

WATER QUALITY ASSESSMENT AND CONSERVATION OF THE RIVER WATER IN REGIONS WITH VARIOUS ANTHROPOGENIC ACTIVITIES IN BULGARIA: A CASE STUDY OF THE CATCHMENTS OF TOPOLNITSA AND LUDA YANA RIVERS

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Abstract

Water is a very important natural resource which is being exploited indiscriminately by humans. The water resources are getting depleted and polluted by anthropogenic sources. One of the key activities to conserve the water including the river water is to achieve a good water quality. Water quality describes the physical, chemical and biological status of water. In this study to define a water quality in a model region with various anthropogenic activities (catchments of Topolnitsa and Luda Yana Rivers) were used fifteen physicochemical parameters: pH, electrical conductivity (EC), dissolved oxygen (DO), ammonium (N-NH₄), nitrate (N-NO₃), nitrite (N-NO₂) and phosphate (P-ortho-PO₄) and such heavy metals as Cu, Fe, Mn, Pb, As, Zn, Cd and Ni. The samples were collected for the period 2019-2021 in six monitoring points of the study area, characterized with intensive and various human impact. The results based on this index and obtained from this research would be useful to the large public and even to land-use planners and environmental management agencies for monitoring and reducing the water pollution, especially for such regions defined as an ecological "hot spot" for many years and their future conservation.

Keywords: Conservation, Water quality, Physicochemical parameters, Heavy metals, Anthropogenic activities, Topolnitsa, Luda Yana

Introduction

Water is a very important natural resource which is being exploited indiscriminately by humans. Water quality is the greatest conservation concern in the watersheds. The water resources are getting depleted and polluted by various anthropogenic sources [1]. The main goals of water conservation are sustainability, energy and habitat conservation [2]. However, despite water being the basic human need, this precious resource is being wasted, polluted and getting depleted [3]. Very often based on the obtained analysis and water quality assessments, conservation measures, including legislations have been suggested in order to conserve (quality and quantity) the river waters. Nowadays in many European countries, including Bulgaria, special attention is paid to the protection of pollution and depletion of environmental

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components, including water resources. The availability of a sufficient quantity of fresh water of the required quality for certain purposes is essential both for the development of modern society and for the normal functioning of aquatic ecosystems.

Due to the transitional nature of the climate in Bulgaria and the diversity of the relief, the distribution of water resources throughout the country is not even. In addition, the minimum of both precipitation and runoff is during the summer months in most regions of the country, when water consumption is higher (for irrigation, cooling in production processes, etc.). Due to these circumstances, the conservation against pollution and the use of water resources is not only an environmental issue, but also an essential factor for sustainable economic growth, especially in conditions of water scarcity and increasing droughts. In our country, the quality of river waters is influenced by various industrial, communal and agricultural activities. In some parts of the river basin, a certain type of pollution is predominant, while in others the "polluters" act together. Like a number of river systems in our country, the Topolnitsa and Luda Yana rivers are also subject to intensive anthropogenic impact within their catchment areas. Due to the diverse and active anthropogenic pressure, the catchment area of the Topolnitsa river is defined as a "hot spot" Along the river are located 11 settlements, including 1 town (Koprivshitsa) and 10 villages, and along the Luda Yana river there are 6 settlements, including 1 town and 5 villages. The river water is mainly used for irrigation and industrial water supply. Both rivers are left tributaries of the Maritsa river. The determination of the main physicochemical properties of surface waters in the two model river basins and the reason for their changes has a decisive contribution to clarifying a number of important issues related to environmental pollution.

The main aim of this study is to assess and analyze water quality by physico-chemical indicators in the catchment areas of the Topolnitsa and Luda Yana rivers for the period 2019-2021 (Fig. 1).

