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DYNAMICS OF THE SELF-PURIFICATION PROCESSES IN THE WATERS OF THE DNIESTER RIVER DURING THE YEARS 2015-2024 (DUBASARI - VADUL LUI VODA SECTION)

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Abstract. It has been evaluated the dynamics of the self-purification processes of the Dniester River waters in the section from Dubasari to Vadul lui Voda based on the analysis of the parameters: biochemical oxygen demand (BOD_5), chemical oxygen demand (COD_{Cr}), thiol content, and the inhibition capacity of the waters in carrying out chemical self-purification processes through free radicals ($\Sigma kiSi$). According to the BOD_5 values, the Dniester waters belong to quality classes II and I, and according to the COD_{Cr} parameter, they fall into quality classes II and III. The thiol content is typical of fresh waters (10^{-6} M), and they are of natural origin. The inhibition capacity classifies the river's waters as slightly and moderately polluted. Along the river, were observed a decrease in biological self-purification processes and an increase in the intensity of free radical processes in the Criuleni area, indicating an additional inflow of reducing compounds into the Dniester waters from its tributary, the Raut River. Additionally, a tendency was noted for the aquatic environment quality restoration in the Vadul lui Voda area.

Keywords: Dniester river, surface water, biochemical oxygen demand, thiol, self-purification process.

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Introduction

The Dniester is the most important aquatic artery of the Republic of Moldova, and the main source of water supply in the country [1,2]. Since the Dniester River flows through many cities and towns and collects runoff, untreated or poorly treated wastewater, domestic sewage, and water from its tributaries, it is constantly affected by both natural and anthropogenic pollution.

The ecological state of the Dniester River is the object of study in various fields, such as ecology, hydrobiology, hydrochemistry, ecological chemistry, *etc.* Research on the ecological chemistry of water has mainly focused on biodegradable, persistent, and xenobiotic organic substances [3-6], which are different types of compounds that greatly impact the ecological state of water ecosystems. Natural sources of organic substances are derived primarily from the decomposition of plant material, bacteria, and algae, as well as various metabolites of these organisms. Anthropogenic sources are much more diverse and include vehicle emissions (oil products), pulp and paper processing plants, meat processing plants (protein compounds), wastewater, household (domestic) wastewater *etc.* Organic pollutants enter aquatic systems through various pathways, primarily *via* surface runoff, wastewater discharge, and atmospheric deposition [7,8]. The impact of anthropogenic sources on the Dniester River is mainly due to poor wastewater treatment. Thus, for 2022, there were 156 treatment plants in the Dniester River basin, of which only 25 (16%) meet the standards of treatment; 92 (59%) discharge insufficiently treated water; and 39 (25%) are not functional [9]. At the same time, sites for the disposal of waste materials increase water pollution, so in the river basin, there are 66 landfills located in the river protection area, and 77% of the basin's territory is used for agriculture [10].

Recent research indicates major pollution with hazardous contaminants in both the waters of the Dniester River and its tributaries, with 150 identified out of a total of over 2000 compounds [11]. These contaminants are predominantly of organic nature, including pharmaceuticals, pesticides, and industrial chemicals. Pollution results from inadequate solid waste and wastewater treatment management by the relevant authorities, which is worsened by the political-administrative issues in the Transnistrian region and the establishment of hydroelectric power plants within Ukrainian territory [12-16].

Even if the biological self-purification capacity of river waters indicates a satisfactory intensity [17], based on pollution indicators [18-20], it must be taken into account that under natural conditions, only biodegradable organic substances are transformed by microorganisms through aerobic biochemical oxidation to carbon dioxide and water [21]. In this case, the oxidation process also consumes the dissolved oxygen from the water. Thus, in aquatic objects with a high content of biodegradable organic matter, a significant amount of dissolved oxygen is used up during their biochemical oxidation, which creates difficulties for the metabolic processes of aquatic organisms. At the same time, the number of organisms tolerant to the critical dissolved oxygen content in water increases. These organisms create an anaerobic environment in the water by producing secondary metabolites, which slows down the enzymatic oxidation processes. Aerobic species may consequently diminish or even disappear. Stated differently, there is constant competition and a dynamic equilibrium between anaerobic and aerobic aquatic organisms in the natural environment.

