Civil and environmental safety problems of the upper reaches of small mountain rivers (on the example of the Tysmenytsia River, Ukraine)

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Abstract

Small rivers are highly important elements of fresh water and sanitary-domestic supplies, local ecosystems functioning, thus they are essential for the environmental and civil safety of local areas. Chemical composition of the upper parts of rivers determines the chemical composition of waters downstream. The article represents the results of long-term researches of the Tysmenytsia upriver and its tributaries. The peculiarity of this area is its location within one of the oldest European oil recovery centers. According to the results of this research, the spatial changes of mineralization and the main components of chemical composition were established: the main ions, nitrogen compounds, petroleum products and phenols. The upper tributaries of the Tysmenytsia are characterized on average by hydrocarbonate calcium-magnesium composition with mineralization of 0,450 g/dm^3, and the waters of the main river streambed by sulfate-hydrocarbonate sodium-calcium composition with mineralization of 0,207 g/dm^3. The waters of the Tysmenytsia upper part on average contain nitrites (NO_2^-) of 0.12–0.20 mg/dm^3, nitrates (NO_3^-) of 1.8–3.4 mg/dm^3, ion ammonium (NH_4^+) of 0.21– 0.24 mg/dm^3, petroleum products of 0.27-0.66 mg/dm^3, phenols of 0.007- 0.010 mg/dm^3 and characterized by a COD value of 7.74-13.6 mgO^2/dm^3. This article also provides explanation of spatial changes of chemical composition of waters, conducts comparison with the composition of other Carpathian mountain rivers. Analyzed waters refer to the 2nd class of water quality. Established facts and analysis of their causes are potent scientific base of forming civil protection measures and environmental safety of investigated areas.

Keywords: civil safety, environmental safety, mountain rivers, small rivers, nitrogen compounds, organic compounds.

Introduction

There are 63029 small rivers and waterways in Ukraine with the total length of 185800 km (Yatsyk A. V., 1991). The object of our research, the Tysmenytsia River, that flows into the Bystrytsia River (the right tributary of the Dnipro), the source of which is located in the Eastern Beskids, also falls under the small rivers category.

Preservation of the small rivers water quality is a challenging task for any European country. Considerable pollution of waters of such rivers leads to reducing the level of environmental safety of the region and to the declaration of the emergency situation in case of stoppage of water supply to human settlements (Karabyn, V. V., 2000; Loboichenko V., 2018). Such situations have occurred in Carpathian region of Ukraine. In case of threat of the emergency situation on

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small rivers, it is of utmost importance for the civil protection services and environmental safety to have high-quality hydrochemical models of these rivers in order to reliably predict the migration parameters of pollutants. The reason is that the change in concentration of pollutants depends not only on the composition and amount of pollutant but also in the composition of containing waters.

Municipal waters of adjacent settlements, as well as industrial and agricultural wastes enter the surface waters of the Tysmenytsa basin. The main industrial enterprises that pollute the Tysmenytsia flows are: "Stebnyk Potassium Factory" ltd., The JSC Automobile Cranes Plant Public Joint Stock Company in Drohobych, Polimineral State Mining and Chemical Enterprise, The JSC Engineering Plant Public Joint Stock Company in Drohobych, "Boryslavvodokanal" Municipal Enterprise (Ekolohichnyi pasport, 2018).

The research is aimed at establishing the basic hydrochemical parameters of the Tysmenytsia River upper part so as to set up hydrochemical model of the small mountain river for civil and ecological safety.

Material and methods

2.1. The object of research. The object is the hydrochemical composition of The Tysmenytsia upriver, Carpathian region of Ukraine.

The source of the Tysmenytsia River, according to zoning schemes by Y. R. Hiletskyi, relates to natural-geographical subzone of the Ukrainian Beskids (Hiletskyi Y.R., 2012).

