Evaluation of the possibility of using the water of the Bystrytsya-Nadvirnyans'ka River in Cherniiv (Ukraine) to supply the population with drinking water

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Abstract
The article presents the results of the research carried out in order to assess the possibility of using surface water of the Bystrytsya-Nadvirnyans'ka River in Cherniiv (western Ukraine), for the public supply of water intended for human consumption. For this purpose an existing database that contains the results of analyses of surface water samples collected in 1999, 2002, 2005, 2008, 2011 and 2014 was used. Each year, from 8 to 13 samples were collected from the Bystrytsya-Nadvirnyans'ka River in Cherniiv. Physicochemical analyses of the samples taken included the determination of pH value, temperature, TDS, alkalinity, hardness, dissolved oxygen, BOD5, COD, suspended solids and ions: Ca2+, Mg2+, Na+, K+, Fe2+, NH4+, Cu2+, Cl-, SO42-, PO43-, HCO3-, NO2-, NO3-. These chemical analyses were verified by calculation of errors based on the ionic balance.

The results of the analyses were referred to the polish applicable requirements for surface water used for public supply of water intended for human consumption and to the regulation regarding the classification of the surface water status and environmental quality standards for priority substances. The results indicate that water of the Bystrytsya-Nadvirnyans'ka River in the area of Cherniiv was out of the class in the years 1999 and 2002 due to exceeding the limit values for category A3 for Cu2+. On the basis of incomplete assessment of the status of the Bystrytsya-Nadvirnyans'ka River water (due to the tests limitation to the physical and chemical components) determined that the water has a bad status because it exceeded the limits for class II for Cl-, SO42-, NO3- and TDS. In the samples collected in 1999 and 2002 it is also observed exceeding the maximum limit concentrations for Cu2+.

Keywords
Surface water, ecological status, chemical status, Cherniiv, Bystrytsya-Nadvirnyans'ka

INTRODUCTION
Through Ukraine flows many great rivers like Dnieper and Dniester. They make up large surface water resources that can be used for public supply. For this purpose appropriate regulations are established to check the water suitability for human consumption and also to define a series of processes through which water have to pass to purify and treat it.

The requirements for surface water which is used to supply the population with water intended for consumption in Poland are set in the Regulation of the Minister of the Environment (RME, 2002). This document defines the requirements that surface water should fulfil, determines the frequency of water sampling, the reference methodology of analysis and the assessment methods, whether the water fulfil the required conditions. The water is classified into three categories A1, A2 and A3 on the base of limit values for water quality indicator included in the regulation.
In Poland the requirements for assessing the status of the surface water bodies (SWB) are specified in the Regulation of the Minister of Environment of the 21 July 2016 (RME, 2016). It defines the criteria and methodology for assessing the status of SWB, including the classification of biological, physicochemical and hydromorphological elements for the 5 surface water quality classes. According to the regulation, the assessment of surface water status is based on the ecological and chemical status of a given SWB.

Assessment of an ecological status is made by assignment one of the five water quality classes to SWB. In turn, the classification of the chemical status is done by comparison the results of analysis with the environmental quality standards for priority substances and other pollutants.

The article presents the assessment of possibility of using the Bystrytsya-Nadvirnyans'ka River water, in Cherniiv, to supply population with drinking water according to the Polish regulations (RME, 2002). This assessment was based on the existing database containing the results of field and laboratory measurements conducted during 6 years (1999, 2002, 2005, 2008, 2011, 2014). In addition, an incomplete assessment of surface water status with the accordance to (RME 2016) was made on the basis of available data.

CHARACTERISTICS OF THE RESEARCH AREA
The study area includes surroundings of Cherniiv. It is a village located in the Ivano-Frankivsk Oblast of western Ukraine, in the Tysmenytsia District, alongside the Bystrytsya-Nadvirnyans'ka River (Fig. 1). Its surface area is 23.35 km², and the population is 3.9 thousand (https://pl.wikipedia.org).

