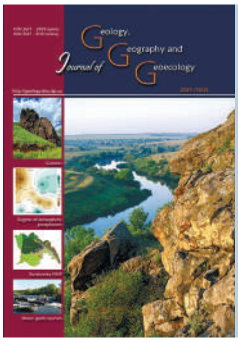

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Hydrochemical characteristics of the Upper reaches of the Tisza River

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Abstract. The purpose of this study is to analyse the hydrochemical regime and surface water quality of the upper reaches of the Tisza River from its source to Tiachiv, which also includes the transboundary section of the river. The data of the Borys Sreznevskyi Central Geophysical Observatory of the State Emergency Service of Ukraine for the period 1984-2018, as well as the results of route surveys during 2015-2018 served as materials for the study. The hydrological parameters of the river, in particular the level and flow of water, the distribution of the flow and the change of power sources throughout the year were analysed. Based on of the collected materials, a detailed analysis of the hydrochemical indicators of the water quality of the Tisza, Black Tisza, and White Tisza rivers was carried out. During the research, the natural conditions of the territory and economic activity were studied and their influence on the values of physic-chemical indicators, main ions and mineralization of water, biogenic substances, heavy metals and specific pollutants was analysed. The ratio of seasonal, average annual, average multi-year and maximum permissible concentrations (MPC) of hydro-chemical indicators was considered to determine their seasonal variability and multi-year dynamics. The role of natural factors in the formation of the chemical composition of river waters is determined, and the main sources of anthropogenic influence are also indicated. Seasonal variability of the indicated groups of indicators was also analysed considering different phases of river water content. It was determined that the waters of the headwaters of the Tisza River are calcium carbonate, moderately fresh with average mineralization (192-245 mg·dm^{-3}) and clear seasonal variability. Cases of increased concentrations of nitrogen-containing compounds in the waters of the upper reaches of the Tisza River due to the intensive decomposition of organic substances from household wastewater were revealed. High concentrations of iron in river waters were recorded, which is related to the peculiarities of the geological structure of the territory. The seasonal variability of the content of synthetic surfactants was established. A decrease in the content of specific pollutants during the study period was observed.

Keywords: Tisza River, hydrochemical regime, water quality, Ukrainian Carpathians.

Гідрохімічна характеристика верхів'я річки Тиса

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Анотація. Метою даного дослідження є аналіз гідрохімічного режиму та якості поверхневих вод верхів'я річки Тиса від витоку до м. Тячів, що включає також транскордонну ділянку річки. Матеріалами для дослідження слугували дані Центральної геофізичної обсерваторії імені Бориса Срезневського Державної служби України з надзвичайних ситуацій за період з 1984 р.

по 2018 р., а також результати маршрутних обстежень впродовж 2015-2018 рр. Проаналізовано гідрологічні параметри вод, зокрема рівень і витрати вод, розподіл стоку та зміна джерел живлення впродовж року. На основі зібраних матеріалів здійснено детальний аналіз гідрохімічних показників якості вод річок Тиса, Чорна Тиса та Біла Тиса. При дослідженні вивчено природні умови території та господарську діяльність та проаналізовано їх вплив на значення фізико-хімічних показників, головних йонів та мінералізацію води, біогенні речовини, важкі метали та специфічні забруднювальні речовини. Розглянуто співвідношення сезонних, середньорічних, середніх багаторічних і гранично допустимих концентрацій ($ГДК_{госп.-поб.}$) гідрохімічних показників для визначення їх сезонної мінливості та багаторічної динаміки. Визначено роль природних чинників формування хімічного складу річкових вод, а також вказано основні джерела антропогенного впливу. Окремо проаналізовано сезонну мінливість вказаних груп показників з урахуванням різних фаз водності річок. Визначено, що води верхів'я річки Тиса є гідрокарбонатними кальцієвими, помірно прісними з середньою мінералізацією (192-245 $мг{\cdot}дм^{-3}$) та чіткою сезонною мінливістю. Виявлено випадки підвищення концентрацій азотовмісних сполук у водах верхів'я Тиси за рахунок інтенсивного розкладу органічних речовин з господарсько-побутових стічних вод. Зафіксовано високі концентрації заліза у річкових водах, що пов'язано з особливостями геологічної будови території та впливом бальнеологічних курортів. Встановлена сезонна мінливість вмісту синтетичних ПАР. Помічено зменшенням вмісту специфічних забруднювальних речовин.

Ключові слова: річка Тиса, гідрохімічний режим, якість води, Українські Карпати.

Introduction

Its largest left tributary, the transboundary river Tisza, is of great importance in the Danube basin, the headwaters of which are in the Ukrainian Carpathians (within the Rakhiv and Tiachiv administrative districts of the Transcarpathian region of Ukraine). This territory is the most mountainous area in Ukraine and has important ecological, economic and cross-border significance. Natural conditions and anthropogenic influence of this territory determine the main features of the chemical composition of the water of the Tisza River downstream. In addition to Ukraine, the Tisza River basin is located in Romania, Hungary, Slovakia and Serbia. Changes in the quality of water in the Tisza River under the influence of natural and anthropogenic factors within these countries are analysed in the works of such scientists as (Babić et al., 2019: Racický et al., 1998: Tanos et al., 2014).

According to the hydrographic zoning of 2016, 9 areas of river basins were allocated on the territory of Ukraine. The Tisza River is separated into a separate sub-basin in the area of the Danube River basin (Khilchevskyi et al., 2019). Ukrainian scientists are constantly interested in studying the chemical composition of the water of the Tisza River. This happens both within the framework of large regional studies (Horiev et al., 1995; Khilchevskyi et al., 2020) and during studies in individual creations. For example, determining the quantitative dependence of mineralization on water consumption in the Tisza-Rakhiv basin (Hopchenko et al., 2012),

Important from the point of view of international cooperation and the implementation of international standards in Ukraine are works in which the ecological state of the surface waters of the Tisza River basin in the section of the Ukrainian-Romanian border was studied using the requirements of the EU Water Framework Directive (Afanasyev, 2010; Leta, 2017; Yarosevych, 2008). Attention was also paid to studying the concentration of heavy metals in the water of the Tisza River (Linnyk et al., 2015; Skobley et al., 2017).

