

State of the Dubossary Reservoir oxygen regime under conditions of river flow regulation and climate change

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Abstract: The aim of the presented work was to analyse the state of the oxygen regime in the Dubossary Reservoir under conditions of the Dniester River flow regulation, aggravated by climatic changes of the last decades. The results of the 2021–2023 scientific expeditions were used. The following parameters of the oxygen regime were analyzed: dissolved oxygen (DO, mg·L⁻¹), biochemical oxygen demand (BOD₅, mgO·L⁻¹) and bichromate chemical oxygen demand (COD-Cr, mgO·L⁻¹). By calculating the BOD₅/COD-Cr ratio, the river sections with a low level of microbiota adaptation were identified. According to the dissolved oxygen concentration and BOD₅ parameter, the water quality of the Dubossary Reservoir during the analyzed period varied within the classes I and II, and according to the COD-Cr parameter it dropped down to class III. It was in such cases that the BOD₅/COD-Cr index decreased to 0.04.

1. Introduction

In 2011, the Parliament of the Republic of Moldova adopted Law No. 272 (Water Law, 2011), which aimed to harmonize national legislation on water policy with European Parliament directives such as No. 91/271/EEC concerning urban waste water treatment, No. 91/676 EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources, No. 2000/60/EC establishing a framework for Community action in the field of water policy, No. 2008/105/EC concerning environmental quality standards in the field of water policy, and some others. In the process of implementing the tasks stipulated by the new Water Law, in 2013, the Republic of Moldova's water legislation was enriched with a number of documents that currently regulate the tasks, methods, and requirements for monitoring, inventorying, and assessing the targeted use of water resources in the Republic of Moldova.

According to the Government Decision No. 890 of November 12, 2013 (Regulation, 2013), the state of water body oxygen regime includes 5 hydrochemical parameters: dissolved oxygen (DO, mg·L⁻¹), dissolved oxygen saturation (DO, %), biochemical oxygen demand (BOD₅, mgO·L⁻¹), manganese chemical oxygen demand (COD-Mn, mgO·L⁻¹) and bichromate chemical oxygen demand (COD-Cr, mgO·L⁻¹). When rivers are regulated through the construction of dams and the formation of artificial reservoirs, the natural hydrological regime of the watercourse is changed, which entails significant modifications in hydrochemical and hydrobiological parameters of these human-altered aquatic ecosystems. The changes in hydrochemical parameters include: decrease in suspended solids concentration and increase in water transparency in the reservoir itself and in the watercourse downstream of the dam (Zubcov, 2012a); increase in the amplitude of fluctuations of oxygen regime parameters, mineral forms of nitrogen,

phosphorus, iron and silicon (Sinelnikov, 1980). Changes in hydrobiological parameters include: reduction in the number of saprophytic microorganisms (due to increased water transparency), overgrowth of riparian zone of the river with higher aquatic vegetation, blue-green algae, etc.

The Dubossary Reservoir was created in 1951–1954 on the territory of the Moldavian SSR as a result of damming the Dniester River near the Dubossary town. This flow-through reservoir was planned to meet the water needs of population and industry, fish farming, irrigation, power generation and flood protection. The Normal Retention Level (NRL = 28 m) of the reservoir was reached in June 1956. The length (from the Camenca town to the Dubossary dam) is 128 km; the average depth – 4.2 m, maximum – 14 m; the width varies from 200 to 1800 m; the water surface is 67.5 km²; the total volume of the reservoir at the moment of reaching the NRL was 485 million m³; the flow velocity varies from 0.05 to 0.15 m·s⁻¹ depending on the hydrological situation in the Upper Dniester (Dubossary Reservoir, 2000).

The Dubossary Reservoir is supplied mainly by the upper sector of the Dniester River. The reservoir's lateral supply area is about 4500 km². From the right bank, the largest tributary is Ciorna River (42 km); from the left bank – Camenca (52 km), Râbnița (45 km) and Iagorlâc (73 km) rivers. Both the right and left tributaries are supplied by groundwater. The annual runoff volume of the largest tributaries is about 70 million m³. Other sources of supply to the Dubossary Reservoir are very limited. For example, the average annual precipitation in the catchment does not exceed 700 mm, which is actually equal to evaporation loss (Environmental Atlas of the Dniester River Basin, 2012).