The territory of investigation is characterized by complex geological structure that is determined by location at the junction of ancient Eastern Europe platforms and the Carpathians. Within the researched area, according to decoding of aerospace images of various scales and space images, there is distinguished the Drohobych-Boryslav ring structure which is characterized by high density of rupture disturbances and localization of various deposits of minerals manifestations (Triska M. T., 2004).

In the stratigraphic aspect, the upper part of the Tysmenytsia River is situated in zone of access to the surface of the Stryiska suite rocks of the Cretaceous and Paleogene rocks. These strata are composed of rhythmic interbedding of sandstones, mudstones and siltstones and belong to the flysch formation. A characteristic feature of most rocks in the studied area are carbonate cement presence, which significantly affects the chemical composition of the underground and, to a lesser extent, surface water.

In the industrial aspect, the area of research is known as the Boryslav Petroleum Region, which is one of the oldest oil production areas in Europe, and oil has been extracted in the territory since the IIX century with the aid of pitsıo In 1893, the drilling of wells was performed by cable way (Hayko H., 2009). As a result of almost a century and a half of oil production, the territory in the vicinity of Borislav is covered with hundreds of oil wells, digs, wells, that created the preconditions for an ecological disaster.

2.2. Methodology. We have been performig monitoring researches to study waters and sediments of the upper part of the Tysmenytsia at 3 points of research and on 4 upper tributaries of the river since 2014. At these points, water samples were taken 4 times a year: in winter, spring, summer and autumn. Selections in winter and summer were carried out in the shortest period, and in spring and summer in the most high-water one.

Analytical studies were performed in the ecological safety laboratory in LSULS. The contents of chlorides (Cl^-) (Unyfitsyrovannye metody, 1987), hydrocarbonates (HCO_3^-) (Metodyka, KND 211.1.4.027-95), calcium (Ca^{2+}) (Unyfitsyrovannye metody, 1987) and magnesium (Mg^{2+}) (Unyfitsyrovannye metody, 1987) were detected with the help of the analysis by titration. In particular: chlorides – with silver nitrate in the presence of potassium chromate; hydro-carbonates – with hydrochloric acid in the presence of methyl orange; calcium and magnesium – with trilon B in the presence of murexide and black erichrome, respectively. Sulphates (SO_4^{2-}) were determined by weight method (barium nitrate sedimentation followed

by annealing the sediment) according to the Guiding Normative Document 211.1.4.026-95. The sodium (Na^+) and potassium (K^+) contents were calculated by the balance of equivalents. The other anions (nitrates (NO_3^-) (Metodyka, KND 211.1.4.027-95) and nitrites (NO_2^-) (Metodyka, KND 211.1.4.023-95) were determined by photocolorimetric method, namely: nitrate content by interaction with sodium salicylate solution in sulfuric acid medium; nitrite – with Griss reagent. Only soluble forms of ions were determined.

Laboratory data were compared with the TLV for water for sanitary and household use (Table 1), the limit values for water quality classes - sources of centralized drinking water supply in accordance with Ukrainian State Standard 4808: 2007 and Directive 98/83/EU. (Table 2).

Table – 1. The value of TLV in water for sanitary and household use for separate components:

Value	BOD_5 mgO_2/dm^3	COD mgO_2/dm^3	Oil products mg/dm^3	Phenols mg/dm^3	NO_2 mg/dm^3	NO_3 mg/dm^3	NH_4
TLV	3,0	15,0	0,3	0,001	0,5	50,0	2,0

Table – 2. Separate classification values of the surface waters quality

Value	Class of water quality			
	1	2	3	4
Oil products, mg/dm^3	<10	10-50	51-200	<200
Phenols, mg/dm^3	<0,001	0,001-0,01	0,011-0,050	>0,050
COD (dichromate), mgO_2/dm^3	<9,0	9,0 – 30,0	31,0-40,0	>40

Results and discussion

3.1. Changeability of the main ions contents. The water of the Tysmenytsia upper part tributaries has mineralization from 0,138 g/dm^3 to 0,310 g/dm^3, the average value is 0,207 g/dm^3. Somewhat higher values, particularly in one of the Tysmenytsia tributaries were obtained during its probable pollution due to drilling of oil and gas well Pivdennoboryslavska-1 in 2013 by P. I. Pavliuk and others (Pavluk M., 2016).

