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Assessment of physico-chemical status of waters in selected sampling sites of Chepelarska River, Bulgaria

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Abstract

Water is not just a commercial product, but a common good and a limited resource that should be protected and used in a sustainable manner, in both terms – of quality and quantity. However, water is under pressure due to variety of uses from different sectors, such as industry, agriculture, tourism, transport, energy, etc. which leads to deterioration in the quality of water resources. The aim of the study is to assess the chemical status of Chepelarska River, right tributary of the main river in Southern Bulgaria – Maritsa, based on more than 10 physico-chemical parameters for the period 2015–2021. Data were provided by the Executive Environmental Agency (ExEA) to the Ministry of Environment and Water (MOEW). The evaluation of the studied river is based on Ordinance No N-4/14.09.2012 (concerning the characterisation of surface waters) and Ordinance on environmental quality standards for priority substances and some other pollutants (Resolution of the Council … 2010), in accordance with the requirements of Directive 2000/60/EU. To achieve the set goal, the Canadian Complex Water Quality Index (CCME-WQI) was applied, through which a complex and differentiated assessment of the status of water in terms of its quality was carried out. The obtained results show constant excesses of the norms for the indicators nitrite-nitrogen ($N\text{-}NO_2$), total nitrogen (TN), total phosphorus (TP) and orthophosphates ($P\text{-}PO_4$). According to them, organic pollution of river waters is mainly of agricultural and municipal-domestic origin. The industrial activities in the area carried out for decades to this day could be considered as a source of a possible pollutant that led to an increased content of heavy metals – copper (Cu), cadmium (Cd), manganese (Mn) and especially zinc (Zn). The obtained new data is a key emphasis in making management decisions to mitigate and prevent current and future pollution of river systems, as a result of various anthropogenic impacts.

Key words: chemical status, complex index, water quality.

Introduction

The protection and use of water in a manner that adequately meets the needs of modern society requires precise monitoring of water quality. This becomes possible through the application of a scientifically based system for assessing of water quality status, aligned with European and national regulatory requirements. At EU level, a key element of water legislation is The Water Framework Directive 2000/60, establishing the framework for action in the field of water policy (European Parliament … 2000). The Water Framework Directive outlines the legal framework for protection and restoration of clean water in the EU and for ensuring its long-term and sustainable use. In this sense, by implementing a complex of programs, plans and measures in accordance with the current regulatory requirements, the member states must strive to achieve at least a 'good' status of water resources.

The status of river waters in physico-chemical aspect is very often determined by one or several parameters. This represents a differentiated assessment of water quality. In general the water quality is influenced by a complex of natural (hydrological, atmospheric, climatic, topographical and lithological) and anthropogenic factors. The suspension of the normal functioning of aquatic ecosystems is a result of the pollution of river waters mainly due to anthropogenic activity. The sources of water pollution (according to the way of entry into the water body) can be grouped into two types: point and diffuse. Regardless of how pollutants enter river waters, they degrade river ecosystems. Agricultural activities, for example, are usually concentrated near rivers, but since river floodplains are fertile enough, pollution can be registered if the cultivated areas are improperly disposed of and overdosed with phosphorus and nitrogen fertilizers. Livestock breeding also has an adverse effect on the quality of river waters. Wastewater from animal breeding complexes is heavily polluted mainly with organic and inorganic suspended substances. Industrial processes are sometimes a source of pollution and discharge into rivers of chemical waste products (e.g. heavy metals such as Fe, Mn, Cd, Cu, Zn). In this sense, water quality assessment is fundamental to the study and use of water. In our days, modern practices of determining the qualitative status of river waters and its change in time and space, the so-called complex assessments, are constantly being developed and applied. The use of new methods for complex determination of water quality is a public challenge of particular importance (Uddin et al. 2021). In this sense, carrying out a complex analysis and evaluation is a good basis for the preparation of environmental policies and the implementation of more effective control in areas marked by significant anthropogenic impact on river systems. Water management is one of the most important aspects of government in any developed country. The modern Bulgarian legislation, which refers to the water sector and is part of the legislation of the EU, is based on the Act on waters – published in the State Gazette No 67 of 27.07.1999, and is in force since 28.01.2000 (Anonymous 2000).