The Dubossary Hydropower Complex was the first experience of regulating the Dniester River. In 1981, the construction of a new hydrotechnical complex was started on the territory of Ukraine. At the given time, the Dniester Hydropower Complex (DHPC) includes: the Dnestrovsk Reservoir (214 km long and from 200 to 3750 m wide), the dam of Hydropower Plant No. 1 (HPP-1), the buffer reservoir, the dam of Hydropower Plant No. 2 (HPP-2) and the Pumped-storage Hydropower Plant (PSHPP) with its technical reservoir. The location of the hydrotechnical constructions on the longitudinal profile of the Dniester River is presented in Figure 1.

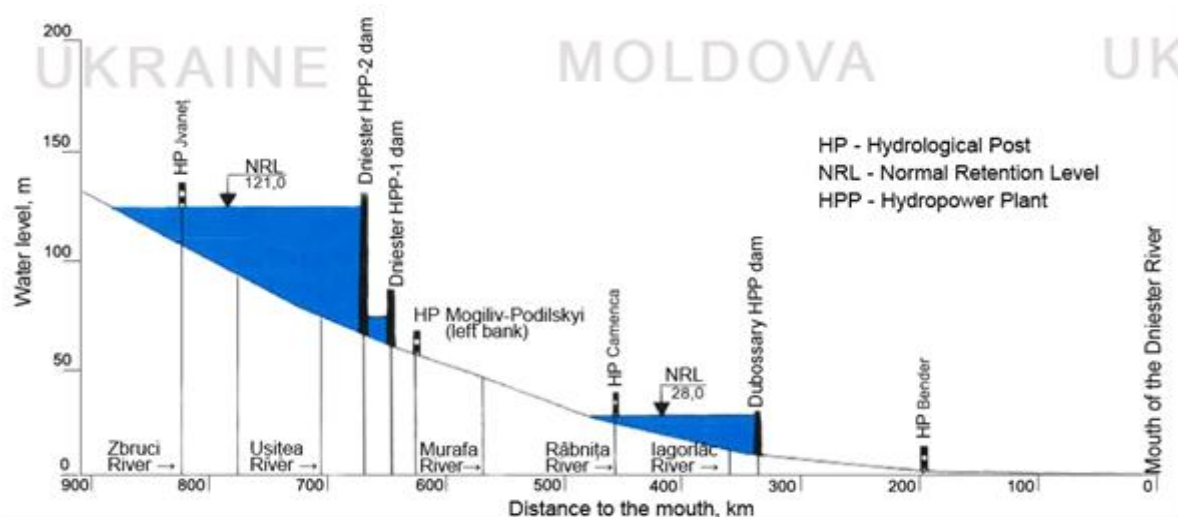


Figure 1. Scheme of location of the water storage reservoirs in the Dniester riverbed (Source: The Rules of Operation of the Dniester Cascade of PSHPPs and HPPs Reservoirs, 2017)

Due to the decrease in flow velocity, reservoirs are subjected to sedimentation processes, which contributes to the reduction of their volume. Before the construction of the DHPC, the sedimentation process in the Dubossary Reservoir was more intensive. In 1988, the bottom sediment layer reached 300 cm. After the Dniester Hydropower Complex was put into operation, the concentration of suspended solids in the Dniester

water at the Camenca–Dubossary sector decreased by 4–6 times (Zubcov, 2012b). At the present time, the degree of siltation in the Dubossary Reservoir is about 52 % (The Management Plan of the Dniester Hydrographic Basin District, 2017).