Upper tributaries of the Tysmenytsia are on average characterized by hydrocarbonate calcium-magnesium composition

$$M_{0,207}\frac{HCO_3 90\,(SO_4 5\,Cl 5)}{Mg\,45\,Ca\,40\,(Na+K\,15)}\,pH\,8{,}2 \qquad (1)$$

The waters of Tysmenytsia River in its upper part are characterized by mineralization from 0.360 g/dm^3 to 0.585 g/dm^3 with the average value of 0.450 g/dm^3.

The chemical composition of water is mainly sulfate-hydrogen carbonate sodium-calcium:

$$M_{0,44}\frac{HCO_3 63\,SO_4 28\,(Cl 10)}{Ca\,51\,Na+K\,36\,(Mg\,13)}\,pH\,7{,}1 \qquad (2)$$

The waters of the upper tributaries are much less mineralized, have slight alkaline reaction and the composition differs from the waters of the Tysmenytsia upper part. That difference is related to the predominantly surface nutrition and small length of tributaries of this part of the river (up to 3 km). As a result, slightly mineralized (0,075 g/dm^3) meteogenic waters of hydrocarbonate magnesium-calcium-sodium composition (Karabyn V. V., 2016) do not have time to react with rocks in order to increase their mineralization considerably. The length of the tributaries is simultaneously sufficient for the contact with clay on the surface which affects increases of these waters' pH (fig. 1).

The amount of dry residue recorded in the upper part of the Tysmenytsia River is slightly higher than in the upper Carpathian waters. For example, waters of the White Cheremosh River above the village Yablunytsia contain 0.305-0.319 g/dm^3 of dry residue (Karabyn V. V., 2013),

waters of the Stryi river above the village Ilnyk contain 0.27–0.33 g/dm3 of dry residue (Borutska Yu., 2015).

The increase in mineralization and the relative content of carbonates, salts of sodium and potassium and sulfites (2) downstream of the river is probably due to geological reasons, particularly due to the river outflows from the flysch deposits of chalk (K_2st) and Paleogene (P_1jm, P_2mn, P_2vg, P_2bs, P_3ml) and its entry into the distribution zone of saline deposits of Paleogene (N_1vr_1).