Surface waters, which are open and complicated systems, also reduce pollution through other self-purification processes than biological ones, but which occur with lower intensity-chemical self-purification processes [22]. The main chemical self-purification processes involve oxidants that come from active forms of dissolved oxygen, like hydrogen peroxide and hydroxyl radicals. The pollution and depollution of aquatic systems by substances with OH radical scavenging properties is evaluated using the parameter inhibition capacity ($\Sigma k_i S_i$) [23].

Determining reducing compounds that consume active forms of oxygen, such as thiols (R−SH), can also assess the intensity of chemical self-purification processes [24]. Information regarding an aquatic object's thiol content may provide details about its ability to undergo chemical and biological self-purification processes.

Therefore, determining the parameters that characterise chemical self-purification processes, which have not received much research, is another part of the complex assessment of water self-purification systems. Using pollution indicators such as dissolved oxygen content, biochemical oxygen consumption, and chemical oxygen consumption, along with the inhibition capacity indicator and thiol content, helps us understand how biochemical and chemical self-purification processes work, which are important for improving water quality. Based on this, the present work aimed to evaluate the dynamics of biochemical and chemical self-purification processes in the Dniester River water in the period from 2015 to 2024.

Experimental

Materials

For the determination of the (biochemical oxygen demand) BOD_5 parameter, chemical reagents of analytical grade were used. The solution for chemical oxygen demand (COD_{Cr}) analysis was purchased from HACH Company. For the determination of thiols and inhibition capacity, 5,5'-dithiobis(2-nitrobenzoic acid), *p*-nitrosodimethylaniline (PNDMA), and hydrogen peroxide were purchased from Sigma-Aldrich (Germany). All solutions were prepared using distilled water (GFL 2001/4).

The sampling points

To achieve the scope of this study, water samples were collected from the Dniester River 4–5 times a year during the years 2015–2024 at three points along its course in the section between Dubasari and Vadul lui Voda, (Table 1 and Figure 1).

The methods used for water sampling were based on the sampling rules. Sampling was carried out at a depth of 30 cm below the water surface. The vessel was lowered into the water with the neck down, filled to the top, and closed in such a way that there was no air above the sample. During transportation, the water samples were protected from sunlight [25]. The measurements included the dissolved oxygen, BOD_5, COD_{Cr}, thiol content, and the inhibition capacity of the waters in carrying out the chemical self-purification processes through OH radicals.

Table 1

The sampling points.

Sampling point	*Source of samples*	*Coordinates*
1	Upstream of the confluence of the Raut River with the Dniester, in the Ustia village, Dubasari district	47°16'29.4"N; 29°07'20.2"E
2	Downstream of the confluence of the Raut River with the Dniester and upstream of the confluence of the Ichel River with the Dniester, in the Criuleni city	47°13'32.1"N; 29°09'48.3"E
3	Downstream of the confluence of the Ichel River with the Dniester, in the Vadul lui Voda city	47°06'14.6"N; 29°04'03.0"E

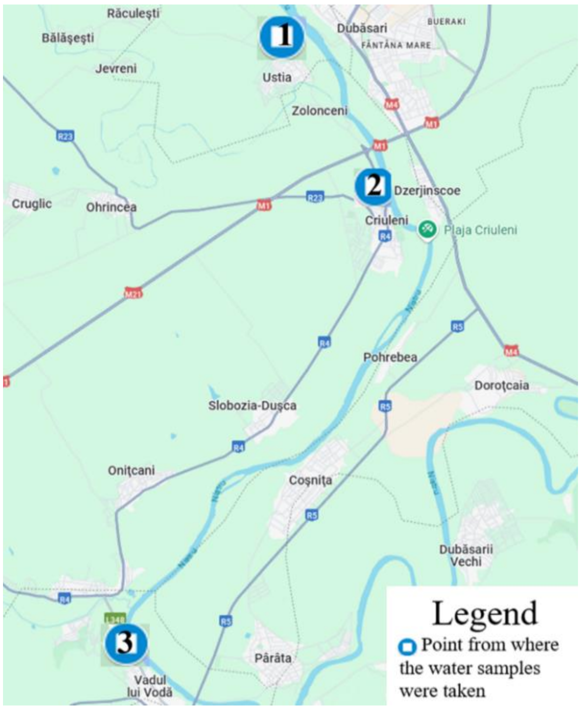

Figure 1. Map with sampling points.