The creation of dams and reservoirs radically changed the hydrological regime of the Dniester River at the territory of the Republic of Moldova (downstream of the HPP-1). Studying these changes is important for understanding the impact on the Dniester ecosystem downstream of hydrotechnical constructions. As Moldovan scientists have repeatedly declared (Zubcov et al., 2021), the construction and exploitation of the Dniester Hydropower Complex causes great ecological damage to the Dniester ecosystem and its biotic communities by constant daily fluctuations in water level, by limitation of water discharge, by disruption of the natural river temperature regime and also by transforming the Dniester River into a technical raw materials for power generation. The aim of the presented work is to analyse the state of the oxygen regime in the Dubossary Reservoir under conditions of the Dniester River flow regulation, aggravated by climatic changes of the current period.

2. Materials and Methods

The Laboratory of Hydrobiology and Ecotoxicology within the Institute of Zoology has been carrying out scientific monitoring of the Dniester River ecosystem for many years. Sampling stations are located along the entire Dniester riverbed within the Republic of Moldova territory, including the sector upstream of the Dubossary Reservoir (Naslavcea, Vălcineț and Soroca stations) and downstream (Vadul lui Vodă, Varnița and Palanca stations). At the Dubossary Reservoir itself, samples are taken at the stations Camenca (upper section), Hârjău (middle section), Goian and Cocieri (lower section). Sampling was carried out according to the international standard for sampling in rivers and other watercourses (ISO 5667-6, 2014).

To analyze the state of the oxygen regime in the Dubossary Reservoir, the results of the 2021–2023 scientific expeditions were used. In 2021 and 2023, three seasonal samplings (spring-summer-autumn) were carried out on the Dniester River. In 2022, due to the outbreak of war in Ukraine (the border with the Republic of Moldova runs along the Dniester River), the spring sampling was skipped, but two samplings were carried out during the summer.

The water temperature was measured during sampling. using the hydrological thermometer with a graduation value of 0.1 °C and, in parallel, was controlled with portable equipment CONSORT C5030.

The concentration of dissolved oxygen in water was determined "in situ" using a multi-sensor measuring device MS 08. In parallel, samples were taken for determination of dissolved oxygen by the classical Winkler method (EN 25813, 1992), while the sedimentation phase of this method was also carried out "in situ".

CCO-Cr was determined in accordance with the international standard (ISO 6060, 1989) in water samples pre-filtered through a paper filter "white tape".

Classical BOD determination by the standard method (Young et al., 2001) is a modelling of the biochemical oxidation processes occurring in a water body under natural conditions. Depending on the duration of the incubation period, the BOD test allows to determine the following: the amount of dissolved oxygen used for the biochemical decomposition of organic compounds (carbonaceous BOD); the oxygen used to oxidize inorganic compounds such as sulfides and ferrous iron; the oxygen used to oxidize reduced forms of nitrogen (nitrogenous BOD), if this process is not prevented by an inhibitor. If an inhibiting chemical is not used, the measured oxygen reduction is the sum of carbonaceous and nitrogenous demands. Depending on the sample specification, 60–70 % of the biochemically oxidizable material is consumed by microorganisms within 5 days of incubation. Thus, the 5-day BOD test has been established as a standard method for measuring carbonaceous and nitrogenous oxygen demand in monitoring programs of the surface water bodies. Standardization of the method is ensured by

observing standard conditions: incubation is carried out in the dark (to exclude photosynthetic processes) at 20 °C. In the Dubossary Reservoir water samples, determination of BOD₅ was performed without inhibiting chemicals, according to the standard EN 1899-2:1998 in undiluted samples by siphoning the water through a 0.45 mm mesh size net to retain zooplankton. The FOC 120E cooled incubator was used to provide a temperature regime of 20 °C.

The water quality of the Dubossary Reservoir was estimated in accordance with the Annex No. 1 (Regulation, 2013), which contains threshold values of five water quality classes (Table 1) for 90 parameters, including temperature and oxygen regimes, acidification state, nutrients, mineralization, metals, organic pollutants, as well as hydrobiological and microbiological parameters. The concept of water body classification laid down in this Regulation is based on European quality standards stipulated by the Water Framework Directive (Directive 2000/60/EC).

