river Tisza, whose headwaters are located in the Transcarpathian region of Ukraine, is the largest left tributary of the Danube and plays an important ecological role in its basin. Apart from Ukraine, the Tisza River basin is located in Romania, Hungary, Slovakia and Serbia.

The significance of studying the formation of the chemical composition and quality of water in the upper reaches of the Tisza River is that it gives an idea of the chemical composition and quality of water in the river, which then flows through the territory of neighboring countries. The chemical composition of the water in the upper reaches of the Tisza River is formed under the influence of high humidity (average annual precipitation is about 1200 mm) and the spread of salt-poor flysch rocks.

The surface waters of the upper reaches of the Tisza River, studied at four monitoring points (Black Tisza - Yasinia, White Tisza - Luga, Tisza - Rakhiv, Tisza – Tiachiv) are hydrocarbonate calcium, moderately fresh with an average mineralization of 192-248. mg·dm⁻³. The clearest connection between hydrological and hydrochemical regimes is manifested for the main ions and mineralization of water.

In case of physicochemical parameters, biogenic substances, trace elements, we can only talk about trends. The results of the study are of great practical importance, in particular for development of a new Tisza River Basin Management Plan; consideration of environmental programs to improve water quality in the Tisza River basin.



Introduction

The transboundary river Tisza, whose headwaters are located in the Transcarpathian region of Ukraine (within the Rakhiv and Tiachiv administrative districts), is the largest left tributary of the Danube and plays an important role in its basin.

This territory is the most mountainous within Ukraine, it is of great ecological, economic and transboundary importance (Leta, 2017). According to the hydrographic zoning of 2016, 9 districts of river basins were allocated on the territory of Ukraine. The Tisza River is defined into a separate sub-basin in the Danube River basin district. Natural conditions and anthropogenic influence within this territory determine the main features of the chemical composition of the water of the Tisza River downstream. Apart from Ukraine, the Tisza River basin is located in Romania, Hungary, Slovakia and Serbia.

The Tisza River is important for the formation of water resources balance of both Ukraine and neighboring countries (Khilchevskiy, 2021), the river basin can also serve as a training ground for research into possible changes in the chemical composition of surface waters under the influence of climate change (Khilchevskiy et al., 2020).

The importance of studying the formation of the chemical composition of water in the upper reaches of the Tisza River is that it gives an idea of the chemical composition and quality of water in the river, which then flows through the territory of neighboring countries.

Materials and research methods. In order to study the chemical composition of surface waters in the upper reaches of the Tisza River, four monitoring points were selected: Black Tisza - Yasinia, White Tisza - Luga, Tisza - Rakhiv, Tisza - Tiachiv. The publicly available stock hydrochemical data of the State Emergency Service of Ukraine (SES of Ukraine) for a multi-year period (1984-2018) were used. It should be noted that since 2011 the State Emergency Service of Ukraine has included hydrometeorological organizations with many years of experience in observing rivers (Osadchyi et al. 2021) in its structure. We also used the results of our own field research during 2015-2018.

Results

1. Characteristics of the study area

The study area of the upper reaches of the Tisza River includes the entire Rakhiv district and most of the Tiachiv district of the Transcarpathian region of Ukraine. The complex morphometry of the territory includes the Chornohora and Svydovets mountain ranges, as well as part of the Maramureş massif, the Yasinia and Solotvyn structural basins. The complexity of the mountainous relief of the territory also affects the density of the river network, represented by the Black Tisza and White Tisza rivers, the confluence of which near the town of Rakhiv (at an altitude of 460 m above sea level) gives rise to the Tisza River. There are also numerous tributaries of the Tisza River, the largest of which are the Kosivska River, the Shopurka River, the Apshytsia River, the Teresva River and others (Leta, Pylypovych 2019; Leta et al., 2019). The dissection of the relief decreases from the source of the Black Tysa River downstream. The area of the research area is $\approx 3420 \text{ km}^2$, and the length of the Tisza River from Rakhiv to Tiachiv is 80 km, of which $\approx 60 \text{ km}$ is the state border between Ukraine and Romania (Table 1, Fig. 1).