Studies of the hydro-ecological condition of the tributaries of the Tisza River: the White Tisza River and the Black Tisza River (Khilchevskyi and Leta, 2016; 2017; Khilchevskyi et al., 2022), the Shopurka River (Leta, 2016), the Kosivska River (Leta and Pylypovych, 2019), the Lazeshchyna River (Leta et al., 2019) have been carried out.

However, these studies do not fully cover the hydrochemical regime and water quality indicators of the Tisza River, in particular around the Ukrainian-Romanian border.

The purpose of this study is to analyse the hydrochemical regime and surface water quality of the upper reaches of the Tisza River (from its sources to Tiachiv), considering the natural conditions of the territory and economic activity.

Being in close connection with the catchment area, the massifs of surface water reflect the ecological state of the entire geosystem. Therefore, determination of physic-chemical and chemical indicators of river waters, research of their seasonal and multi-year dynamics will allow to identify the factors of formation and influence on water quality within particular sections of the river.

Material and methods

To study the chemical composition of the surface waters of the upper reaches of the Tisza River, four monitoring points were chosen: Black Tisza – Yasinia, White Tisza – Lugy, Tisza – Rakhiv, Tisza – Tiachiv (Fig. 1, Fig. 2). Publicly available stock hydrochemical data of the Borys Sreznevskyi Central Geophysical Observatory of the State Emergency Service of Ukraine (ESES of Ukraine) for a multi-year period

(1984-2018) were used. It is worth noting that since 2011, hydrometeorological organizations with many years of experience in observing rivers have been included in the structure of the National Emergency Service of Ukraine (Osadchyi et al., 2021). The results of own field research during 2015-2018 were also used.

To determine the chemical components in water, methods were used according to the handbook (Nabyvanets et al., 2007). The chemical composition of river waters is represented by the following groups of components: physical and chemical indicators; main ions and water mineralization; nitrogen compounds; heavy metals; specific pollutants. The quality of surface waters of the Tisza River headwaters was assessed according to the hygienic water quality standards of water bodies to meet the drinking, household, and other needs of the population, as well as requirements for fisheries water bodies − maximum permissible concentrations (MPC) (Ministry of Agrarian…, 2012: Ministry of Health…, 2022).

The data set for 35 years allows to analyse in detail the multi-year dynamics and seasonal variability of indicators of the chemical composition of river waters, as well as to identify their regime characteristics. Characterization of the chemical composition of river waters was carried out based on the average values of the components for three phases of the water regime: spring flood, summer-autumn ebb, winter ebb.

For the surface waters of the upper reaches of the Tisza River, a control system was used, which consisted of several consecutive checks (logical, mathematical and statistical), which served as a kind of filter of hydrochemical data (Dubenok et al., 2003). The main ones were: detection of extremely possible values for the measured indicators; comparison of individual indicators among themselves, obtained within the limits of one sampling; comparison of individual indicators with each other in the context of spatio-temporal variability; comparison of the obtained results with normative indicators, i. e. MPC in the water body; comparison of measurement results with retrospective information. Piper's diagram was used to find out the genetic relationship of the chemical composition of water at different hydrological stations of the upper reaches of the Tisza River.

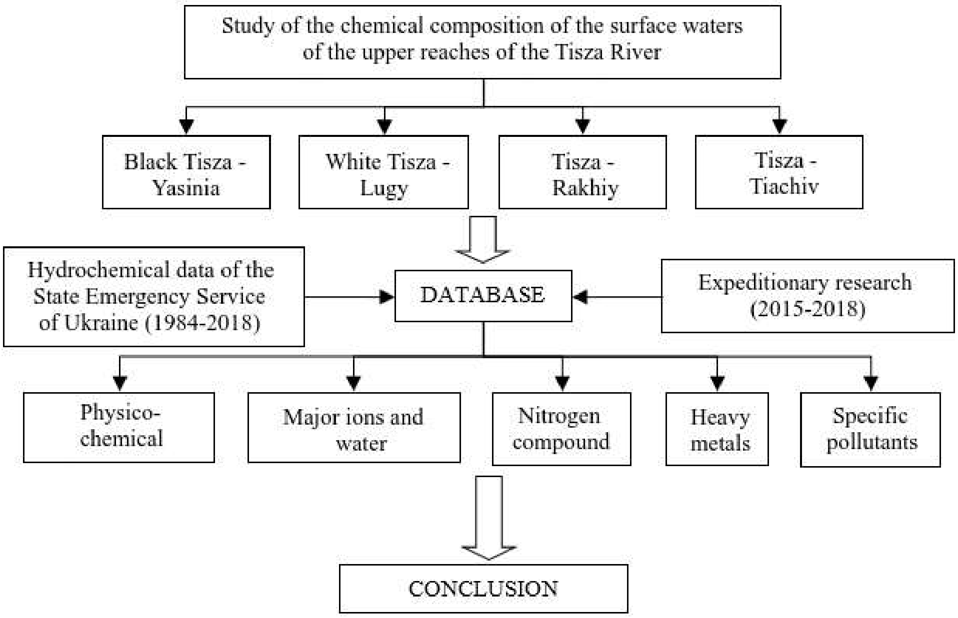

Fig. 1. Block diagram of the methodology for researching the chemical composition of the surface waters of the upper reaches of the Tisza River

Characteristics of the research area

The studied territory of the headwaters 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 Maramureș massif, the Yasinian and Solotvy basins. The complexity of the mountainous topography of the territory also affects the density of the river network, which is represented by the Black Tisza and White Tisza rivers, the confluence of which near 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. The dismemberment of the relief decreases from the sources of the Black Tisza River downstream. The area of the research territory is ≈ 3420 km^2, and the length of the section of the Tisza River from Rakhiv to Tiachiv is 80 km, ≈ 60 km of which is the state border between Ukraine and Romania (Table 1).