Table 1. Threshold values for oxygen regime parameters

Parameter	Units	WQC I	WQC II	WQC III	WQC IV	WQC V
Dissolved oxygen	mg·L ⁻¹	> 8	> 7	> 5.5	> 4	< 4
BOD ₅	mgO·L ⁻¹	3	5	6	7	> 7
CCO-Cr	mgO·L ⁻¹	< 10	15	30	90	> 90

Within the analyzed group of oxygen regime parameters, the BOD₅/COD-Cr ratio in the collected water samples was calculated to assess the potential of self-purification processes in the Dubossary Reservoir under conditions of anthropogenic load and climatic challenges.

3. Results and Discussion

Hydromorphological characteristic of the Dubossary Reservoir is not uniform (Figure 1). This was taken into account when establishing sampling points. The Camenca station is located in the upper sector (left bank), where the water body still has a river-like character. It should be noted that the main manufacturing enterprise in the Camenca town is the Camenca Cannery, located at a distance of no more than 1 km from the reservoir bank. The wastewater from fruit and vegetable processing may contain high concentrations of organic matter. There are sewage treatment facilities in Camenca, but they were built back in the 1960s.

The Hârjău station (left bank) is located 5 km upstream of the Rezina-Râbnîța agglomeration. It is the beginning of the middle sector of the reservoir, where the estuaries of the tributaries Ciorna, Rezina and Râbnîța are situated. The Dniester water intake in Hârjău is one of the three sources of water supply for the Râbnîța city. The main environmental polluters in this section of the Dniester basin are two cement plants (in Rezina and Râbnîța) and the Moldavian Metallurgical Plant. In 2021, construction of the municipal wastewater treatment facilities started in Rezina. The urban and industrial sewage from Râbnîța is subjected to complete biological treatment at the municipal wastewater treatment facilities commissioned in 1964–1985.

The Goian and Cocieri stations (left bank) are located in the lower sector of the Dubossary Reservoir. The Goian station is situated at the estuary of the Iagorlâc River, the left tributary of the Dniester (Figure 2), and the Cocieri station is located not far from the Dubossary HPP dam. In this sector of the reservoir, the depth in some places reaches 12–16 m in the former riverbed of the Dniester River. The morphological and hydrological particularities of this part of the reservoir determine special habitat conditions for hydrobionts.

Dissolved oxygen concentration, along with water temperature, are the most important parameters of water habitat, the seasonal dynamics of which determined the

evolution of adaptation mechanisms of aquatic biota. Concentration of dissolved oxygen in a surface water body can be contributed by both natural factors such as aeration (diffusion/convection), fluctuations of water temperature and photosynthetic processes, and anthropogenic ones such as wastewater discharge, operation of hydrotechnical facilities, washouts from surrounding areas and landfills in the absence of water protection zones, etc. Thus, the oxygen concentration at the sampling point is the result of a dynamic balance between processes of natural aeration, photosynthetic production of oxygen and its use for chemical, biochemical and biological (respiration of hydrobionts) consumption.



Figure 2. Iagorlâc river estuary (Source: <https://www.himoldova.md/en/md/state-reserve-iagorlic>)

Dependence of oxygen solubility on water temperature determines its seasonal and spatial dynamics in river ecosystems. The Dniester River crosses the territory of the Republic of Moldova from northwest to southeast for 657 km. The natural increase in water temperature between the northernmost and southernmost sampling point of the Dniester within this territory is 2–4 °C (Jurminskaia et al., 2023). The water temperature seasonal fluctuations in the Dubossary Reservoir during 2021–2023 hydrological periods varied in the range of 5.20–28.4 °C, while the concentration of dissolved oxygen ranged from 7.2 to 12.7 mg·L⁻¹. To assess the extent to which the variability of oxygen concentration in the reservoir is due to fluctuations in water temperature, a correlation analysis of the data was performed (Figure 3).