The aim of the study is to assess the chemical status of Chepelarska River, right tributary of the main river in Southern Bulgaria – Maritsa, based on more than 10 physico-chemical parameters for the period 2015–2021.

A distinctive innovation in this study is the achievement of a comprehensive assessment of water quality of Chepelarska River. The waters are mainly used for electricity production, irrigation, industrial water supply and to satisfy the domestic needs of the population. In addition, historically, the waters of the river have been heavily polluted by the lead and zinc industries, located near the town of Laky (European Parliament … 2010, Hristova 2012, Basin Directorate … 2018, Radeva 2022). The problem studied in the present article is also partially examined by Dospatliev et al. (2015), who studied the content of Pb and Cd for the period 2010–2013. Gartsiyanova 2022 evaluated the water quality of Maritsa River basin and respectively partially referred the research for Chepelarska River. New analysis was performed by Gecheva et al. in 2023 when the authors studied the accumulated heavy metals and trace elements in aquatic plants, and on this basis they obtained a macrophyte-based assessment of ecological status. The various studies by far conducted on Chepelarska River are too limited. Taking into account this fact, it is necessary to conduct a regional study of its physico-chemical status. In this sense, the assessment of river water quality is based on Ordinance No N-4 of 14.09.2012 concerning the characterisation of surface waters (according requirements for good condition) and Ordinance on environmental quality standards for priority substances and some other pollutants (Resolution of the Council … 2010, MOEW 2012).

Materials and Methods

Study area

Chepelarska River (known also as Asenitsa or Chaya) is a right tributary of Maritsa River with a length of 85.9 km and a catchment area of 1010 km² (Hristova 2012). The river originates in the area of Rozhen saddle, in the Western Rhodopes. Near the town of Chepelare and the village of Hvoyna, it flows in a narrow valley with valley extensions (small hollows). It changes its direction several times from northeast to northwest. In the Upper Thracian lowland, it divides into arms and flows as a right tributary into Maritsa River in the area of Katunitsa village. Its river network is characterised by a high density in its upper course, draining the eastern slopes of Chernatitsa and Dobrostan hills. The average multi-year runoff is determined by the changing weather conditions throughout the year and due to the trends in climate change. Chepelarska River has a rain-snow recharge with a maximum in the period April–May and minimum – September and August. It flows into Maritsa River at 148 m a.s.l., 2.5 km south of the village of Rogosh (Basin Directorate … 2018).

Nowadays the qualitative status of the surface waters in Chepelarska River basin is a direct reflection of the diverse and dynamic combinations of natural and anthropogenic factors. Its analysis and assessment are based on data for the period from 2015 to 2021 and provided by the Executive Environmental Agency to MOEW. Due to the specificity of the sampling and completeness of the source data, three sampling sites presented in Table 1 and Figure 1 were selected to achieve the purpose of the present study. In addition, the sampling sites of the studied watersheds were chosen so as to be representative both for the areas with developed agricultural activity and animal husbandry, tourism, and for those with industrial production. Chepelarska River after the town of Chepelare (Ch1) and near village of Bachkovo (Ch2) belongs to

Table 1. Sampling sites of the study.

Sampling sites	Code of the sampling sites	Coordinates, °	Code on the map
Chepelarska River after the town of Chepelare	BG3MA05295MS0630	N 41.73509 E 24.68886	Ch1
Chepelarska River near village of Bachkovo	BG3MA00523MS0600	N 41.94440 E 24.85281	Ch2
Chepelarska River before mouth	BG3MA05213MS0570	N 42.14570 E 24.87722	Ch3