Table 1. The main morphometric parameters of the investigated rivers of the headwaters of the Tisza River (in Ukraine)

River	Where it flows	Length, km	Area, km^2	Slope, m·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. * – within the studied area / within the entire Transcarpathian region of Ukraine

With the help of the ArcGIS 10.4.1 software and the selection of appropriate tools, a map of the location of water monitoring points within the upper reaches of the Tisza River was drawn up (Fig. 2).

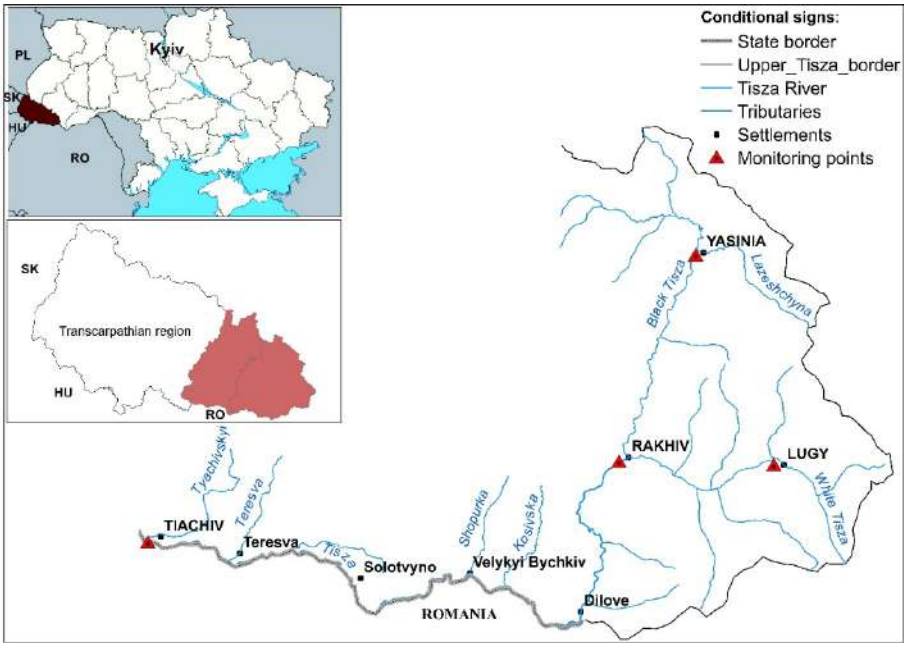

Fig. 2. Water monitoring points in the upper reaches of the Tisza River, Transcarpathian region, Ukraine (concluded by the authors)

Brief description of economic activity

Within the studied area, there are enterprises of the wood-chemical, pulp and paper, metallurgical, light and food industries, which during the 1990s and early 2000s were the main anthropogenic sources of water pollution of the Black Tisza River, the Shopurka River and the Tisza River itself (Leta, 2016). Route surveys of the Black Tisza River, the White Tisza River, and the Tisza River along the Ukrainian-Romanian border made it possible to identify the impact on the waters' quality of agriculture, household waste, spontaneous landfills, and summer animal camps within coastal protection strips and floodplains.

The analysis of economic activity within the Rakhiv and Tiachiv districts made it possible to highlight a list of the main enterprises and institutions whose activities during the studied period posed a direct or indirect threat of pollution of the Tisza river waters or its tributaries: communal enterprises of Rakhiv, Kobyletska Polyana, Solotvyn, Tiachev; marble mining enterprises «Trybushany» and «Bilkam»; woodworking enterprises «VHSM» and «Karpaty», as well as Velykobychkiv forest chemical plant and Rakhiv cardboard factory; tourist shelter «Kozmeschyk», resort «Dragobrat», sanatorium «Hirska Tisza». We especially want to point out the danger of pollution of the waters of the Tisza River in the section from the city of Rakhiv with solid household waste, organic and synthetic substances entering the river waters from the landfill located directly on the left bank of the river.

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 different sources of river nutrition, which cause fluctuations in the chemical composition of water.

The presence of floods (Ovcharuk and Goptsiy, 2022) caused by snowmelt during winter thaws, frequent spring rains, and intense precipitation in the summer-autumn period (May-October) is a typical feature of the rivers of the Tisza headwaters. At the Tisza – Rakhiv hydrological station (catchment area 1070 km^2), the average long-term water consumption is 25.4 m^3·s^{-1}; the highest water consumption – 938 m^3·s^{-1} (March 5, 2001); minimum – 1.14 m^3·s^{-1} (February 2, 1963).

Minimum water levels are observed under conditions of low summer-autumn water level and insignificant spring irrigation. At the same time, the most catastrophic floods also occur in the summer-autumn period, which is caused by intense rains. It is worth noting that the amplitude of level fluctuations varies in the range from 3.1 m to 6.8 m. Instead, water levels on the Tisza River and its tributaries are unstable during the winter period, which is due to frequent thaws and rains.

Spring irrigation begins in the second half of March – early April, accompanied by active melting of the snow cover, and sometimes active rainfall. Taking this into account, irrigation on the Tisza River and its tributaries within the Rakhiv District may take place in several stages. At high waterholes, the water level can rise by 150-200 cm/day, at low ones – by 5-15 cm/day. According to the data of the Tisza – Rakhiv hydrological station for the period 1950-2016, the highest water level recorded on 03/05/2001 was 575 cm. The spring period is characterized by elevated water levels even in years with average water content.