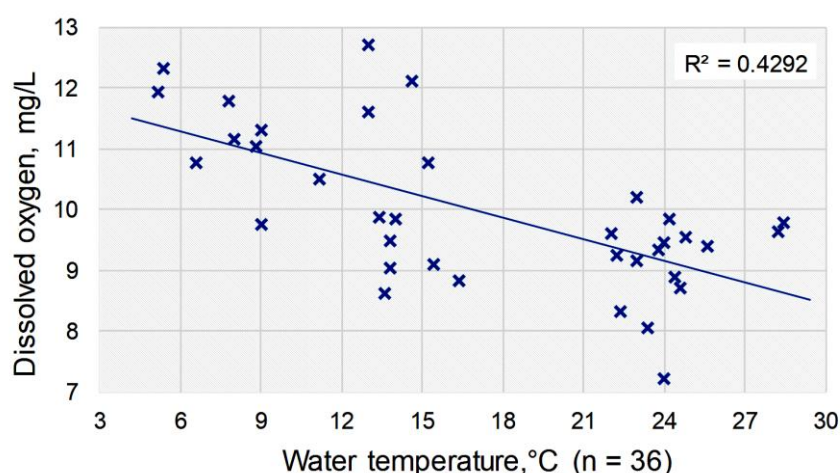


Figure 3. Relationship between water temperature and dissolved oxygen concentration in the Dubossary Reservoir (2021 – 2023)

The analysis showed a relatively strong negative correlation between oxygen concentration and water temperature in the Dubossary Reservoir: $r = -0.66$. The negative correlation for these parameters is natural, but the significant scatter of oxygen data, associated with the temperature range 12–15 °C (spring and autumn seasons), indicates the influence of other factors on oxygen concentration not only water temperature. The most significant variability was registered at the Camenca station: the

lowest concentration in the summer of 2021 and the highest in the autumn of 2022 (Figure 4). The deficiency of dissolved oxygen at this station can be provoked by the ecological state of the river section upstream, when untreated wastewater from the Soroca town (whose treatment facilities are not functioning) is discharged into the Dniester River. At the same time, the oxygen deficiency may be caused by the high intensity of biochemical consumption under the discharge of wastewater from the Camenca cannery, which contains high concentrations of organic matter formed during the processing of horticultural raw materials.

It was of research interest to compare the current seasonal-spatial dynamics of dissolved oxygen in the Dubossary Reservoir with data from the 1971–1973 period (Gorbatenkiy & Byzgu, 1977), when the Dubossary HPP dam was the only on the Dniester River, and facilities for biological treatment of wastewater were commissioned in every industrial town in the Dniester basin (Figure 4).

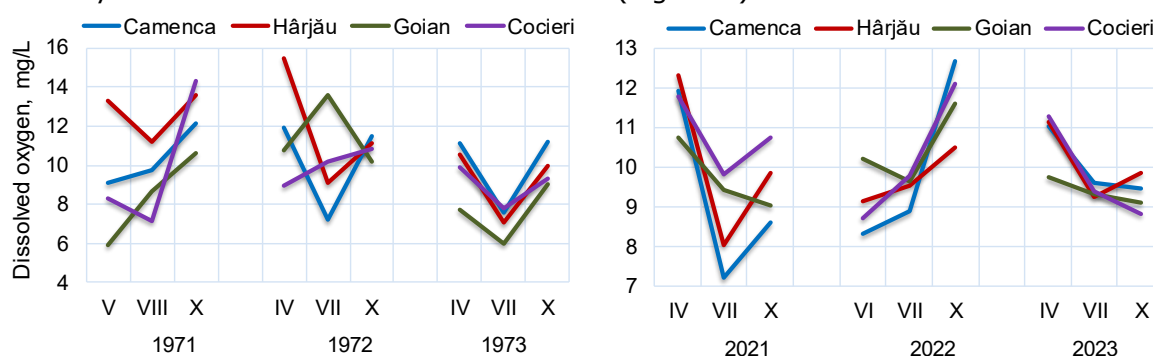


Figure 4. Retrospective analysis of dissolved oxygen seasonal dynamics in the Dubossary Reservoir

The result of the graphical analysis demonstrates that the natural seasonal dynamics of dissolved oxygen in the Dubossary Reservoir during the compared periods was registered only in 1973. Both 50 years ago and at present, local oxygen fluctuations in the reservoir water in most cases do not have natural seasonal dynamics, and thus are subject to the impact of other factors. But despite all the variability of this parameter, its values in the reservoir are within the limits of I–II WQC (Table 1).