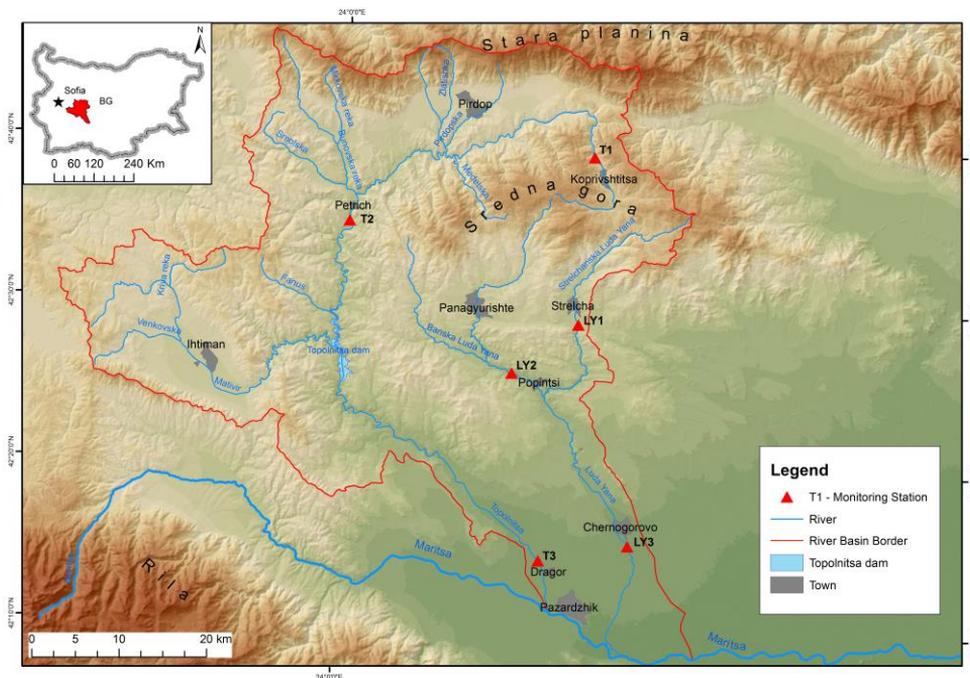


Fig. 1. Map of the study area

In practice, the obtained results popularized in the current research are the final stage of a three-year study with clear practical applicability and in close connection with the requirements of the National Strategy for Research in the Republic of Bulgaria 2017-2030. The conclusions made regarding the spatio-temporal transformations of the physicochemical state of the Topolnitsa and Luda Yana rivers will help to increase the quantity and quality of fundamental research in the field of environmental protection, as well as raising the standard of living. The performed detailed analysis of the condition of surface waters in terms of their quality can serve as a good basis for making long-term management decisions for conservation and sustainable water management in the study area.

Study Area

The catchment areas of the Topolnitsa river and the Luda Yana River, which are the subject of research in this project, are within the boundaries of the Basin Directorate (DB) "East Aegean Region". Detailed information about the two river basins is presented in previous studies by the authors [4]. This article focuses on the physicochemical state of surface waters in selected points of river flows, the origin and nature of pollutants, the extent and degree of water pollution in the two model catchments, which are characterized by diverse and intense anthropogenic activity. The catchments of the studied rivers are subject to long-term anthropogenic pressure. Along the Topolnitsa river are some large enterprises that pose a potential risk to water and subsequently to the environment. Pollution from industry, agriculture, solid waste disposal and wastewater discharge from settlements increase the content of heavy metals, some anions (nitrates, nitrites, sulfites, etc.) and organic components. The deterioration of water quality as a result of the metallurgical plants, non-ferrous metal plants, mines and tailings ponds that have been operating for years is particularly significant. The end result of their production activity is pollution of river waters with heavy metals (copper, lead, zinc, etc.). Although the waters of the Topolnitsa river and the Topolnitsa dam have a complex application, the information on the degree of heavy metal pollution in the study area and the consequences of this is extremely limited.