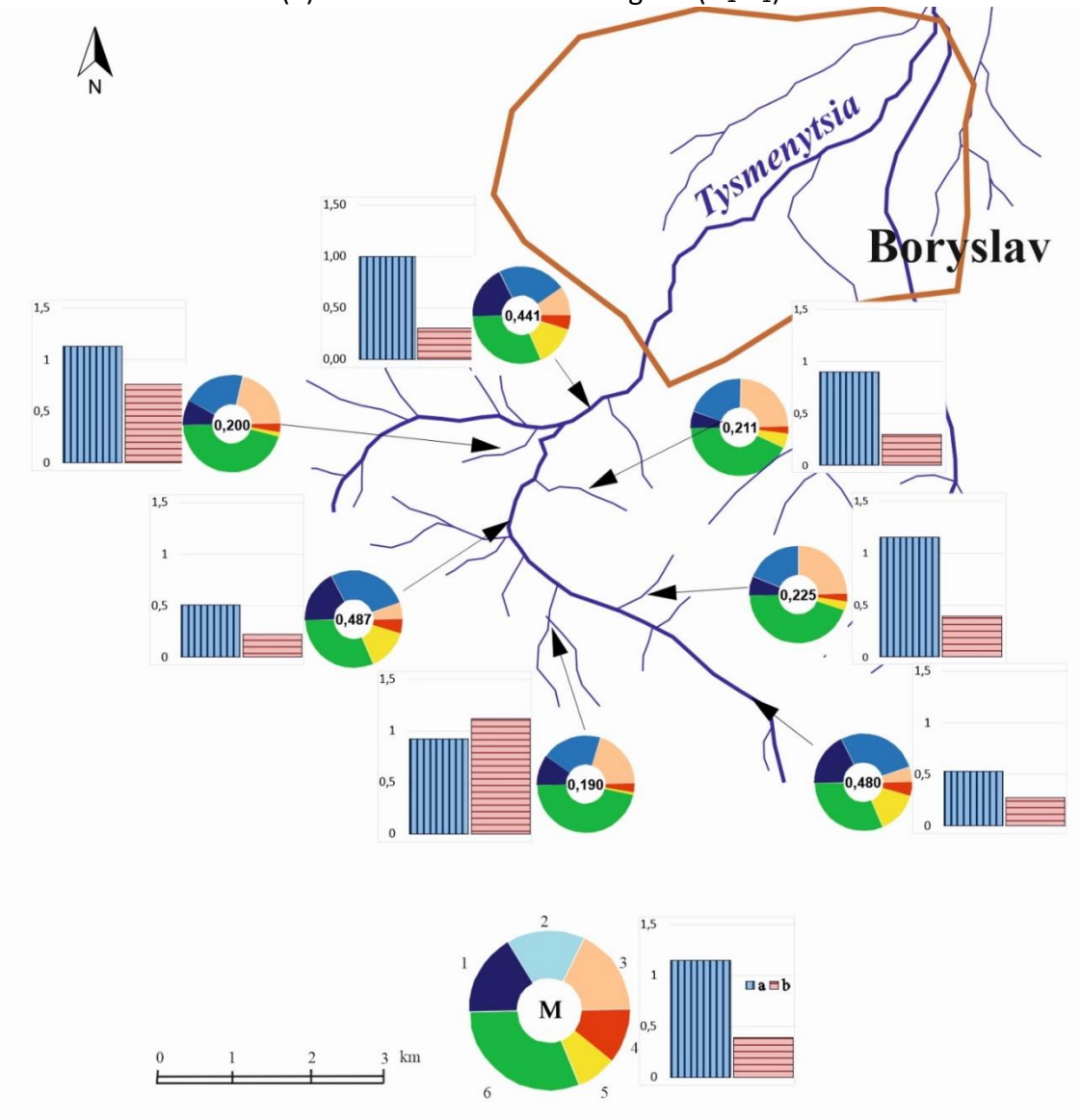

Fig 1. Map of the chemical composition of the upper part of the river Tysmenytsia water: 1 – Na^++ K^+, 2 – Ca^{2+}, 3 – Mg^{2+}, 4 – Cl^-, 5 – SO_4^{2-}, 6 – HCO_3^-, M – mineralization, a – phenols, b – oil products. M in g/dm^3, phenols 10n mg/dm^3, other water components in mg/dm^3

3.2. Changeability of nitrogen compounds content. The nitrites (NO_2^-) of upper tributaries of the Tysmenytsia are 0.20 mg/dm^3, nitrates (NO_3^-) – 3.4 mg/dm^3, ammonium ion (NH_4^+) – 0.24 mg/dm^3. In the water of the Tysmenytsia in the area above the city of Boryslav average concentrations of nitrites (NO_2^-) are 0.12 mg/dm^3, nitrates (NO_3^-) – 1.8 mg/dm^3, ammonium ion – 0.21 mg/dm^3. The mentioned concentrations do not exceed the TLV. One of the reasons for the nitrogen compounds presence in the upper reaches of the river is global and regional nitrogen

pollution of the atmosphere. In particular, in melt water from snow in this territory we have detected nitrates in the amount from 3,078 mg/dm^3 to 4,012 mg/dm^3 and ammonium ions in the amount from 1.05 mg/dm^3 to 1,32 mg/dm^3.