Results and analysis

The chemical composition of the water in the headwaters of the Tisza River is formed under the influence of high humidity (average annual precipitation of about 1200 mm) and the spread of salt-poor flysch rocks. These conditions determine the hydrocarbonate-calcium type of river waters and low water mineralization. Seasonal and multi-year changes in the hydrological regime affect water mineralization and the concentration of major ions. There is a clear inverse relationship between water consumption and mineralization values – an increase in water consumption leads to a decrease in mineralization and vice versa (Fig. 3).

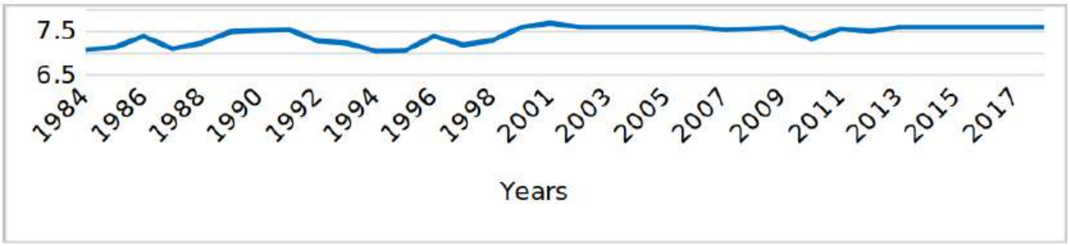

Fig. 3. The relationship between water consumption and mineralization on the example of the Black Tisza River – Yasinya, 2007

Physical and chemical indicators

Within the scope of this study, we have analysed in detail indicators important for the habitat of hydrobionts, namely the hydrogen index (pH) and the content of oxygen (O_2) dissolved in water.

The change in water pH is influenced by calcium bicarbonates $Ca(HCO_3)_2$ and magnesium $Mg((HCO_3)_2$, as well as various soil-forming rocks (granite-gneisses, sandstones, carbonates, etc.). The analysed pH indicators do not go beyond the MPC – 6.5-8.5 (Ministry of Health..., 2022). Thus, the range of average annual pH values in river waters during 1984-2018 is as follows: Black Tisza River – 7.1-8.2; the White Tisza River is significantly larger in water – 6.4-8.2; Tisza River – Rakhiv – 7.0-8.6; the Tisza River – Tiachiv – 7.1-7.7 (Fig. 4). Thus, the waters of the upper reaches of the Tisza River can be classified as weakly alkaline.

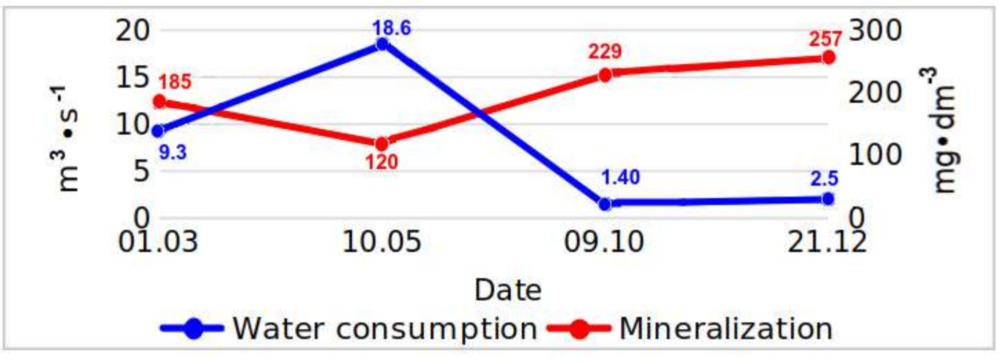

Fig. 4. Dynamics of average annual pH values in the Tisza River – Tiachiv water (1984-2018)

Seasonal variability of hydrogen index (pH) values is caused by changes in water content and nutrition regime. Thus, during the spring flood and the summer-autumn threshold pH values in the upper reaches of the Tisza are somewhat higher.

An important indicator of water quality and the suitability of the aquatic environment for the existence of hydrobionts is the content of dissolved oxygen (O_2) in the water. The seasonal variability of the oxygen content in the water of the studied rivers has a clear character, which depends on the intensity of production and costs for the processes of oxidation of organic compounds. A decrease in the oxygen content in the waters of the Black Tisza, White Tisza, and Tisza downstream, in particular, is observed during the summer-autumn border due to a decrease in the water level and the consumption of oxygen for the mineralization of organic substances. The ranges of average annual values of O_2 concentrations do not reach the limit of 6 mg·dm^{-3} and are as follows: Black Tisza – 7.5-14.3 mg·dm^{-3}, White Tisza 8.0-13.9 mg·dm^{-3}, Tisza – Rakhiv – 7.1- 13.2 mg·dm^{-3}, Tisza – Tiachiv – 9.4-12.7 mg·dm^{-3} (Fig. 5).

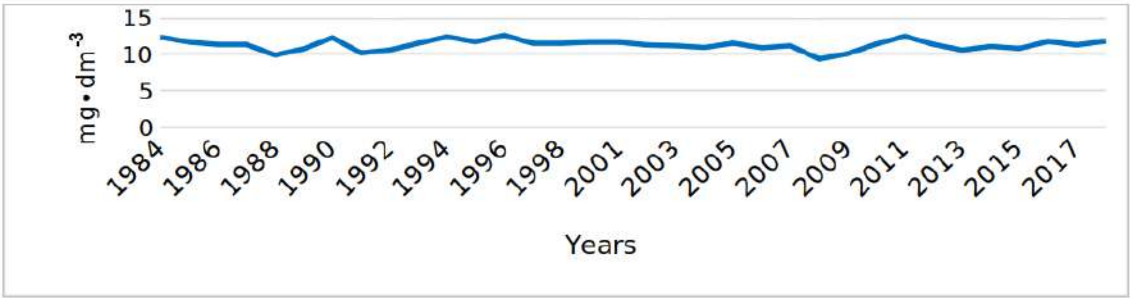

Fig. 5. The dynamics of the average annual values of the content of dissolved oxygen O_2 in the water of the Tisza River – Tiachiv (1984-2018), mg·dm^{-3}

Major ions and water mineralization

The main ions contained in natural waters include: HCO_3^-, SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, 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 water.