Biochemical oxygen demand, BOD₅. As noted above, dissolved in water oxygen is consumed for respiration of aquatic biota, chemical and biochemical oxidation. The rate of oxidation depends on different factors, including water temperature. Dependence on water temperature is determined by the structure of microbial communities and the specific adaptive mechanisms of their participants.

The correlation between BOD₅ parameter and water temperature in the Dubossary Reservoir is presented in Figure 5. For these parameters, correlation is positive, less strong ($r = 0.41$), with outliers at the temperature 15 °C (Cocieri, October 2022; Goian, October 2023) and 28 °C (Goian and Cocieri, July 2022). The most significant outlier (Goian, June 2022: 4.15 mgO·L⁻¹, WQC II) had to be excluded from the correlation analysis. To explicate the high BOD₅ value at the Goian station in June 2022, the spatial dynamics of this parameter was analyzed: both at upstream (Camenca, Hârjău) and downstream (Cocieri) stations, the BOD₅ values did not exceed 2 mgO·L⁻¹ (WQC I). Thus, the high value of BOD₅ at the Goian station associated with the high value of COD-Cr (Figure 6) suggests the local water pollution at the date of sampling. On the other hand, high autumn BOD₅ values at low COD-Cr values (Cocieri, October 2022; Goian, October 2023) are associated with secondary pollution by the biomass of dying hydrophytes that actively vegetated in the reservoir (with slow water flow and high transparency) during the summer season. The water quality of the Dubossary Reservoir in terms of BOD₅ fluctuated between classes I and II during the period under review.

Bichromate chemical oxygen demand, COD-Cr. The composition and quantity of chemically oxidizable substances at a certain river site depends on many factors, such

as surface runoff, which can be aggravated by the rainfall; the ecological state of the tributaries, which can have a diluting effect or, on the contrary, cause pollution; the hydrochemical reactions of internal processes in the river ecosystem; the composition of discharged wastewater, etc.

Depending on the hydrological season, the COD-Cr values in the samples from the Dubossary Reservoir (Figure 6) varied as follows (*min – max*, mgO·L⁻¹): in spring, from 12.3 (Hârjău) to 24.9 (Camenca); in summer, from 9.8 (Cocieri) to 31.5 (Camenca); in autumn, from 13.2 (Cocieri) to 22.0 (Camenca). Thus, according to the national Regulation (Table 1), the water quality of the Dubossary Reservoir in terms of COD-Cr varied between classes I and II, and in some cases corresponded to class III.

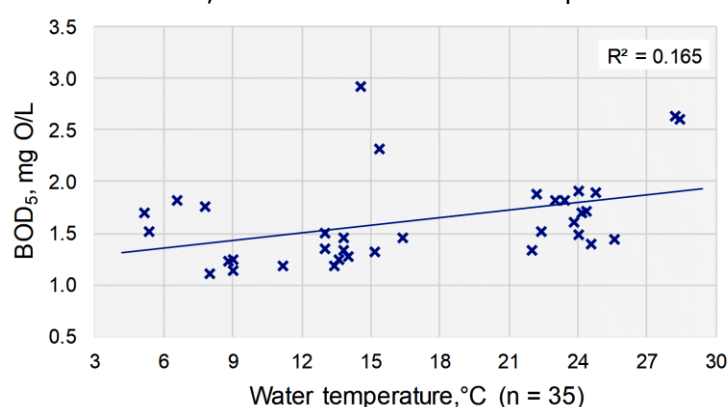


Figure 5. Relationship between water temperature and BOD₅ values in the Dubossary Reservoir (2021 – 2023)

The spatial dynamics of the COD-Cr parameter as a whole for the vegetation period 2021–2023 was distributed like this (*mean ± standard error of the mean*, mgO·L⁻¹): Camenca – 20.6±5.3; Hârjău – 18.9±5.2; Goian – 18.6±5.0; Cocieri – 17.1±3.9. Thus, there is a decreasing trend for chemically oxidizable organic load from the upper sector of the reservoir to the dam. The largest variability of this parameter is registered at the Camenca station and could be caused by the ecological state of the Dniester River downstream the Soroca town which is considered an area of environmental disaster in the last decades (Zubcov et al., 2017).