These and other economic activities also determine the presence of pollutants that adversely affect many of the general physicochemical parameters and some priority substances and specific pollutants: pH, electrical conductivity, dissolved O₂, ammonium nitrogen (N-NH₄), nitrite nitrogen (N-NO₂), orthophosphates (P-PO₄), total phosphorus, iron, manganese, copper, arsenic, zinc, cadmium, lead, nickel. It is important to note that not all industrial enterprises of the above-mentioned productions, even with established WWTPs, effectively treat their wastewater. Very often the WWTPs are not in good operating condition and do not work at full capacity. Accidental bursts of untreated industrial wastewater as a result of accidents are still allowed. On the other hand, another significant source of so-called diffuse pollution is agricultural land, which is widely treated with fertilizers and plant protection products. Rainwater and agro-ameliorative waters support their migration into soils, groundwater and surface water. The registered pollutants are according to the indicators - content of biogenic elements and some specific chemical pollutants. Livestock, as well as improper use and storage of animal manure are other sources of diffuse surface water pollution in the study area.

In the settlements without or with partially built sewerage network, the domestic, economic and industrial waters are collected in septic tanks or absorbent cesspools. These pits are usually not watertight and insulated and wastewater seeps and contaminates water sources most often with organic and biogenic elements.

Taking into account the fact that the two model river basins, especially the one on the Topolnitsa river, collect all polluted wastewater from industrial enterprises and settlements, it is imperative to apply an integrated approach, taking into account the economic, social and environmental aspects of society. In order to protect water in terms of its quality, it is crucial to

introduce programs and measures for sustainable management and use of water resources, including the promotion of scientific and applied research for efficient production, recycling and reduction of waste through its conversion into raw materials [5, 6].

Methods and Materials

Sampling and sample location

Samples were collected once time every month during March 2019 and July 2021. Sampling was performed according to the accepted rules for surface water sampling. Polyethylene bottles with a capacity of 500 ml were pre-washed with non-ionic detergents, rinsed in tap water, in 1:1 hydrochloric acid, and finally with deionized water were used to store the samples. Immediately after collection, the samples were analyzed for cited above parameters: pH, nitrates (NO_3^-), nitrites (NO_2^-), phosphates (PO_4^{3-}), as well metals as Fe, As, Mn, Pb, Cd, Cu, Zn and Ni.

The main sampling points were identified as hubs for the Topolnitsa and Luda Yana rivers (Table 1) with possible accumulations of pollutants and are as follows: Topolnitsa river: T1 (Topolnitsa river after Koprivshitsa), T2 (Topolnitsa river near the village of Petrich), T3 (Topolnitsa river near the village of Dragor - confluence with Maritsa), Luda Yana river: LY1 (Luda Yana river under Strelcha), LY2 (Panagyurska Luda Yana river, near Popintsi), LY3 (Luda Yana river near the village of Chernogorovo).

Table 1. The sampling stations of Topolnitsa and Luda Yana basins, Bulgaria

Sampling stations	Location
T1	GPS: N 42 38 49, E 24 21 18 (Topolnitsa river after Koprivshitsa)
T2	GPS: N 42 35 58, E 24 00 40 (Topolnitsa river near the village of Petrich)
T3	GPS: N 42 15 36, E 24 18 54 (Topolnitsa river near the village of Dragor)
LY1	GPS: N42 29 53, E 24 19 30 (Luda Yana river under Strelcha)
LY2	GPS: N 42 29 33, E 24 11 16 (Panagyurska Luda Yana river, near Popintsi)
LY3	GPS: N42 16 13, E 24 23 31 (Luda Yana river near the village of Chernogorovo)

Regulations

In order to assess the quality of river water and in relation with the anthropogenic effects, natural state and future uses, the best way of preventing pollution is to capture pollutants before they are able to reach the watercourse. The evaluation of the quality of water bodies, including the surface water in rivers, is of fundamental importance to the study and use of river water.

In accordance with the requirements of the EU Water Framework Directive and the implementation of the Water Act in the country, a significant number of bylaws are being developed and adopted - ordinances, orders, regulations etc. [7, 8]. In this sense, the water quality in the studied catchments according to selected physicochemical indicators is based on Ordinance N-4 on surface water characterization of 2012 and Ordinance on environmental quality standards for priority substances and some other pollutants of 2010 (Ordinance EQSPSSOP 2010) [9, 10].