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 (Khilchevskyi et al., 1994). Seasonal fluctuations in the value of mineralization of river waters depend on the wetting 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 medium mineralization (100-225 mg·dm^{-3}).

Table 2. Average seasonal concentrations of major ions and water mineralization in the headwaters of the Tisza River (1984-2018), mg·dm^{-3}

River – point / Ion	HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	$Na^+ + K^+$	Mineralization
Spring flood							
Black Tisza – Yasinia	107	30.2	11.7	30.5	5.72	16.9	205
White Tisza — Lugy	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	192
Tisza – Tiachiv	94.7	27.5	18.0	29.4	7.76	11.9	196
Summer-autumn low water							
Black Tisza – Yasinia	123	28.3	14.7	36.5	6.62	14.3	226
White Tisza – Lugy	103	26.2	12.8	29.8	7.70	12.7	193
Tisza – Rakhiv	113	24.9	11.8	33.4	5.41	12.2	208
Tisza – Tiachiv	106	28.4	32.1	31.8	6.82	22.4	236
Winter low water							
Black Tisza – Yasinia	134	30.6	13.0	40.6	7.68	11.6	242
White Tisza – Lugy	127	25.8	12.8	36.5	7.46	13.7	227
Tisza – Rakhiv	126	39.7	15.8	38.2	7.27	11.0	245
Tisza – Tiachiv	90.2	20.1	26.3	26.8	5.89	17.6	193

Fluctuations in water mineralization of the Black Tisza River, the White Tisza River, and the Tisza River 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. 6).

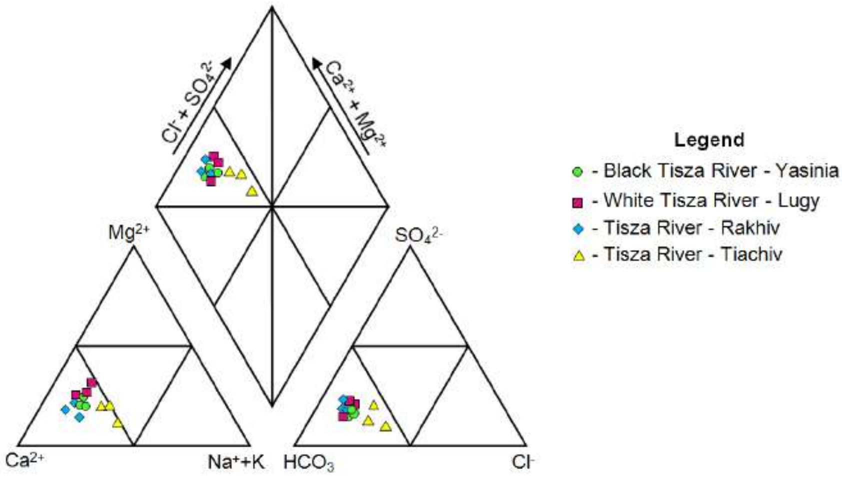

Fig. 6. Average long-term values of water mineralization of the Tisza River – Rakhiv during different water phases, mg·dm^{-3}

Piper's diagram shows that the chemical composition of surface waters in the upper reaches of the Tisza River has low values of variability in terms of major ions (Fig. 7). The figure shows that the ion-salt composition of the water of the Black Tisza, White Tisza, and Tisza rivers is identical in terms of the ratio of components. In general, all surface water samples are projected into the IV zone of the geochemical facies (Ca^{2+} – Mg^{2+}– HCO_3^-), which corresponds to the 5th type of water (Ca^{2+} – Mg^{2+} та HCO_3^- + CO_3^{2-}). Thus, Piper's diagram proves the genetic closeness of the chemical composition of the studied surface waters in the headwaters of the Tisza River at four monitoring points.

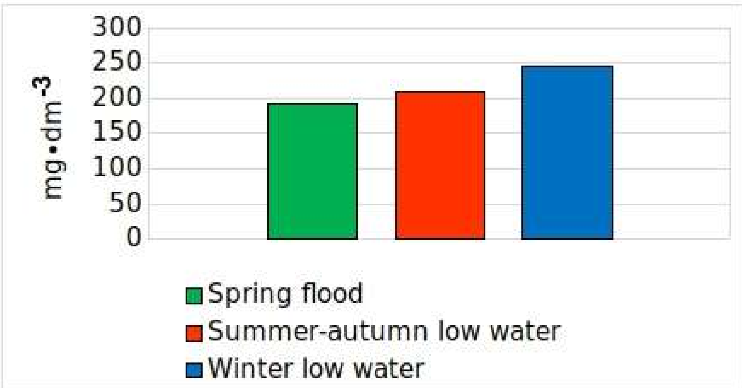

Fig. 7. Piper's diagram for the main ions in the water of the rivers: Black Tisza – Yasinia; White Tisza – Lugy; Tisza – Rakhiv; Tisza – Tiachiv

Biogenic substances – nitrogen compounds

Among biogenic substances, the following nitrogen compounds were studied: ammonium (NH_4^+), nitrites (NO_2^-), nitrates (NO_3^-). Their presence in the waters of the Black Tisza River, the White Tisza River, and the Tisza River is due to the life processes of organisms, the decay of their remains, as well as surface runoff from coastal areas of agricultural use and wastewater from communal enterprises and private households, which enter the river waters directly.