Table 1 The main morphometric parameters of the investigated rivers of the upper reaches of the Tisza River

River	Where the river flows	Length, km	Area, km^2	Slope, $\text{m}\cdot\text{km}^{-1}$
Black Tisza	Tisza	49	567	19
White Tisza	Tisza	28	489	10
Tisza	Danube	80/265	3420/12777*	3.6/1.4*

Note. * - parameters within the study area / within the entire Transcarpathian region of Ukraine



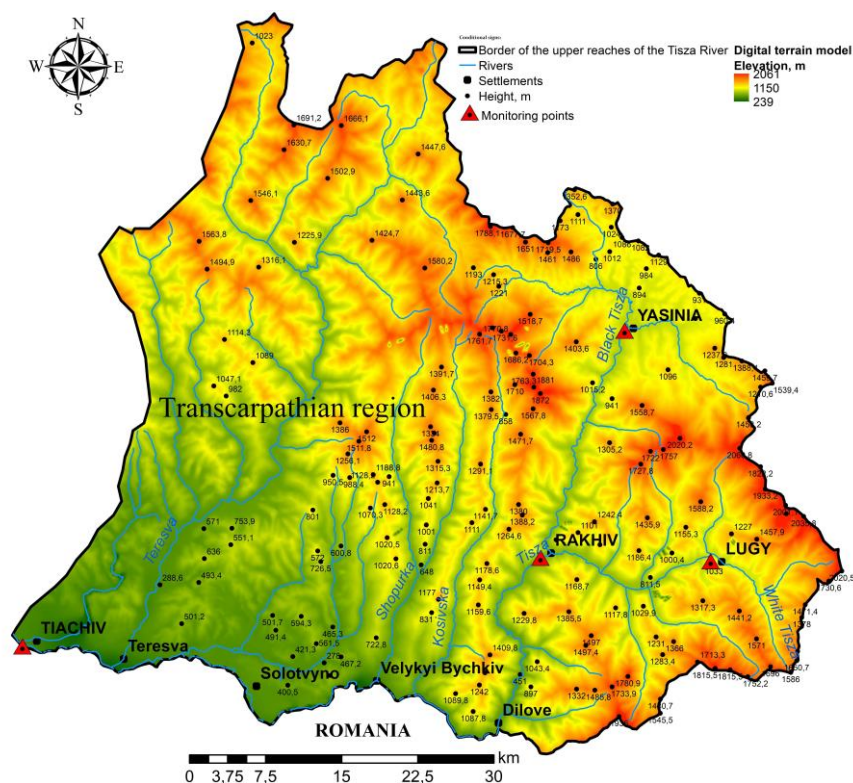


Figure 1 Study area location map - the sources of the Tisza River in the Transcarpathian region, Ukraine (compiled by the authors on the basis of a topographic map at a scale of 1:25 000)

2. Brief hydrological characteristics

The hydrological regime of rivers, which is characterized by the presence of spring floods, summer-autumn and winter low tides, affects the change in the share of various sources of river supply, causing fluctuations in the chemical composition of water. Therefore, the hydrological regime largely affects the formation of the hydrochemical regime.

In addition, the existence of floods (Ovcharuk and Goptsiy, 2022) is a characteristic feature of the rivers of the upper reaches of the Tisza, which is caused by snow melting during winter thaws, frequent spring rains, and intense precipitation in the summer-autumn period (May-October). At the Tisza-Rakhiv hydrological station (catchment area 1070 km²), the average long-term water consumption is 25.4 m³·s⁻¹; the highest water consumption - 938 m³·s⁻¹ (March 5, 2001); minimum – 1.14 m³·s⁻¹ (February 2, 1963).

3. Characteristics of the chemical composition of water

The chemical composition of the water in the upper reaches of the Tisza River is formed under the influence of high humidity (average annual precipitation is about 1200 mm) and the spread of salt-poor flysch rocks. These conditions determine the bicarbonate-calcium type of waters of low mineralization.

Main ions and mineralization of water. The main ions contained in natural waters are: HCO₃⁻, SO₄²⁻, Cl⁻, Ca²⁺, Mg²⁺, Na⁺, K⁺. Their content in fresh waters is 90-95%, and in highly mineralized waters - more than 99% of all salts. The main ions determine the chemical type of waters.

The mineralization of the surface waters of the upper reaches of the Tisza River depends on natural factors, in particular, the presence of soluble minerals calcite, dolomite, and limestone cement in



sandstones, as well as the ingress of these salts with wastewater from agricultural lands (Khilchevskiy, 1994). Seasonal fluctuations in the of river waters value depend on the moistening conditions of the territory and the feeding regime of the rivers. The dominant ions in the surface waters of the upper reaches of the Tisza River are hydrogen carbonate anions (HCO_3^-) and calcium cations (Ca^{2+}) (Table 2). The surface waters of the upper reaches of the Tisza River are bicarbonate calcium, moderately fresh with an average mineralization ($192\text{-}248 \text{ mg}\cdot\text{dm}^{-3}$).