Methods for determination of metals, pH, electrical conductivity (EC), dissolved oxygen (DO), NO_3^- , NO_2^- , PO_4^{3-} and ammonium (N-NH_4) in samples

Standard ICP-OES method (Inductively Coupled Plasma Optical Emission Spectroscopy, method: ISO 011885) by properly calibrating the equipment with a multi element

standard solution ('Ultra scientific', Lot: P00332) containing 24 elements in 5% HNO₃ (Al, Ba, Be, Bi, B, Cd, Ca, Cr, Co, Cu, Ga, Fe, Pb, Li, Mg, Mn, Ni, K, Se, Na, Sr, Te, Tl and Zn) at concentration 100 ±5 mg·L⁻¹ of each element (for arsenic As standard solution (As in 5% HNO₃) 1000 ±3 mg·L⁻¹ (VHG Labs, Lot: 112-0017)) was used. The ICP-OES spectrometer (Prodigy High Dispersion ICP-OES, Teledyne Leeman Labs, USA equipped) was working at the following parameters: a dual view torch, cyclonic spray chamber, and concentric nebulizer with follow conditions: coolant gas 18L·min⁻¹, auxiliary gas 0.5L·min⁻¹, nebulizer gas 34 psi, RF power 1.2kW, pump rate 1.2mL·min⁻¹, sample uptake time 30s, integration time 40s. High purity Ar 99.999% was used to sustain plasma and as a carrier gas.

The pH of water was measured at room temperature (25°C) with digital Janway pH meter (±0.01) immediately after sample collection. A CDM92 conductivity meter was used to measure the conductivity values of samples.

The equipment used to measure the energy absorbed and registered of absorption spectra for all analytes was a double-beam UV-Vis "Varian-Cary" with 1cm path length synthetic quartz glass cells spectrophotometer. The nitrates were determined by spectrophotometric method, ISO 7890-3 using sulfosalicylic acid [11].

The method is based on measuring the signal of a yellow solution of a compound obtained by reacting nitrates with sulfosalicylic acid (formed by adding sodium salicylate and sulfuric acid to the sample) after treatment with a base. The ethylenediamino tetraacetic acid disodium salt (Na₂EDTA) is added to the solution at the same time as the base is added to prevent the precipitation of the calcium and magnesium salts. The interfering effect of nitrites is removed by the addition of NaN₃. Standard solutions with nitrate ion concentration in the range 0.003 - 0.013mg/L were used to calibrate the analytical function using an external standard calibration method. The spectrophotometric method [12] using the formation of a reddish-purple azo dyes (pH = 2.0) by coupling diazotized sulfanilamide with N-(1-naphthyl)-ethylenediamine dihydrochloride was used for nitrite ions determination [13]. Winkler titrimetric method (a standard procedure, EN 25813:1993 and ISO 5813:1983) was used for the determination of dissolved oxygen (DO) in the analyzed water samples and the ammonium molybdate spectrometric method (ISO 6878) for determination of phosphates content [14].

Methods for assessment and analysis of water quality

A water quality index is a means to summarize large amounts of water quality data into simple terms (e.g. good) for reporting to management and the public in a consistent manner. WQI is a set of standards used to measure changes in water quality in a particular river reach over time and make comparisons from different reaches of a river. A WQI also allows for comparisons to be made between different rivers. This index allows for a general analysis of water quality on many levels that affect a stream's ability to host life [15]. Water quality index can be evaluated on the basis of various physical, chemical and bacteriological parameters. Numerous water quality indices have been formulated all over the world which can easily judge out the overall water quality within a particular area promptly and efficiently [16].

To calculate the river water quality, the CCME Water Quality Index (WQI) was applied to obtain an integrated complex assessment. This index is widely used in hydroecological practice and gives representative results [17]. The CCME index was chosen because of its ease of application and the flexibility provided in the choice of water quality parameters. The CCME WQI is not designed to replace the detailed analysis of variables, but rather as a tool for reporting the overall state of water in terms of its quality, while the intermediate results of the index used offer information on leading pollutants, the degree and the intensity of pollution and how it spreads over time and space. Once the CCME WQI value is determined, water quality is classified by referring to one of the following categories according to the value of WQI - Excelent 95 - 100, Good 80 - 94, Fair 65 - 79, Marginal 45 - 64, Poor 0 - 44. The article reveals how these wide variations in different parameters can be reduced to a single number through applying a CCME WQI method.