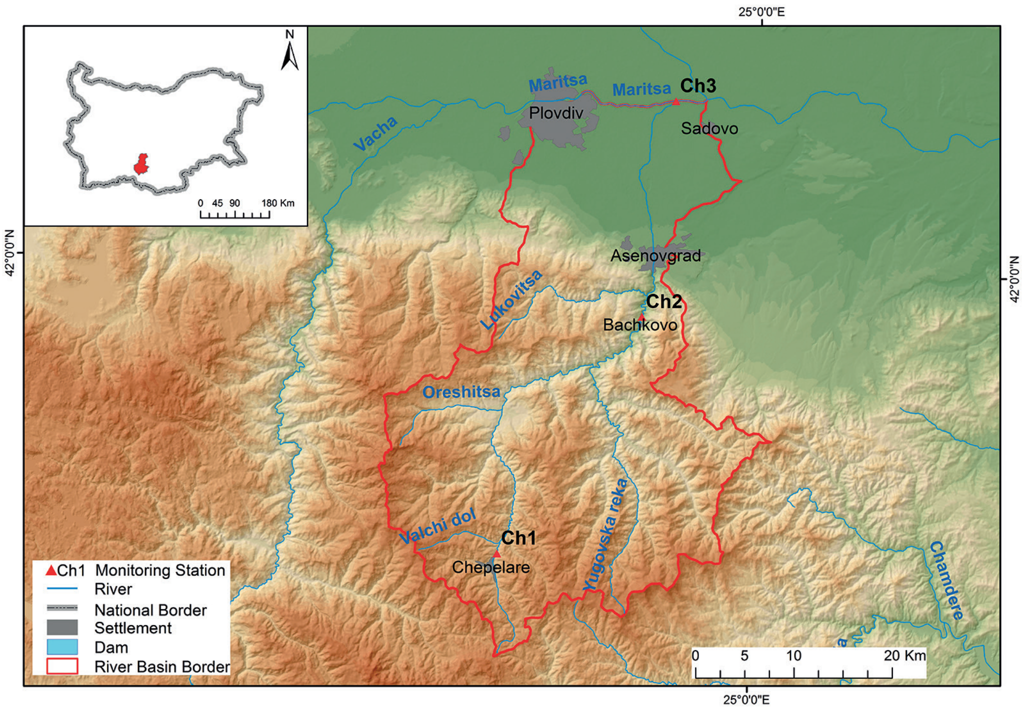

Fig. 1. Study area.

R3 (mountain) water type, and Chepelarska River before mouth (Ch3) is defined as water type R5 (semimountain) (Basin Directorate … 2018).

Methods

Water quality assessment and monitoring of rivers have been globally used all over the world to determine the sources of pollutants and their effects in temporal and spatial aspect. Evaluation of surface water quality usually is a complicated process due to undertaking multiple parameters which impact the overall water quality (Jafarabadi et al. 2016).

The quality status of the sampling sites in this study was assessed by following physico-chemical parameters: pH, electrical conductivity, dissolved oxygen, ammonium nitrogen ($N\text{-}NH_4$), nitrates

($N\text{-}NO_3$) and nitrites ($N\text{-}NO_2$), orthophosphates (P-ortho-PO_4), content of total nitrogen and phosphorus (TN and TP), biochemical oxygen demand (BOD_5) and the concentration of eight chemical elements – iron (Fe), manganese (Mn), cadmium (Cd), lead (Pb), arsenic (As), copper (Cu), nickel (Ni), zinc (Zn). The physico-chemical parameters were collected at least 4 times a year (MOEW 2012).

In order to provide a standardised method for comparing the status and changes in water quality based on selected parameters and summarizing the obtained data in an easily expressed and easily understood format, a number of quality index assessments have been developed and are being developed. According to studies by some authors, more than 20 water quality indices are applied worldwide today (Uddin et al. 2021). Complex index assessments have a number of advantages compared to the differentiated ones used in hydroecological practice. They provide an opportunity not just a complex assessment to be received, but also a differentiated assessment of water quality. Complex indices provide a generalised assessment of the status of water quality, by obtaining a simple or rank value that can be easily understood by the public, water distributors, planners, managers and policy makers (Lumb 2006). Questions related to the quality of river waters in our country have become more relevant since the end of 1990s. Varbanov and Gartsiyanova (2015, 2017) have significant contribution to the application of the complex methods for assessment and analysis of the status of surface water bodies in Bulgaria.