The content of ammonium (N-NH_4^+) in the water of the Tisza River ranges from 0.2 mg·dm^{-3} to 1.9 mg·dm^{-3} in Rakhiv and from 0.1 mg·dm^{-3} to 1.8 mg·dm^{-3} in Tiachiv. The indicators of ammonium content are also high in the rivers Black Tisza 0.1-1.9 mg·dm^{-3} and White Tisza – 0.1-2.2 mg·dm^{-3}, which indicates isolated cases of exceeding the normative value of N-NH_4^+ 2.0 mg·dm^{-3} (Ministry of Health…, 2022). Exceeding the MPC norms can be a consequence of conducting economic activities within the floodplains of rivers, in particular within the boundaries of the Yasinian basin and along the Tisza River from the village of Velykyy Bychkiv to the Tiachiv town, and by economic and domestic wastewater and natural garbage dumps along the riverbeds. Average long-term values of ammonium content indicate a decrease in the concentration of nitrogen-containing compounds during the baseflow period, on the other hand, the highest values were recorded during the spring flood (Table 3).

The anthropogenic influence on the growth of ammonium nitrogen concentrations in the water of the Black Tisza River occurs due to wastewater that enters from numerous tourist and recreational facilities, most of which are located directly on the banks of the river or its tributaries. The influence of such objects on the water quality of the White Tisza River is somewhat smaller. As the water level of the Tisza River rises during the spring flood, the content of NH_4^+ downstream also increases, which indicates the increasing influence of surface runoff from agricultural land, farmland, manure storage and landfills, in particular in the city of Rakhiv, and communal and domestic wastewater from private sector in settlements located along the Tisza River.

Nitrites (NO_2^-) in river waters are in soluble form and are formed because of ammonium oxidation and subsequent formation of nitrates (NO_3^-). A part of nitrogen-containing compounds can come with atmospheric precipitation and surface runoff, and seasonal fluctuations in the content of nitrites ($N\text{-}NO_2^-$) in the range of 0.006-0.012 mg·dm^{-3} can be caused by an increase in the intensity of decomposition of organic matter during the spring flood. An increase in the nitrite content in the waters of the Tisza headwaters may continue until the end of the summer-autumn period (Table 3). Indicators of nitrite nitrogen content with the highest annual average values in the waters of the Black Tisza River – Yasinia 0.025 mg·dm^{-3}, the White Tisza River – Lugy – 0.039 mg·dm^{-3}, the Tisza River – Rakhiv – 0.77 mg·dm^{-3}, Tisza – Tiachiv river – 0.017 mg·dm^{-3} do not reach the normative value of $N\text{-}NO_2^-$ mg·dm^{-3} (Ministry of Health…, 2022).

Nitrate content ($N\text{-}NO_3^-$) in the water of the Tisza River varies from 0.12 mg·dm^{-3} to 1.76 mg·dm^{-3} in Rakhiv and 0.07-2.15 mg·dm^{-3} in Tiachev, as well as 0.08-2.4 mg·dm^{-3} and 0.11- 5.6 mg·dm^{-3} in the waters of Black Tisza River and White Tisza River, respectively, which is many times less than the limit of 45 mg·dm^{-3} for the NO_3^- content (Ministry of Health…, 2022). The seasonal nature of the change in nitrate content in the waters of the upper reaches of the Tisza and its tributaries has its own characteristics. Thus, in the spring period, when work is actively carried out on agricultural land, the indicators increase. In the summer-autumn border period, nitrate concentrations reach minimum values, often at the limit of detection. On the other hand, during the winter low water, we observe an increase in nitrate nitrogen due to the formation of mineral forms of nitrogen during the decomposition of organic substances.

Table 3. Average seasonal long-term concentrations of biogenic substances in headwaters of the Tisza River (1984-2018), mg·dm^{-3}

Indicator	$N\text{-}NH_4^+$	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$	$N\text{-}NH_4^+$	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$	$N\text{-}NH_4^+$	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$
River – point / Season	Spring flood			Summer-autumn low water			Winter low water		
Black Tisza – Yasinia	0.56	0.012	0.65	0.76	0.006	0.43	0.8	0.008	0.54
White Tisza – Lugy	0.82	0.011	0.75	0.66	0.011	0.43	0.67	0.007	0.44
Tisza – Rakhiv	0.75	0.01	0.63	0.74	0.012	0.39	0.71	0.007	0.48
Tisza – Tiachiv	0.81	0.009	0.73	0.7	0.008	0.58	0.65	0.01	0.62

Heavy metals

The content of heavy metals copper (Cu), zinc (Zn), total iron (Fe), and chromium was analysed among trace elements in the waters of the Black Tisza, the White Tisza, and the Tisza rivers (Cr^{-6+}).

In the water of the studied rivers during 1984-2018, wide ranges of fluctuation of the average annual values of the concentration of total iron (Fe) were recorded, which indicates the risks of water pollution and the inadmissibility of using the surface waters of the Tisza River for economic and drinking needs. Yes, the range of iron concentrations in the waters of the Black Tisza River is the largest, namely 0.02-1.75 mg·dm^{-3}, the range of values in the waters of the White Tisza is somewhat smaller – 0.04-1.2 mg·dm^{-3}. In the Tisza waters from Rakhiv to Tiachiv, the range of average annual indicators varies from 0.01-0.96 mg·dm^{-3} to 0.02-0.43 mg·dm^{-3}, respectively. On the other hand, the average long-term values of the content of total iron in the waters of Black Tisza and White Tisza are 0.24 mg·dm^{-3}, and in the Tisza it decreases downstream from 0.31 mg·dm^{-3} in Rakhiv to 0.13 mg·dm^{-3} in Tiachiv. The upper threshold of the absolute and average annual values of iron in the waters of the studied rivers exceeds the limit values (0.3 mg·dm^{-3}) in the water of water bodies to meet the drinking, household, and other needs of the population.

Seasonal variability of total iron (Fe) concentrations in the waters of the Tisza headwaters occurs under the influence of hydrological conditions. The highest values were recorded during the spring period in the active phase of spring irrigation (Fig. 8). High levels of total iron (Fe) in surface waters are influenced by natural rock weathering processes, surface runoff (during heavy rains) from soils with high iron content (Khilchevskyi and Leta, 2016). The seasonal variability of the total iron content indicates the natural nature of river water pollution of the upper reaches of the Tisza River and its tributaries.