Results and discussion

According to the criteria and norms for "good" physicochemical condition set in Ordinance № N-4 for characterization of surface waters, the upper course of the Topolnitsa river (river waters at the point after Koprivshitsa) in 2019 do not meet the requirements, the waters are defined as heavily polluted, almost always threatened or deteriorated by the anthropogenic activity. In 2020 and 2021 the river in this section improves its condition and falls into the category of "good". The water quality is in their natural status by registering isolated cases of anthropogenic load and pollution (Fig. 2).

The deterioration is mainly due to the "poor" values of dissolved oxygen, nitrate and nitrite nitrogen (N-NO₃ and N-NO₂) and orthophosphates (P-PO₄), which generally indicates organic pollution. Exceedances of the registered values are most often up to 10 times, with the exception of the established values for the orthophosphate indicator, when on 29.10. and on 17.12.2019 the extreme values of 10.10 and 2.90mg/L were reported, respectively. Deviations from the permissible norms are over 25 times. The reasons for the detected pollution can be found in the still non-functioning WWTP regardless of its started construction under the settlement. There are several livestock complexes in the town, which are possible diffuse source of water pollution. The intermediate results of the applied water quality index show deviations of up to 10 times from the standards for Fe, Cd and Cu indicators.

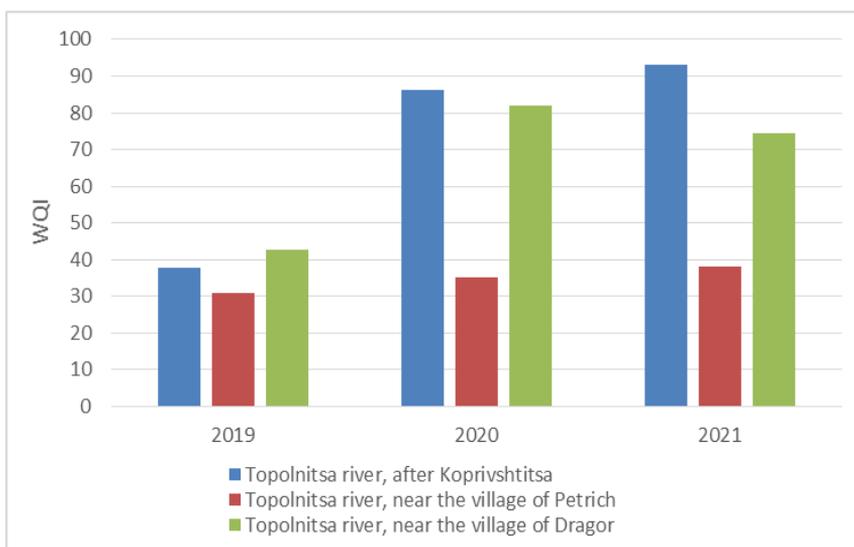


Fig. 2. Values of WQI for Topolnitsa river

The waters of the Topolnitsa river in the middle course at the point near the village of Petrich are defined as highly polluted, almost constantly subjected to intense anthropogenic stress. WQI values do not even reach the upper limit (44) of the "poor" water quality category (Fig. 2). As a result of the calculations, it was found that almost all analyzed physicochemical parameters (dissolved oxygen, pH, electrical conductivity, ammonium nitrogen (N-NH₄), nitrates (N-NO₃), nitrites (N-NO₂) total P and orthophosphates (P-PO₄) for quality show exceeding up to 10 times the norms in the study period. Exceptions are dissolved oxygen and pH indicators for which single cases of non-compliance up to 10 times above the reference values are found. The constant "jumps" from the permissible content of the orthophosphate's indicator (P-PO₄), are indicative, and on 30.10 and 18.12.2019 values exceeding the norms over 25 times were registered - respectively 3.12 and 3.22mg/L. The values of heavy metals - iron (Fe), cadmium (Cd) and manganese (Mn) are most often characterized by ten times exceeding

the standards, with the exception of the established values of copper (Cu), which exceed the set standards most often above 25 times. For example, only on March 19, 2019, the content of copper (Cu) exceeds the permissible concentration 10 times. In all other sampling deviations from the standards were found more than 25 times, and the highest value - 679 μ g/L was registered on 21.10.2020.