In order to achieve the set goal, the Canadian Water Quality Index was applied in the present study (CCME 2001). The anthropogenic impact affecting the status of water bodies by physico-chemical parameters or quality elements using this index is determined by using three components. The first one is the range of impact (F_1), which reflects the range of quality indicators that do not meet the normatively defined threshold values. The second component is frequency (F_2), showing the ratio of the values at which the content of potential pollutants with a concentration above the permissible norms was found and the total number of values according to the studied indicators. The third indicator – amplitude (F_3), expresses the degree of deviation of the values that do not meet the legal norms, compared to the corresponding reference values. The water quality index is calculated according to the formula (1):

$$WQI = 100 - \left(\frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732} \right), \qquad (1)$$

The divisor 1.732 normalises the obtained value in the interval from 0 to 100, where 0 means ‘worst quality’, 100 – ‘best quality’ of water. CCME-WQI applied model also offers the following differentiation of the water quality status: excellent (WQI = 95–100), good (WQI = 80–94), fair (WQI = 65–79), marginal (WQI = 45–64), poor (WQI = 0–44) (CCME 2001).

Results and Discussion

The waters of Chepelarska River at the sampling site Ch1, both at the beginning and in the end of the study period are defined as ‘highly polluted’. For 2017 and 2018, CCME-WQI values classifies the river in ‘good’ condition category. From 2019 to 2021, the values of WQI again place the river in this section in the category of ‘poor’ condition, with the lowest value WQI being recorded in 2020 (figs 2 and 3).

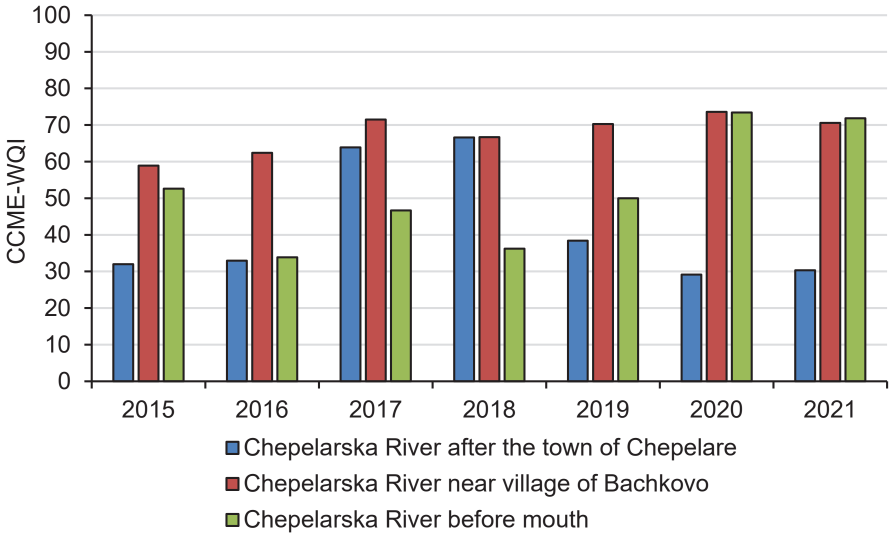

Fig. 2. Change in *WQI* values calculated for Chepelarska River in the period 2015–2021.

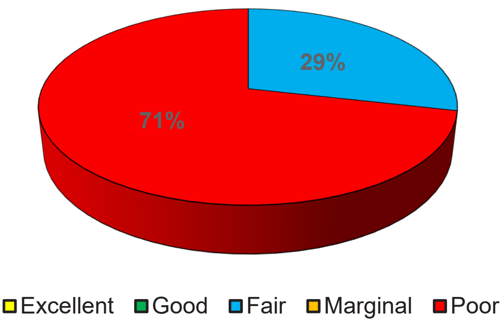

Fig. 3. Distribution of water quality status of Chepelarska River at the point Ch1 by categories for the period 2015–2021.