Method for the determination of BOD_5

The intensity of biological self-purification processes was estimated by determining the biochemical oxygen demand over five days (BOD_5). BOD_5 was calculated as the difference between the dissolved oxygen content on the day of sampling and that measured five days after collection, with the sample being stored in the dark at a temperature of 20°C. The dissolved oxygen concentration was determined using the Winkler titrimetric method [20].

Method for determination of COD_{Cr}

For chemical oxygen demand determination, a spectrophotometric method developed by HACH was used [26].

The proportion of biodegradable substances in the total organic content was calculated using Eq.(1), proposed based on the water self-purification index (*WSPI*) [27].

$$WSPI = \frac{BOD_5}{COD_{Cr}} \cdot 100\% \qquad (1)$$

where, BOD_5 - biochemical oxygen demand;
COD_{Cr} - chemical oxygen demand.

Method for determination of inhibitory capacity [23]

Radical self-purification processes were evaluated by the inhibition capacity method (*ΣkiSi*). The method is based on the determination of the rate of discoloration of the dye *p*-nitrosodimethylaniline (PNDMA) under forced conditions of hydroxyl radical initiation upon UV irradiation in distilled water and the natural water sample. The inhibition capacity (*ΣkiSi*) may be determined by Eq.(2).

$$\Sigma k_i[S_i] = \frac{V_{tot.}}{V_{n.w.}} \cdot k(\mathrm{PNDMA}) \cdot [\mathrm{PNDMA}]_0 \cdot [\frac{W_{d.w.}}{W_{n.w.}} - 1] \qquad (2)$$

where: $W_{a.d}$ ($W_{a.n.}$) - the initial rate of PNDMA discoloration upon photolysis of hydrogen peroxide in distilled (natural) water, $M \cdot s^{-1}$;
k_{PNDMA}= $1.25 \cdot 10^{10}$ - bimolecular rate constant of the reaction of the dye with OH radicals, s^{-1};
$[\mathrm{PNDMA}]_0$ - PNDMA initial concentration, M;
V_{tot} - the total volume of the mixture, mL;
$V_{a.n.}$ - the volume of natural water in the mixture, mL.

Determination of thiol content in natural waters

The thiol content in natural waters was determined using the Ellman spectrophotometric method, adapted for the analysis of natural water samples [28]. This method is based on the interaction between 5,5′-dithiobis-(2-nitrobenzoic) acid (DTNB) and the –SH thiol group, which at pH= 8, leads to the formation of 2-nitro-5-thiobenzoic acid (TNB). Subsequently, at pH= 8, TNB dissociates, forming the TNB^{2-} anion, which exhibits a maximum absorption at a wavelength of λ= 412 nm, with a molar extinction coefficient of ε= 14150 M^{-1} cm^{-1}.

Statistical analysis

Statistical analysis was conducted by calculating linear correlation coefficients using the Pearson linear function in Microsoft Excel 2019. This analytical method enables the identification of potential relationships between variables, as well as the assessment of their strength and direction [29].

Results and discussion

Considering that biological self-purification plays a predominant role among all self-purification processes in aquatic systems, the monitoring of biodegradable organic substances in the waters of the Dniester River was conducted by determining the biochemical oxygen demand over a standard period of 5 days (BOD_5) (Table 2).