Table 2 Average seasonal concentrations of major ions and mineralization of river waters in the upper reaches of the Tisza River (1984-2018), $\text{mg}\cdot\text{dm}^{-3}$

River - point / Ion	HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	$\text{Na}^+ + \text{K}^+$	Mineralization
Spring flood							
Black Tisza - Yasinia	107	25.2	10.5	31.6	4.74	14.3	193
White Tisza - Luga	98.4	32.0	13.3	29.3	5.74	13.0	192
Tisza - Rakhiv	112	23.7	11.2	31.9	4.96	12.6	196
Tisza - Tiachiv	98.7	28.5	19.0	31.4	8.76	12.9	199
Summer-autumn low water							
Black Tisza - Yasinia	123	28.3	14.7	36.5	6.62	14.3	223
White Tisza - Luga	103	28.2	12.8	29.8	7.70	12.7	194
Tisza - Rakhiv	113	24.9	11.8	33.4	5.41	12.2	201
Tisza - Tiachiv	106	28.4	32.1	31.8	6.82	22.4	227
Winter low water							
Black Tisza - Yasinia	134	30.6	13.0	40.6	7.68	11.6	238
White Tisza - Luga	127	25.8	12.8	36.5	7.46	13.7	223
Tisza - Rakhiv	126	39.7	15.8	38.2	7.27	11.0	238
Tisza - Tiachiv	132	40.6	15.9	39.3	8.28	12.0	248
Average annual							
Black Tisza - Yasinia	121	28.0	12.7	36.1	6.31	13.4	218
White Tisza - Luga	109	32.6	12.9	32.4	7.13	13.1	207
Tisza - Rakhiv	117	29.4	12.9	34.5	5.78	12.1	212
Tisza - Tiachiv	112	32.5	22.3	34.2	7.95	15.8	225

Fluctuations in water mineralization of the Black Tisza, White Tisza, and Tisza rivers throughout the year are related to the hydrological regime - the lowest values are observed during the spring flood, and increase during the summer-autumn and winter low tides (Fig. 2).

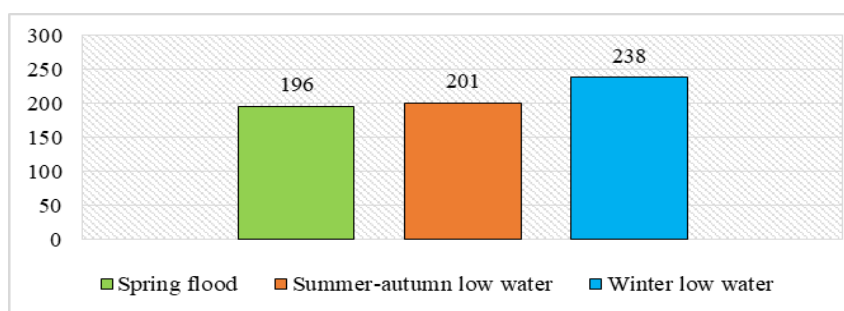


Figure 2 Average long-term values of water mineralization of the Tisza River - Rakhiv during different water phases (spring flood, summer-autumn low water, winter low water), $\text{mg}\cdot\text{dm}^{-3}$



In addition to the main ions, the chemical composition of the river waters of the upper reaches of the Tisza River was also studied according to physicochemical indicators, nitrogen compounds, some heavy metals, and specific pollutants. Water quality was assessed according to hygienic water quality standards of water objects to meet drinking, household and other needs of the population (Ministry of Health of Ukraine, 2022).

Conclusions

1. The surface waters of the upper reaches of the Tisza River, studied at four monitoring points (Black Tisza - Yasinia, White Tisza - Luga, Tisza - Rakhiv, Tisza - Tiachiv) are hydrocarbonate calcium, moderately fresh with an average mineralization of 192-248 mg·dm⁻³.
2. The clearest connection between the hydrological and hydrochemical regimes is manifested for the main ions (HCO₃⁻, SO₄²⁻, Cl⁻, Ca²⁺, Mg²⁺, Na⁺+K⁺) and water mineralization. In case of physicochemical parameters (pH, O₂), biogenic substances, trace elements, we can only talk about trends.
3. The obtained research results have important practical significance, in particular for development of a new Management Plan for the Tisza River basin; determination and implementation of measures of environmental control of economic entities in the upper Tisza basin; consideration of environmental programs for improving water quality in the Tisza River basin.

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