From the analysis of the available data and the results obtained for the physico-chemical pollution of surface waters by each component, it is clear that their deteriorated condition is mainly due to the 'bad' values of the following indicators: dissolved oxygen, $N\text{-}NO_2$, in rarer cases of $N\text{-}NO_3$, TN and TP, $P\text{-}PO_4$ and BOD_5. The excesses of the registered values are most often up to 10 times. An exception is the measured values for the indicator $N\text{-}NO_2$, for which values in 2015 and 2016 exceedance by more than 25 times from the permissible thresholds were reported (for example on 08.08.2016 – 0.77 $mg\cdot L^{-1}$). In 2016, single excesses between 10 and 25 times over the permissible values for the TP, $P\text{-}PO_4$ indicators were also recorded. From 2019 to the end of the research period, the average excess of the normative thresholds for the values of the indicator TP, is between 10 and 25 times, and the cases of deviation exceeding 25 times are not rare (e.g. 08.05.2020 – 2.48 $mg\cdot L^{-1}$, 05.02.2021 – 0.90 $mg\cdot L^{-1}$). The results obtained on the basis of the available data show that during the research period only Mn was in concentrations not exceeding the standards by more than 10 times. The maximum content was established on 10.11.2020 – 72.1 $\mu g\cdot L^{-1}$.

As a result of the applied complex WQI, it was concluded that Chepelarska River at the sampling site Ch2 in 2015 and 2016 was in a 'critical' quality status. River waters are defined as 'polluted'. From

2017 to the end of the period, according to the calculated values of CCME-WQI, the river in this section changes its category and meets the regulatory requirements for 'good' surface water quality. The applied index has the highest value in 2020 – 73.6 (figs 2 and 4).

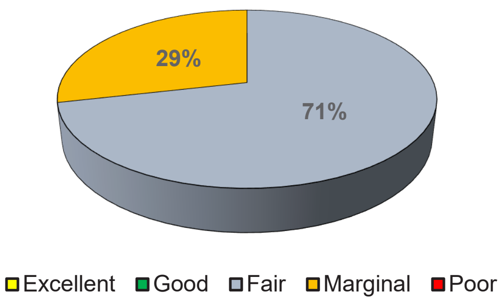

Fig. 4. Distribution of water quality status of Chepelarska River near Ch2 by categories for the period 2015–2021.

The obtained results designate that of the analysed indicators, N-NO_2, P-PO_4, TN and TP showed an excess of norms up to 10 times. An exception is the pH indicator, for which individual cases of discrepancies up to 10 times the reference values are detected. On 11.13.2021, a maximum content of TP of 0.36 mg·L^{-1} in this section of the river course was detected, exceeding the legal requirements between 10 and 25 times. Heavy metal values generally met the quality standards except for Cu and Zn. The content of these metals was usually 10 times higher than the permissible level. A single deviation from the reference content for Cd was registered in 2016. In February 2017 and 2018 (respectively on 08.02 and 26.02) the concentration of Cu exceeded the permitted thresholds between 10 and 25 times (the detected values are 12.7 μg·L^{-1} and 11.6 μg·L^{-1}). From 2019 to 2021, the content according to this indicator registered deviations from the norms up to 10 times.

According to the values of the quality index, from the beginning of the period to 2019, in the lower courses the surface waters of Chepelarska River, before flowing into Maritsa River, are defined as 'polluted' and 'highly polluted'. Therefore, the river in this section does not meet the requirements for 'good' physico-chemical condition. The lowest CCME-WQI score was registered in 2016 and was just 33.9. In 2020 and 2021, the quality status of the river waters slightly improves and the river reaches the criteria for good quality status, the index values are 73.4 and 71.9, respectively (figs 2 and 5).

The main indicators reflecting the anthropogenic impact in the estuarine area are electrical conductivity, N-NO_2, N-NH_4 and TN. Their values usually exceed the norms up to 10 times. In 2016 (11.08.2016 and 08.11.2016, 4.00 μg·L^{-1} and 3.00 μg·L^{-1}, respectively) a N-NO_2 content exceeding 25 times the permissible limit was detected. From 2019 to 2021, dissolved oxygen, N-NO_3 and P-PO_4 were added to the quality indicators listed above that do not meet the legally defined criteria for good water quality. Thus, in practice at this control point, almost all analysed indicators,