Figure 1. Location of the research area

The Bystrytsya-Nadvirnyans'ka River originates on the northern foothills of Small Syvulia mountain (Gorgany mountain massif). Its total length is 82 km and the area of its catchment is 795 km². It joins the Bystrytsia of Solotvyn north of Ivano-Frankivsk creating the Bystrytsia River and finally flows into Dniester as its right-bank tributary. The river has some tributaries: Manyavka, Sadzhavka, Radchanka, and Great Lukavets (https://alchetron.com).
METHODOLOGY
To determine the usefulness of surface water as a water for human consumption, and to assess the status of water in the Cherniiv area, an existing database was used. It contains the results of analyses of surface water samples collected in 1999, 2002, 2005, 2008, 2011 and 2014. Each year, from 8 to 13 samples of surface water were collected from the Bystrytsya-Nadvirnyans'ka River in Cherniiv. Sampling and analysis were done in accordance with the guidelines of Ukrainian Ministry of Ecology and Natural Resources of Ukraine. The analysis included determination of TDS, total hardness, pH, alkalinity, temperature, dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD) and ions: Ca$^{2+}$, Mg$^{2+}$, K$^+$, Fe$^{2+}$, NH$_4^+$, Cu$^{2+}$, Cl$^-$, HCO$_3^-$, SO$_4^{2-}$, NO$_2^-$, NO$_3^-$, PO$_4^{3-}$. In further calculation average results from each year were used.

Due to the lack of detailed data on the methodology, it was possible only to verify the correctness of the analysis by calculation of the errors based on the ionic balance. The values of this error were within the range from 3.76% to 6.68%. For sum of main ions [mval/L] lower than 5 mval/L the maximum allowed error is 10% according to polish standard (PN-C-04638-02). On this basis it was found that all analyses were conducted correctly.

RESULTS OF WATER PHYSICOCHEMICAL ANALYSES
The dominant hydrochemical types of Bystrytsya-Nadvirnyans'ka River in Cherniiv, according to Szczukariew-Prikołński classification, are two-ionic water: bicarbonate-calcium (HCO$_3$-Ca) in 2005, 2008 and three-ionic water: bicarbonate-sulfate-calcium water (HCO$_3$-SO$_4$-Ca) in 2011 and 2014, bicarbonate-calcium-potassium (HCO$_3$-Ca-K) in 1999 and bicarbonate-calcium-magnesium (HCO$_3$-Ca-Mg) in 2002.

Average value of mineralization for all samples taken during these years is 222.4 mg/L. The highest mineralisation is observed in 2014 (238.4 mg/L) and the lowest in 2011 (203 mg/L). The mineralization is similar for all years and does not show upward or downward trends.

Table 1 presents minimum, maximum and average concentrations of selected physicochemical elements in the tested points as well as threshold values for good status (RME, 2016, Attachment 1, Type of river: 12 - flysch stream) and limit values of the analysed water quality indicators (RME, 2002, Attachment 1). Bold values indicate that threshold values for good status are exceeded.

ASSESSMENT OF SUITABILITY OF SURFACE WATER AS SUPPLY WITH WATER USED FOR HUMAN CONSUMPTION
The assessment of suitability of surface water as water for human consumption the average values of the measured physicochemical elements from each year were compared with the threshold values of the water quality indicators (Tab. 1). The exceeding of threshold values (RME, 2002) for category A3 (the worst category) were found in 2 samples taken in 1999 and 2002. In both cases it concerns copper concentration. In the next years (2005, 2008, 2011, 2014) the copper concentration was not measured, but it does not mean that it was absent in this water. On the contrary it can be expected that during these years the copper concentration also could be much higher than limit value for category A3. The other indicators for all studied years are in the range of the threshold values for the category A1. According to the regulation (RME, 2002), it is permissible to exceed the limit values for a selected category not marked with an asterisk (*) in 10% of samples if they are not hazardous to human health and in subsequent water samples, no threshold values were exceeded. But in this case high concentrations of copper are observed in both years 1999 and 2002. Even though copper is not particularly hazardous for human health, it belongs to substances that are harmful to the aquatic environment.
### Table 1. Statement of the selected physicochemical elements of the Bystrysya-Nadvimyans'ka River’s water