The applied water quality index (WQI) in the study period places the Topolnitsa river at the point near the village of Dragor, before the estuary in three different categories. In 2019, WQI has a value of 42.5, which speaks of highly polluted waters exposed to active anthropogenic impact. The calculated values of the index for 2020 and 2021 are respectively 81.9 and 74.4. These meanings categorize river waters into two relatively more favorable categories - "good" and "fair". This means that the water quality is in their natural status by registering isolated cases of anthropogenic load and pollution for the first category and the water quality is usually protected, but a number of cases of anthropogenic pressure have been registered for the second category and the waters are defined as slightly polluted (Fig. 2). The performed component-by-component analysis of the physicochemical state of the waters shows that in this part of the valley, as a whole the values of the indicators meet the normative requirements. The only thing that is impressive is the pollution according to the indicator - nitrates (N-NO₃), the values of which exceed the norms up to 10 times during the whole studied period, and on 09.07.2019 a maximum value of 8.40mg/L was registered. Isolated cases of "bounce" (up to 10 and between 10 and 25 times) of the criteria for "good" status of river waters are determined by the indicator's orthophosphates (P-PO₄) and total P. The values of heavy metals iron (Fe), manganese (Mn), cadmium (Cd) and copper (Cu) are most often characterized by ten times the standards, but in some cases the values of copper (Cu) exceed the set norms between 10 and 25 times (March 18, 2019, December 17, 2019, respectively 151 and 185 μ g/L).

The results obtained for WQI on the waters of the Strelchenska Luda Yana rivers at the point after Strelcha indicate a deteriorating condition. At the beginning of the period the calculated value of the index is 30.7 (2019), subsequently WQI reaches 66.2 (2020) and at the end of the study period is 42.5 (2021) (Fig. 3).

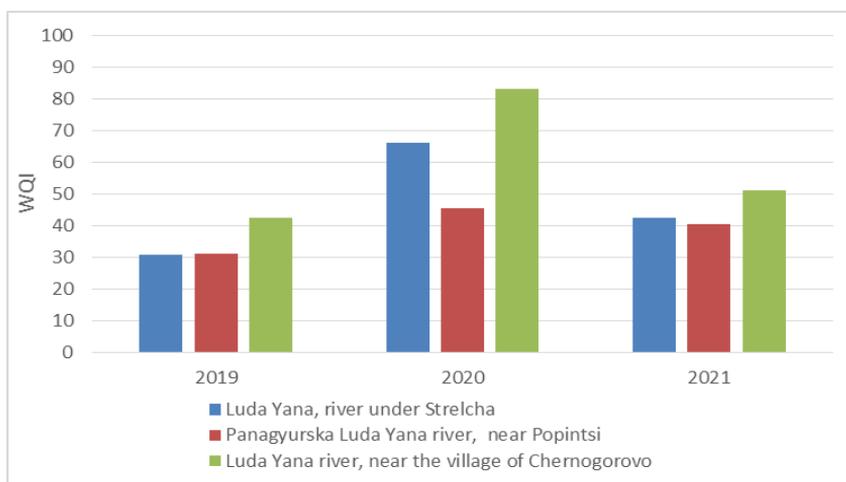


Fig. 3. Values of WQI for Luda Yana river

In 2019 and 2021 the condition of the river in this section is defined as almost always threatened or deteriorated by the anthropogenic activity, the water is heavily polluted. In 2020 the water quality is usually protected, but a number of cases of anthropogenic pressure have been registered. The water quality is defined in the "fair" category. According to the research, it is established that the requirements of Ordinance N-4/2012 for achieving "good" status of

surface waters are not met mainly on the indicators of nitrates (N-NO₃), dissolved oxygen, orthophosphates (P-PO₄) and total P. The most significant are the exceedances (up to 10 times and over 25 times) of the reference values for the indicators - orthophosphates (P-PO₄) and total P. Their maximum values were registered on October 29, 2019 (25mg/L) and on May 28, 2019 (2.61 mg/l). The analysis unequivocally shows that the river waters after the town are under significant anthropogenic pressure, which is mainly expressed in the discharge of domestic and fecal waters. The functions of Strelcha as a resort center leads to an increase in the discharge of insufficiently treated communal waters. During the field observations, a specific smell of sewage is registered.