During the monitoring period, BOD_5 values varied within the range of 0.3–7.4 mgO_2/L. The multiannual average values downstream of the Dubasari Dam and Criuleni city were 3.3 mgO_2/L and 3.1 mg O_2/L, respectively. The BOD_5 values classify the waters of the Dniester River within quality class II (Good) according to Government

Decision No. 890 [30], which is aligned with Directive 2000/60/EC of the European Parliament [31], suggesting that these waters were only slightly affected by anthropogenic pollution. At the Vadul lui Voda sampling point, the multiannual average of this quality parameter was 2.5 mgO_2/L (Table 2). Throughout the monitoring period, the water in this section of the Dniester River fell within quality class I, except in 2016, when it was classified as quality class II. Water quality classes I and II mean that there were no major changes in the water and that the concentrations of biodegradable organic substances did not reach levels characteristic of pollution, thus ensuring the proper functioning of the aquatic ecosystem [30]. Additionally, the multiannual average values demonstrate a 24% decrease in BOD_5 from Dubasari to Vadul lui Voda, which means there is less water pollution by biodegradable organic substances.

To determine the origin of biodegradable organic substances in the waters of the Dniester River, the average seasonal values of BOD_5 were calculated (Figure 2). At all sampling points, seasonal variations in BOD_5 values were observed, with maximum values recorded in the summer and minimum values in the autumn. This trend indicates that the biodegradable organic substances in the Dniester River mainly come from the activities of living organisms in the water. It is well known that summer water temperatures provide optimal conditions for their development. Also, the rise in biodegradable organic matter in spring and especially summer might be affected by the grazing and watering of farm animals in the Dniester floodplain, which adds different biological waste to the water.

At all sampling locations, the highest amount of biodegradable organic substances is found in the summer, with about a 33% rise at Dubasari, around 14% after the Raut tributary flows into the Dniester, and about 26% after the Ichel tributary flows in. Pollution with biodegradable organic substances, primarily of animal origin, in the waters of the Dubasari reservoir and its tributaries is responsible for this increase. The main sources are the reservoir's eutrophication and the unregulated domestic animal grazing and watering in the Dniester streams' floodplains.

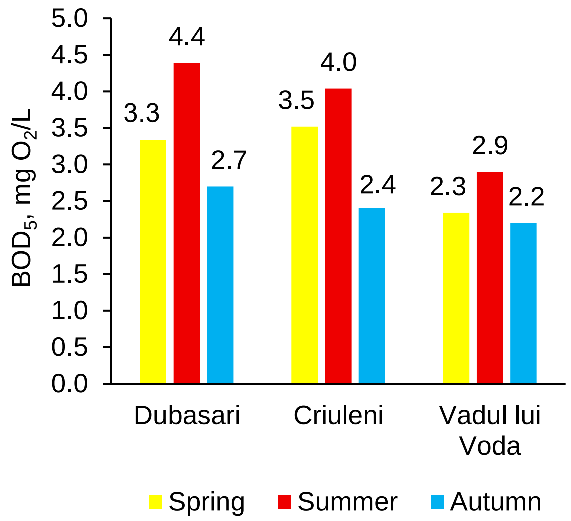

Figure 2. Seasonal variations of BOD_5 values at the three sampling points along the Dniester River during the period 2015–2024.

Table 2

Minimum, maximum, annual, and multiannual average values of BOD_5 along the Dniester River during the period 2015–2024.

Year	*Sampling point*											
	Dniester (downstream of Dubasari dam)				*Dniester (Criuleni)*				*Dniester (Vadul lui Voda)*			
	BOD_5, mg O_2/L			*Quality class*	*BOD_5, mg O_2/L*			*Quality class*	*BOD_5, mg O_2/L*			*Quality class*
	min	*max*	*average*		*min*	*max*	*average*		*min*	*max*	*average*	
2015	0.3	5.3	3.5	II	1.4	4.2	2.3	I	0.6	3.8	2.2	I
2016	1.1	3.0	1.7	I	0.5	2.1	1.4	I	0.3	2.4	1.1	I
2017	0.8	7.1	4.5	II	3.5	7.2	5.0	II	2.1	4.9	3.7	II
2018	0.7	5.7	3.4	II	2.9	7.1	4.4	II	1.3	3.3	2.2	I
2019	2.2	4.9	3.0	I	1.5	4.3	3.2	II	1.8	2.9	2.4	I
2020	0.6	4.8	2.7	I	0.5	6.8	2.6	I	0.9	4.4	2.2	I
2021	0.6	7.4	3.8	II	1.6	4.3	2.6	I	1.4	4.3	2.6	I
2022	1.5	3.8	2.9	I	1.9	4.1	3.1	II	2.4	3.0	2.7	I
2023	2.1	6.0	3.9	II	1.8	5.9	3.7	II	2.0	3.6	3.0	I
2024	2.6	5.6	3.7	II	1.3	4.0	3.0	I	2.4	2.6	2.5	I
Multiannual average	1.3	5.4	3.3	II	1.7	5.0	3.1	II	1.5	3.5	2.5	I