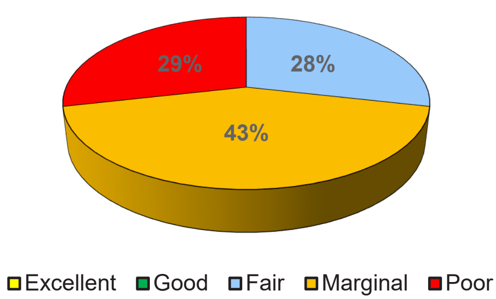

Fig. 5. Distribution of water quality status of Chepelarska River in Ch3 by categories for the period 2015–2021.

which determine the physico-chemical status of the river waters, register excesses over the reference values. Regarding heavy metal pollution in this section of the studied watershed, the deteriorated water quality is due to the high content, in addition to Zn and Cu, also to the excessive concentration of Mn and Cd. Values exceeding the standards up to 10 times for the metals listed above are relatively constant over time. An exception to the values exceeding, often 25 times the regulated standards, is indicated only by Cu. For example, on 11.08.2016, an extreme value of 1160.00 $\mu g \cdot L^{-1}$ was reported for Zn, and on 10.10.2018, Cd had a content of 265.00 $\mu g \cdot L^{-1}$.

Based on the results obtained from the applied CCME-WQI, the following summary can be made:

- Spatially, the cleanest are the waters of Chepelarska River at the sampling site on the bridge for the village of Bachkovo, and the most polluted is the river before it flows into Maritsa River.

- The quality status of the surface water varies, both in the individual years of the research period, and also in the different points, and no direction of deterioration or improvement of its quality is established.

- Leading and constant are the excesses of the norms for the nitrite nitrogen ($N\text{-}NO_2$), especially for Chepelarska River after the town of Chepelare (over 25 times), total nitrogen (TN) and total phosphorus (TP) and orthophosphates ($P\text{-}PO_4$) (up to 10 times the requirements for 'good' condition). The deviations from the regulated values for the other physico-chemical indicators are not determined to be so frequent.

- The increased content (very often up to 10 times, not rarely between 10 and 25 times and in some cases over 25 times exceeding the standards) of copper (Cu), cadmium (Cd), manganese (Mn) and especially zinc (Zn) (the most often more than 25 times of excess) at the sampling site of Chepelarska River before it flows into Maritsa River, determines the extremely poor quality of the river waters in terms of heavy metal content.

- Due to the nature of the identified polluting substances, a negative impact on the quality status of the surface waters of Chepelarska River in the studied sampling sites is caused by the discharge of untreated or insufficiently treated communal-household (incl. and faecal) waters. Additional peril to the quality of surface waters is the presence of numerous micro-dumps, as well as landfills that do not meet the regulated requirements. A significant problem are the settlements with a partially constructed or unconstructed sewage system and, last but not least, agricultural activities – crop farming on one hand, through excessive fertilization and use of plant protection products, and livestock farming on the other, by improper storage of significant amounts of manure.

- CCME-WQI can be used for assessment of water quality for specific purposes. For example – drinking, aquatic life, recreation, irrigation and livestock. Due to the aim of this study it is possible the calculation of the index for these needs to be performed by the authors in the future.

Conclusions

The present study provides important new knowledge for water quality status of Chepelarska River. The quality assessment is obtained by applying of CCME-WQI. The results reveal the advantages of the used complex index, allowing to obtain complex and differentiated assessments for different temporal and spatial generalisations, both for the whole river and for separate sections of it. It can be assumed that the lack of a wastewater treatment plant in the town of Chepelare and the proximity of Pamporovo resort complex are the main possible reasons for the deteriorated water quality in the relevant section of the studied basin. It is recommended treatment facilities to be built after larger settlements (especially resort complexes) and to reduce pollution from agriculture in the lower reaches of the river, by application of good agricultural practices. One of the limitations in this study was the lack of official information regarding the main diffuse and point pollutants. In this sense providing an up-to-date picture of the physico-chemical status of Chepelarska River is a basis for future planned activities in the catchment area of the river for identifying the specific anthropogenic sources of pollution. This research would be a key emphasis in making management decisions for development and implementation of a complex of programs, projects and measures, specialised in limiting and preventing current and future pollution. At the end, the results obtained of Chepelarska River study contribute to the regional research in the field of water quality and could be used in the future for preparation of a regional qualitative categorization of surface waters in the country.

Acknowledgments

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