The obtained results show that throughout the whole period the heavy metals iron (Fe), manganese (Mn), cadmium (Cd) and copper (Cu) are in concentrations exceeding the permissible ones up to 10 times.

The WQI values calculated for the Panagyurska Luda Yana river near the village of Popintsi the river flow in this section in the categories "marginal" and "poor". Thus, the waters do not meet the criteria for "good" status during the study period. WQI indicates contaminated or heavily polluted water significantly or almost always threatened or deteriorated due to the anthropogenic impact. The values obtained for 2019, 2020 and 2021 are respectively 31.3, 45.5 and 40.5 (Fig. 3). According to the differentiated analysis of the quality indicators, the main discrepancies from the reference values are the indicators pH, total P, nitrites (N-NO₃) and ammonium nitrogen (N-NH₄). The largest exceedances (usually over 25 times) of the regulatory requirements are for nitrite values (N-NO₃). Regarding the concentration of heavy metals, the high content of iron (Fe), cadmium (Cd) and copper (Cu) is usually accepted, the values of which from almost all samples do not meet the quality standards (10 above them). Although insignificant, there is an improvement in this section of the river in terms of manganese (Mn) content.

Downstream, the surface waters of the Luda Yana river at the point near the village of Chernogorovo are in the categories of "poor", "good" and "marginal" quality status according to the norms for "good" status, regulated in Ordinance N-4/2012. The values of the WQI applications for 2019, 2020 and 2021 are respectively 42.4, 83.3 and 51.3 (Fig. 3).

There is a slight improvement in the condition of the river according to the studied physicochemical indicators, which is explained by the more liberal norms of the respective indicators for the plain type of rivers and the possibilities for self-purification of the river. The main pollution, similar to the river sections analyzed above, remains with heavy metals - iron (Fe), manganese (Mn), cadmium (Cd) and copper (Cu). Values exceeding the standards (up to 10 times and between 10 and 25 times) for the amount of copper (Cu) are relatively constant the only registered value exceeding the quality standard more than 25 times was established on October 29, 2019 and is 310µg/L.

As a result of the analysis of the water quality index according to the requirements of Ordinance N-4/2012 for the period 2019-2021, the following summaries can be made for the two model valleys:

- For the Topolnitsa river, the point where the surface waters are in the worst quality condition is the one near the village of Petrich, and the upper course of the river, after Koprivshitsa has the most favorable quality characteristics.
- Regarding the quality of the Luda Yana river, the point near the village of Popintsi is the most polluted and the best surface water quality is established for the river waters near the village of Chernogorovo.
- The quality of river waters as a whole slightly improves towards the lower reaches of the studied river basins, which is explained by the more liberal norms of the respective physicochemical indicators for the plain type river and the possibilities for self-purification of river flows.

Conclusions

During the study period the waters of the Topolnitsa river and the Luda Yana river are subjected to active anthropogenic impact of various directions. In total, the rivers meet the criteria for good physicochemical condition only four times. This is evidenced by the established values of the applied complex water quality index. While the values of nitrates (N-NO₃), nitrites (N-NO₂), ammonium nitrogen (N-NH₄), dissolved oxygen, orthophosphates (P-PO₄) and total P vary in space and time, the values of heavy metals iron (Fe), manganese (Mn), cadmium (Cd) and especially copper (Cu) remain constant and significant, not meeting quality standards.

As some of the largest enterprises of the mining and processing industry in the country are located and operate in the study area, its sustainable development is related to the application of an integrated approach, taking into account the economic, social and environmental aspects of society. To conserve the water and reduce the pollution demands immediate intervention in the management, especially through an integrated approach for water policies, and related issues.

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