In comparison to the summer, the concentration of biodegradable organic substances in the Dniester decreased in the autumn. The decreases were approximately 40% at Dubasari, about 32% in the sampling point of the Criuleni city (after the Raut River discharge), and around 18% at the Vadul lui Voda sampling point (after the Ichel River discharge). The phenomenon occurs because, following hot and dry summers, the water flow from the reservoir and the Dniester's tributaries decreases significantly in the fall, which reduces their impact on the river's biodegradable organic matter content.

The BOD_5 measurements only partially reflect the oxidation processes of biodegradable substances involving dissolved oxygen. So, the COD_{Cr} (chemical oxygen demand) was also measured to give a complete assessment of water quality and to determine how much of the total dissolved organic matter in the river is biodegradable. This parameter indicates the total content of both biodegradable and chemically hard-to-break down organic substances. Throughout the monitoring period, COD_{Cr} values (Table 3) ranged from 1 to 57 mgO/L. The multiannual average downstream of the Dubasari Dam was 14.6 mgO/L, while at the intake points in Criuleni and Vadul lui Voda, the average values were 19.3 mgO/L and 19.2 mgO/L, respectively. These results indicate that along the river course, from Dubasari to Vadul lui Voda, the average COD_{Cr} values increased by 32%. Thus, at the Dubasari sampling point, the waters of the Dniester River exhibited a lower degree of organic pollution. However, anthropogenic influences caused a moderate alteration in physicochemical and biological quality parameters at the Criuleni and Vadul lui Voda sampling points. This finding suggests a moderate disruption in the functioning of the ecosystem.

The study showed the following patterns over several years in the seasonal changes of hard-to-break down organic compounds (Figure 3), as shown by the COD_{Cr} measurement.

During the spring period, along the river, an increase in the content of hard-to-degrade organic substances was recorded, with approximately 38% at the Vadul lui Voda sampling point compared to the sampling point downstream of the Dubasari dam. This phenomenon can be explained by the ongoing anthropogenic pollution from the settlements situated along the riverbanks.

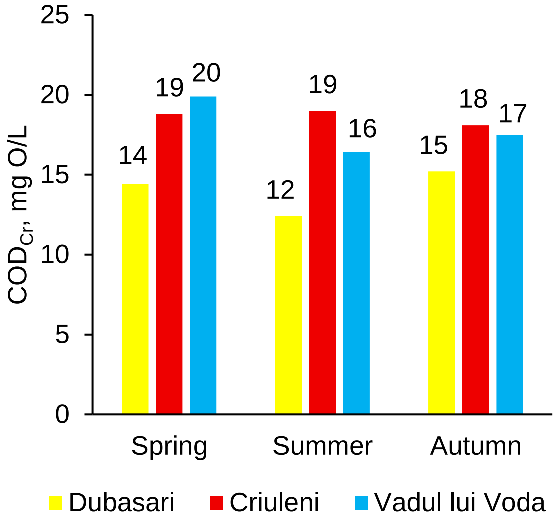

Figure 3. Seasonal variation of the average content of hard-to-degrade organic substances in the waters of the Dniester River in the Dubasari – Vadul lui Voda section during the period 2015–2024.

Table 3

Minimum, maximum, annual, and multiannual average values of COD_{Cr} along the Dniester River during the period 2015–2024.