| Elements                      | 1999   | 2002   | 2005   | 2008   | 2011   | 2014   | Mean   | Min    | Max    | Threshold value for good status, II class (RME, 2016) | Threshold values of the water quality indicators (RME, 2002) |
|-------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------------------------------------------------------|----------------------------------------------------------|
| TDS [mg/L]                    | 221.6  | 203.1  | 225.2  | 161.9  | 200.2  | 236.8  | 208.1  | 161.9  | 236.8  | 203                                                 | -                                                        |
| Total hardness [mg CaCO₃/L]   | 107.0  | 111.1  | 114.7  | 105.9  | 107.6  | 118.5  | 110.8  | 105.9  | 118.5  | 144                                                 | -                                                        |
| pH [-]                        | 8.22   | 7.91   | 7.72   | 7.75   | 7.43   | 7.67   | 7.78   | 7.43   | 8.22   | 7.4-8.4                                              | 6.5-8.5                                                 |
| Alkalinity [mg CaCO₃/L]       | 97.6   | 87.59  | 99.6   | 95.60  | 91.59  | 101.6  | 95.60  | 87.59  | 101.6  | 219.0                                               | -                                                        |
| Temperature [°C]              | 8.88   | 11.5   | 9      | 10.62  | 10.08  | 9.67   | 9.96   | 8.88   | 11.5   | 24                                                  | 25*                                                     |
| Suspension [mg/L]             | 4.125  | 5.8    | 3.42   | 9.62   | 3.33   | 9      | 5.88   | 3.33   | 9.62   | 17.3                                               | 25                                                       |
| DO [mg O₂/L]                  | 9.79   | 9.96   | 10.07  | 10.06  | 11.05  | 10.83  | 10.29  | 9.79   | 11.05  | >8.9                                                | -                                                        |
| BOD [mg O₂/L]                 | 2.55   | 2.24   | 2.11   | 1.5    | 1.38   | 1.6    | 1.90   | 1.38   | 2.55   | 2.9                                                | 3                                                       |
| COD [mg O₂/L]                 | -13.66 | 10.08  | 8.45   | 5.78   | 7.03   | 9.00   | 5.78   | 7.03   | 13.66  | 14                                                  | 25                                                      |
| Cations and anions [mg/L]     |        |        |        |        |        |        |        |        |        |                                                     |                                                          |
| Ca²⁺                          | 33.63  | 33.4   | 37.08  | 34.62  | 33.17  | 36.83  | 34.79  | 33.17  | 37.08  | 51                                                 | -                                                       |
| Mg²⁺                          | 5.04   | 6.7    | 5.38   | 4.11   | 5.93   | 6.82   | 5.66   | 4.11   | 6.82   | 11.7                                               | -                                                       |
| NH₄⁺                          | 0.27   | 0.3    | 0.15   | 0.4    | 0.21   | 0.12   | 0.24   | 0.12   | 0.4    | 0.54                                                | -                                                       |
| Cl⁻                            | 18.88  | 19.8   | 18.33  | 11.31  | 9.82   | 13.5   | 15.27  | 9.82   | 19.8   | 12.8                                               | 250                                                     |
| SO₄²⁻                          | 24.5   | 23.8   | 24.75  | 26.54  | 26.5   | 34.25  | 26.72  | 23.8   | 34.25  | 28.2                                               | 250                                                     |
| NO₃⁻                          | 0.04   | 0.03   | 0.02   | 0.04   | 0.007  | 0.024  | 0.027  | 0.007  | 0.04   | 0.082                                               | -                                                       |
| NO₂⁻                          | 6.98   | 5.26   | 4.33   | 3.19   | 1.97   | 2.38   | 4.02   | 1.97   | 6.98   | 6.64                                               | 50                                                      |
| PO₄³⁻                          | -0.031 | 0.035  | 0.02   | 0.02   | 0.021  | 0.031  | 0.028  | 0.02   | 0.035  | 0.21                                               | 0.4                                                     |

| Substances that are particularly harmful to the aquatic environment [mg/L] |        |        |        |        |        |        |        |        |        |                                                     |                                                          |
| Cu²⁺                          | 3.03   | 2.3    | -      | -      | -      | -      | 2.67   | 2.3    | 3.03   | 0.05                                               | 0.05                                                     |

Explanations: TDS – total dissolved solids, DO – dissolved oxygen, BOD – biochemical oxygen demand, COD – chemical oxygen demand, * derogations allowed due to exceptional conditions, as defined in the Regulation (RME, 2002).
On this basis surface water of the Bystrytsya-Nadvirnyans'ka River should be classified as out of the category in 1999 and 2002 because of high concentration of copper, which means that they cannot be used for human consumption. During years 2005, 2008, 2011 and 2014 this surface water belong to category A1 and could be used for public supply. Surface water which belongs to category A1 are water requiring simple physical treatment, in particular filtration and disinfection.