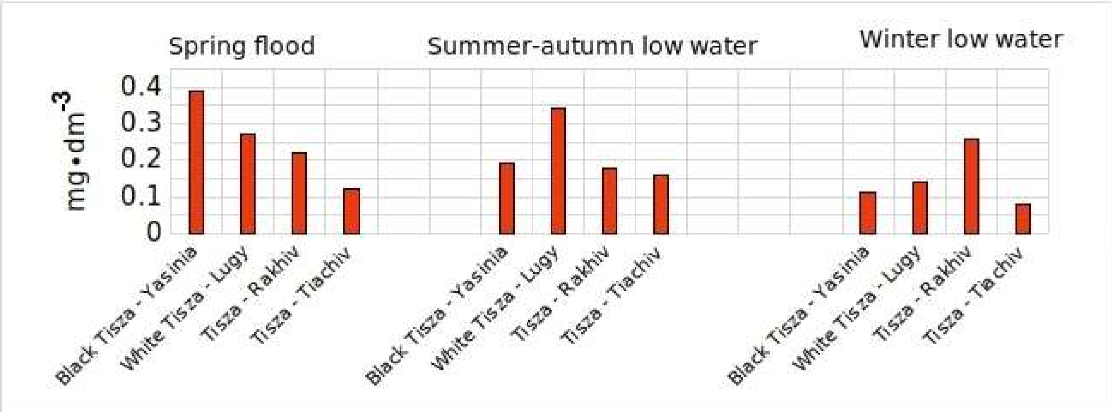

Fig. 8. Average long-term values of the content of total iron (Fe) in the waters of the headwaters of the Tisza River during the periods of different water phases, mg·dm^{-3}

Copper is a heavy metal that can enter surface waters because of the weathering processes of rocks containing this element: oxides, carbonates, silicates. From anthropogenic sources within the studied territory, we can single out the influence of wastewater from the territories of the Transcarpathian rebar plant in the village of Kobyletska Polyana and the Velykobychkiv forest chemical plant.

Average long-term values of copper (Cu) content in the waters of the Black Tisza River vary in the range of 0.3-32 mkg·dm^{-3}, the White Tisza River – 0.3-29 mkg·dm^{-3}, the Tisza River – 0.2-26.5 mkg·dm^{-3}, which is significantly less than the limit standards, which are 1,000 mkg·dm^{-3} (Ministry of Health…, 2022). Significant fluctuations in the concentration of copper were recorded several times, in particular, in the summer of 1990, in the Tisza River in Tiachiv, the copper content was recorded at the level of 120 mkg·dm^{-3}, which indicates a sharp anthropogenic pollution of the river. We observed isolated increases in copper concentrations in the waters of the upper reaches of the Tisza River until 2004, when powerful industrial enterprises that were the main polluters of the surface waters of Shopurka – the right tributary of the Tisza River within the boundaries of the Velykyy Bychkiv settlement – ceased to function in the Rakhiv district.

Zinc is a heavy metal that is quite common in water and soil, but its concentrations can vary from the level of analytical zero to several hundred mkg·dm^{-3}, and they often depend on the phase of the water regime. The average annual values of zinc content in the water of the Tisza River do not exceed the MPC of 1,000 mkg·dm^{-3}, but range from 1.1 mkg·dm^{-3} to 108.5 mkg·dm^{-3}. Much smaller ranges in the waters of Black Tisza River and White Tisza River, namely 1.3-28 mkg·dm^{-3} and 1.8-26.5 mkg·dm^{-3}, respectively. The zinc content increases downstream of the Tisza River. The highest zinc content was recorded in 1990 in the waters of the Tisza River at the level of 378 mkg·dm^{-3}.

Chromium is a heavy metal with toxic properties for living organisms. Chromium-containing rocks and minerals, as well as wastewater from chemical and light industry enterprises of the Rakhiv district, are sources of chromium within the catchment area of the Upper Tisza River. Chromium limits (Cr^{6+}) constitute 50 mkg·dm^{-3} (Ministry of Health…, 2022), and the maximum value was recorded in 1994 at the level of 22.9 mkg·dm^{-3}. Dynamic seasonal or multi-year changes in chromium content in the waters of the studied rivers were not detected (Table 4). The largest range of changes in the average annual values of chromium concentration in the waters of the Tisza River is 1.8-12.5 mkg·dm^{-3}.

Specific pollutants

Among the specific pollutants that can be found in river waters, the content of synthetic surfactants and petroleum products was analyzed. Synthetic

Table 4. Average seasonal concentrations of heavy metals in the waters of the headwaters of the Tisza River (1984-2018), mkg·dm^{-3}

Indicator	Cu	Zn	Cr	Cu	Zn	Cr	Cu	Zn	Cr
River – point / Season	Spring flood			Summer-autumn low water			Winter low water		
Black Tisza – Yasinia	6.01	8.22	3.41	7.48	12.8	333	5.85	11.1	4.08
White Tisza – Lugy	6.38	1.9	3.03	5.64	8.8	4.43	6.47	13	2.86
Tisza – Rakhiv	5.77	14	3.17	6.85	9.9	2.95	4.62	12.9	2.13
Tisza – Tiachiv	6.77	16.1	3.06	8.12	1.5	4.42	7.27	16.6	3.46

surfactants are contained in detergents, disinfectants and emulsifiers, which can enter river waters with surface runoff from coastal areas or floodplains, within which unauthorized dumping sites are often found. The largest sources of surfactants are domestic wastewater, which is discharged into rivers without treatment and in the absence of a centralized sewage network, as well as wastewater from light industry enterprises, particularly in the village of Yasinia. The content of surfactants in surface waters is not standardized, and the average long-term values in the waters of Black Tisza, White Tisza and Tisza rivers vary within 0.02-0.04 mg·dm^{-3}. Individual increases in indicators during the year are associated with an increase in the water content of rivers during the active phase of spring floods and frequent floods during the summer-autumn period. Frequent thaws during the winter border cause an increase in synthetic surfactants content in the waters of the Tisza in Rakhiv.