Analysis of the COD-Cr parameter in the Dubossary Reservoir also reveals significant interannual variability (Figure 6): the well pronounced seasonal dynamics in 2021, when minimum values occurred in mid-summer and maximum were triggered by June rainfall; the seasonal dynamics of the COD-Cr parameter in 2022 has the opposite direction: the maximum values were recorded in summer, with local pollution at Goian station in spring; the complete absence of any seasonal or spatial dynamics in 2023, which indicates the impact of anthropogenic load on the reservoir ecosystem. In general, during the analyzed period, the quality of the Dubossary Reservoir water in terms of COD-Cr parameter varied from WQC I to WQC III.

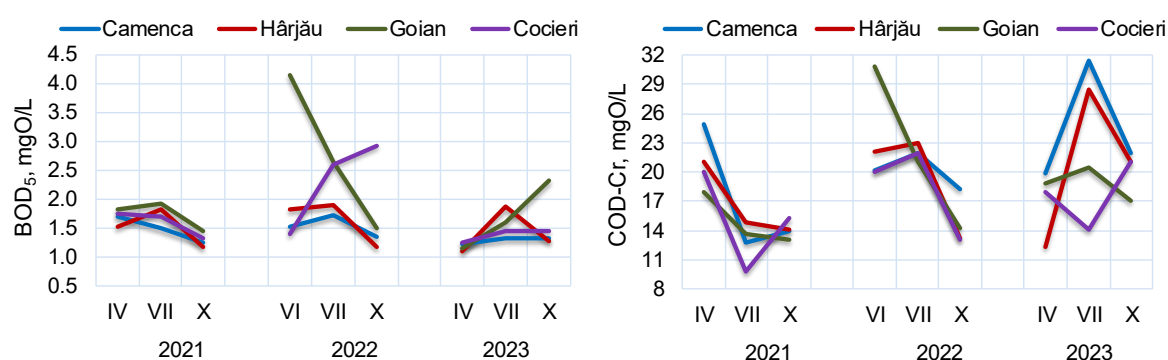


Figure 6. Seasonal dynamics of the BOD₅ and COD-Cr values in the Dubossary Reservoir

Ratio of chemically and biochemically oxidizable components. The processes of chemical and biochemical oxidation in aquatic ecosystems occur simultaneously. Saprophytic microflora is able to adapt to biodegradation of a wide variety of organic substances, but any adaptation in natural conditions occurs over a certain period. Therefore, the highest biochemical activity is characteristic of river sites exposed to permanent pollution. In bioreactors of biological treatment facilities, the efficiency of biochemical oxidation process is regulated by technological parameters, such as the concentration of dissolved oxygen in the system, the dose and age of activated sludge, the degree of its regeneration, etc.

In fact, all wastewater (treated and untreated) is eventually discharged into recipient water bodies, increasing the load on autochthonous heterotrophic (chemoorganotrophic) bacteria. The Dniester River, including the Dubossary Reservoir, is the recipient of all discharged waters (domestic and industrial) in the Dniester Hydrographic Basin District (The Management Plan, 2017). Calculation of the BOD₅/COD-Cr ratio in the collected water samples allows to predict the efficiency of biochemical processes that are the basis of self-purification in aquatic ecosystems, as well as of the technology of biological wastewater treatment. When the BOD₅/COD-Cr ratio is > 0.5, it is reasonable to apply biological treatment, in which the value of this index in treated effluent decreases to 0.2–0.04 (Zhmur, 2003).