To use surface water of the Bystrytsya-Nadvirnyans'ka River for human consumption, it is necessary to control copper concentration in the river and also to undertake measures to eliminate the causes of this high concentration. High copper concentrations may be associated with electrotechnical, pharmaceutical, rubber and dye industry or anthropogenic pollution (leachate from municipal landfills). Copper is also a part of plant protection products and some mineral fertilizers (Witczak et al., 2013), which easily can reach the surface water along with the precipitation water. This is the most probable cause of its high concentration in surface water, because of an agricultural use of this area.

**ASSESSMENT OF THE CHEMICAL STATUS**

Relating the values of the physicochemical elements of surface water in the individual monitoring points to the threshold values for good water status (RME, 2016), exceeding of threshold values for class II (Tab. 1) were found for: TDS and Cl⁻ in samples collected in 1999, 2002, 2005 and 2014, \( \text{SO}_4^{2-} \) (2014), \( \text{NO}_3^- \) (1999) and \( \text{Cu}^{2+} \) in samples collected in 1999 and 2002 (Fig. 2). Not fulfilling the requirements for class II means a status below good for physicochemical elements.
Figure 2. Exceeding threshold values (RME, 2016 – black lines) for: a) TDS, b) Cl\(^{-}\), c) SO\(_4^{2-}\), d) NO\(_3^{-}\) and e) Cu\(^{2+}\).

According to the regulation, not fulfilling the requirements for class I (very good status) means that the status is below good for hydromorphological elements.

In order to classify ecological status it is necessary to include also biological elements. Due to the absence of biological analysis, in this paper the assessment of ecological status was made only on the basis of the physicochemical analyses results. For the whole investigated area the analysed waters belong to water with poor ecological status in the range of analysed indices.

According to the Regulation (RME, 2016), chemical status is assessed on the basis of not less than 12 results of priority substances and other pollutants measurements. However, only copper was identified in the tested samples, hence the assessment of chemical status is incomplete. Exceeding the maximum allowable concentrations for copper is observed only in samples collected in 1999, 2002. This exceedance determines that the chemical status of the surface water is below good for years 1999 and 2002. For other years the chemical status of this surface water is good most probably because of absence of copper concentration measurement.

The assessment of SWB status is made by comparison of the results of the classification of ecological and chemical status. Classifying studied surface water to poor ecological status and chemical status below good (for 1999 and 2002) or good chemical status (for 1999, 2002, 2005, 2014) results in poor surface water status. Hence, in the area assessment, surface water of the Bystrytsya-Nadvirnyans'ka River in Cherniiv is characterized by poor status.

CONCLUSIONS
The assessment of the usefulness of the surface water of the Bystrytsya-Nadvirnyans'ka River in Cherniiv, in the context of their use as a supply of drinking water for human consumption, was based on the existing database containing the results of field and laboratory analyses conducted during 6 years (1999, 2002, 2005, 2008, 2011, 2014). Each year from 8 to 13 samples were collected from the river and then have been analysed in the laboratory. These results (average values of indicators for each year) have allowed the classification of surface water to the appropriate category of the suitability for consumption and the incomplete assessment of the status of these water.

The dominant hydrochemical type of Bystrytsya-Nadvirnyans'ka River in Cherniiv, according to Szczukariew-Prikłoński classification, are two-ionic water: bicarbonate-calcium (HCO\(_3\)-Ca) in
2005, 2008 and three-ionic water: bicarbonate-sulfate-calcium water (HCO₃-SO₄-Ca) in 2011 and 2014, bicarbonate-calcium-potassium (HCO₃-Ca-K) in 1999 and bicarbonate-calcium-magnesium (HCO₃-Ca-Mg) in 2002.

Based on the results of analyses, water of Bystrytsya-Nadvirnyans'ka in Cherniiv is out of the category for years 1999 and 2002, which means that the water cannot be used for human consumption, because of high concentration of copper. For other years the analysed surface water is classified to category A1 and could be used for public supply, however the copper concentration was not measured during these years. In addition, incomplete assessment of the status of these water has shown that both in point and area assessment it has a poor status.

Presented evaluation is a simplified assessment. In order to obtain a reliable results, it is necessary to carry out a study covering the full range of indicators listed in the Regulation in an accredited laboratory, in accordance with the sampling collection procedures described in international standards (e.g. ISO 5667-3, 5667-6, 5667-14).

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