Average annual values of surfactants content in the waters of the studied rivers during 1984-2018 are decreasing (Fig. 9). The positive dynamics regarding the reduction of the content of synthetic pollutants can be explained by the decline of production capacities in the Rakhiv and Tiachiv districts, as well as the decrease in industrial wastewater, as well as the increase in the network of centralized drainage in populated areas. Thus, according to the data of the water quality monitoring point in Tiachiv, the range of average annual values varies from 0.13 mg·dm^{-3} in 1985 to the level of analytical zero (2013-2016).

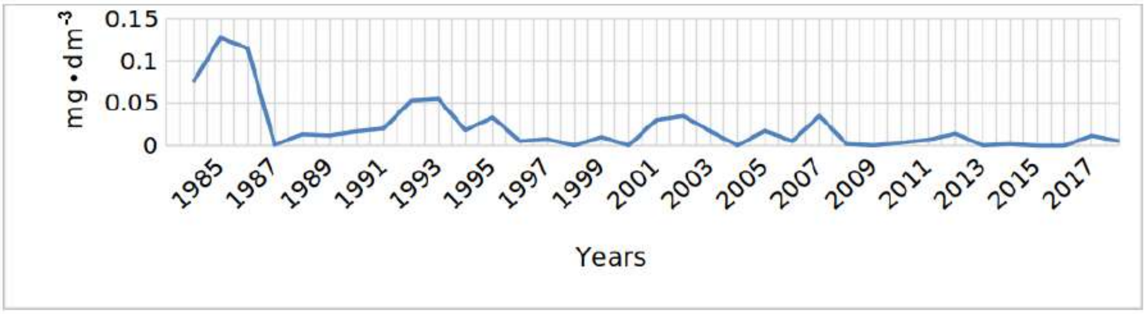

Fig. 9. Dynamics of average annual values of the content of synthetic surfactants in water of the Tisza River – Tiachiv (1984-2018), mg·dm^{-3}

Petroleum products are ones of the most dangerous organic compounds that enter river waters due to economic activities within the catchment area, in particular due to surface runoff from the territories of industrial facilities, territories polluted by fuel and lubricant substances and the surface of highways that extend along the Tisza River network. The limit rate of the content of oil products (high-sulfur oil) in surface waters is 0.1mg·dm^{-3} (Ministry of Health…, 2022).

Clear seasonal variability of the content of oil products in the waters of the studied rivers was not recorded, and high average multi-year values during the period of different water phases indicate the constant influence of anthropogenic sources of surface water pollution with a slight increase during the flood period and frequent floods in the warm period of the year (Fig. 10). And since 2013, the content of petroleum products in the waters of the Black Tisza, the White Tisza and the Tisza rivers in the section from Rakhiv to Tiachiv is less than 0.002 mg·dm^{-3} or even drops to the level of analytical zero.

Conclusion

1. The waters of the headwaters of the Tisza River from the source to the town of Tiachiv are hydrocarbonate-calcium, moderately fresh with an average mineralization in the range of 192-245 mg·dm^{-3}. The researchers conducted by us testify to the genetic closeness of the chemical composition of the surface waters of the upper reaches of the Tisza River.

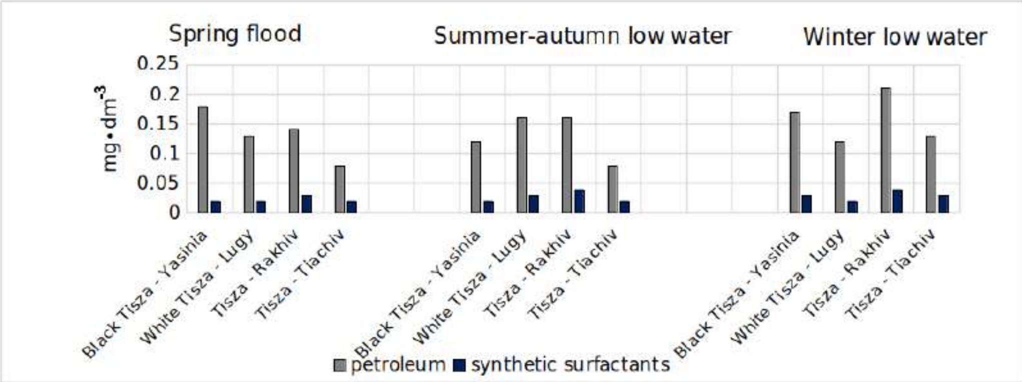

Fig. 10. Average long-term values of the content of petroleum products and synthetic surfactants during the period of different water phases in water of the Tisza River, mg·dm^{-3}

2. A clear connection was recorded between the hydrological regime and the regime of the main ions (HCO_3^-, SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+) and water mineralization. For physical and chemical indicators (pH, O_2), nitrogen-containing compounds and trace elements no seasonal fluctuations were detected.

3. Individual seasonal increases in the content of nitrogen-containing ammonium compounds ($N\text{-}NH_4^+$), nitrites ($N\text{-}NO_2^-$), nitrates ($N\text{-}NO_3^-$) in the waters of the Tisza headwaters are associated with the intensive decomposition of organic substances that enter the rivers with household wastewater.

4. A tendency towards the decrease in the concentrations of synthetic surfactants (during 1984-2018) and petroleum products (after 2013) in the waters of the upper reaches of the Tisza River was revealed.

5. The results of the study have important practical significance and can be used, in particular, in the development of a new Management Plan for the Tisza River Basin; determined and implemented in the actions of environmental control of business entities in the upper Tisza basin; consideration of environmental programs to improve water quality in the Tisza River basin.

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