Surface watercourses cannot be regulated by any technological parameters other than flow regulation, but this regulation provokes ecosystem instability both at the level of hydrochemical parameters and at the level of biocenoses functioning. Under conditions of constant daily fluctuations of the Dniester water level, the ratio of chemically and biochemically oxidizable substances downstream of HPP-2 dam is in constant dynamics, which makes it difficult for riverine bacterioplankton to adapt to the habitat composition, even taking into account the high rate of its generation. Using the BOD₅/COD-Cr ratio, the locations with a low level of microbiota adaptation were identified (Figure 7).

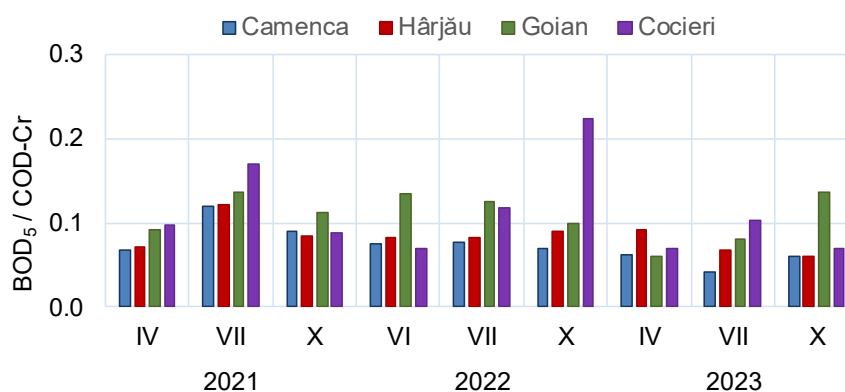


Figure 7. Seasonal, spatial and interannual variability of the BOD₅/COD-Cr index in the Dubossary Reservoir

During 2021–2023 vegetation period, the value of BOD₅/COD-Cr index ranged from 0.04 at Camenca station (July 2023) to 0.22 at Cocieri station (October 2022). The spatial dynamics of the index in most cases tends to increase in the direction from the upper sector of the reservoir (Camenca station) to the lower sector (Cocieri station), where fluctuations of the Dniester level are minimized due to the large depth of the water mass, and the impact of hydrological droughts (caused by climate changes) is not as critical as at shallow sectors. For the reservoir as a whole, the value of the BOD₅/COD-Cr index constituted 0.1 ± 0.04 . This result is comparable to the results obtained for used waters that have undergone complete biological treatment (Zhmur, 2003). Thus, in the analyzed period, the anthropogenic load associated with the regulation of the Dniester flow under conditions of climatic changes, as well as with pollutions washed off from

adjacent territories and discharged with used waters, has not yet exceeded the adaptation resource of the Dubossary Reservoir heterotrophic microbiota.

4. Conclusions

The analysis of oxygen regime parameters demonstrates that their fluctuations in the Dubossary Reservoir in most cases do not have natural seasonal dynamics. The retrospective analysis of the obtained results with data from 50-years ago shows that the anthropogenic load on the reservoir ecosystem has remained actual for the present. During 2021–2023 vegetation periods, the spatial dynamics of analyzed parameters revealed the presence of a tendency to decrease this load in the direction from the upper section of the reservoir (Camenca station) to its lower section (Cocieri station). This trend is also demonstrated by the change in the ratio between the BOD and COD parameters: the value of BOD₅/COD-Cr index ranged from 0.04 (Camenca) to 0.22 (Cocieri).

According to the dissolved oxygen concentration and BOD₅ parameter, the water quality of the Dubossary Reservoir during the analyzed period varied within the classes I and II, and according to the COD-Cr parameter it dropped down to class III. It was in such cases that the BOD₅/COD-Cr ratio decreased to 0.04 (Camenca, July 2023).

Conditions for effective biochemical activity of microbial communities are more favorable in the lower section of the Dubossary Reservoir. The upper section is affected by different anthropogenic factors, including regulation of the Dniester flow, discharge of insufficiently treated wastewater, shoaling of the Dniester and its tributaries due to hydrological droughts, unauthorized discharges that provoke local pollution.

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