The increased contents of nitrogen compounds are peculiar to many European rivers and also to their upper parts. In particular, for 66% river trials of the surface and alluvial waters of the Oja and Tirón river basins in Spain do not meet the European requirements for a maximum content of NO_3^- (50 mg/L^{-1}) (Arauzo M., 2011).

3.3. Variability in the content of organic compounds. The upper tributaries of the river Tysmenytsia contain on average 0,66 mg/dm^3 of oil products, phenols – 0,010 mg/dm^3 and they are characterized by the COD value of 13,6 mgO_2/dm^3. Similar characteristics have also waters of the upper part of the Tysmenytsya: oil products 0,27 mg/dm^3, phenols – 0,007 mg/dm^3, COD – 7,74 mgO_2/dm^3. Among the natural causes for the presence of such quantities of organic substances in the waters of the upper part of the Tysmenytsia River is the drainage by the river of sediments of the Paleogene menilite suite, the rocks of which are enriched with organic substances of bituminous composition. Technogenic ones should include the drilling ground of deep oil and gas well located in the basin of upper reaches of the Tysmenytsia.

In general, the waters of the Tysmenytsia River meet the demands for the quality of surface water of the first class for the most part. However, the concentration of phenols and the amount of chemical oxygen demand in the upper tributaries of the Tysmenytsia River and the main riverbed correspond to the second class of water quality.

According to the Emergency Classifier in Ukraine (Klasyfikator, 2010), one of the grounds for declaring a state of emergency is a 100-fold exceedance of the maximum permissible concentration of a pollutant in the water. In this aspect, in the basin of the Tysmenytsa river it is important to monitor the concentration of organic substances, especially phenols, the maximum concentration of which according to our data was 0.036 mg/dm3. This concentration exceeded the maximum permissible concentration 36 times during the period when there were no accidental spills of oil, petroleum products and other organic substances. This circumstance indicates a real danger of reaching 100 times the maximum permissible concentration in the event of an oil spill.

The research region is saturated with mining, which has already affected the surface water quality. Further development of minerals should be carried out on a new "environmentally friendly" basis (Khorolskyi A., 2019).

The established facts and the analysis of their causes are the significant scientific basis for the formation of civil protection measures and environmental safety of the studied area. They point out to the inability to use the water of the upper part of the Tysmenytsa safely for drinking water supply in case of emergency. These data are also important for estimating changes in the chemical composition of downstream waters.

Conclusions

The water of the upper part of the Tysmenytsia River and its tributaries has mineralization of 0.207-0.450 g/dm^3. The upper tributaries of the Tysmenytsya are characterized on average by a calcium carbonate magnesium composition, and the waters of the main channel by sulfate-bicarbonate sodium-calcium one. The increase in mineralization and the relative content of carbonates, salts of sodium and potassium and sulfites downstream of the river is probably due to geological reasons, namely the exit of the river from flysch deposits of chalk (K_2st) and Paleogene (P_1jm, P_2mn, P_2vg, P_2bs, P_3ml) and its entry into the distribution zone of saline deposits of the Vorotyshchyn suite of Paleogene (N_1vr1).

The waters of the upper part of the Tysmenytsia River on average contain nitrites (NO_2^-) in the amount of 0.12-0.20 mg/dm^3, nitrates (NO_3^-) – 1.8-3.4 mg/dm^3, ion- ammonium (NH_4^+) – 0.21-0.24 mg/dm^3, oil products – 0.27-0.66 mg/dm^3, phenols – 0.007-0.010 mg/dm^3 and the waters are characterized by a COD value of

7.74-13.6 mgO_2/dm^3. Among the natural causes for the presence of organic liquids high content in the waters of the upper part of the Tysmenytsia is the drainage by the river of the Paleogene menilite suite sediments, the rocks of which are enriched with organic substances of bituminous composition. Technogenic causes include the oil and gas well drilling site located in the basin of the upper Tysmenytsia River.

The studied waters correspond to the second class of water quality. The established facts and the analysis of their causes are the significant scientific basis for the formation of civil protection measures and environmental safety of the research area.

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