Year	*Sampling point*											
	Dniester (downstream of Dubasari dam)				*Dniester (Criuleni)*				*Dniester (Vadul lui Voda)*			
	COD_{Cr}, mgO/L			*Quality class*	*COD_{Cr}, mgO/L*			*Quality class*	*COD_{Cr}, mgO/L*			*Quality class*
	min	*max*	*average*		*min*	*max*	*average*		*min*	*max*	*average*	
2015	1.0	5.0	3.8	I	4.0	20.0	11.0	II	2.0	26.0	9.5	I
2016	4.0	22.0	15.0	II	7.0	28.0	16.4	III	8.0	49.0	31.5	IV
2017	9.0	17.0	13.3	II	13.0	37.0	19.6	III	10.0	32.0	16.5	III
2018	10.0	14.2	12.1	II	11.6	17.3	14.9	II	9.2	15.7	12.3	II
2019	12.0	18.0	14.3	II	12.0	21.0	17.3	III	11.0	14.0	13.0	II
2020	13.2	15.0	14.0	II	18.1	20.5	19.5	III	14.4	16.5	15.5	III
2021	16.0	20.3	18.2	III	20.1	27.0	23.2	III	16.0	19.0	18.1	III
2022	7.7	23.3	16.1	III	6.2	24.2	18.2	III	5.6	19.1	13.5	II
2023	20.8	21.0	20.9	III	27.0	36.4	31.7	IV	35.0	57.0	46.0	IV
2024	15.6	20.6	18.1	III	14.7	27.5	21.4	III	13.2	19.1	16.1	III
Multiannual average	10.9	17.6	14.6	II	13.4	25.9	19.3	III	12.4	26.7	19.2	III

During the summer, pollution with hard-to-break-down organic substances was 50% higher at the Criuleni sampling point (downstream of the Dniester confluence with the Raut tributary) than at the Dubasari sampling point. This disparity arises from the intensified anthropogenic pollution caused by the discharge of tributary waters. At the Vadul lui Voda sampling point, dilution effects lessened the influence of these pollutants because they mixed with cleaner water, resulting in only a 32% increase in the COD_{Cr} level compared to the Dubasari sampling point.

Similar trends were observed during the autumn period, when at the Criuleni sampling point, the increase in the COD_{Cr} parameter compared to the Dubasari sampling point was 19% and then decreased to 15%.

By examining the average BOD_5 and COD_{Cr} values, it was found that in the Dniester waters at the Dubasari sampling point, around 23% of the total organic substances are biodegradable. In the Criuleni sampling point, this proportion is about 16%, and in the Vadul lui Voda sampling point, it is 13% (Table 4). Those results indicate that the Raut and Ichel rivers, which flow into the Dniester, greatly raise the amount of non-biodegradable substances, mostly caused by human activities, thereby highlighting the negative impact of human activities.

According to calculations based on [32], the level of biodegradable organic compounds decreased by 25% along the Dniester from the Dubasari to the Vadul lui Voda during the monitoring period. In contrast, the proportion of hard-to-degrade organic substances, like organic carbon (C_{org}) and total organic substances (*TOS*) in the water increases by about 32% (Table 4).

The analysis of the average seasonal content of biodegradable and hard-to-degrade organic substances, as well as the ratio between them, indicates the presence of seasonal dynamics in the ratio between the BOD_5 and COD_{Cr} parameters (Table 5).

The multiannual seasonal variation in the origin of organic substances present in the waters of the Dniester River can be shown by changes in the ratio between the content of biodegradable organic substances (BOD_5) and hard-to-degrade organic substances (COD_{Cr}) (Figure 4).

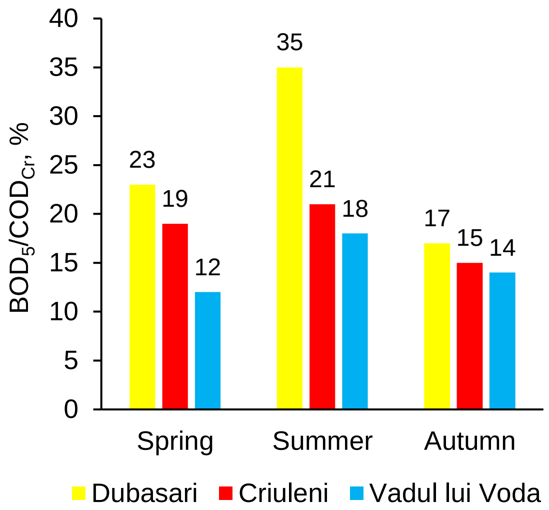

Figure 4. Multiannual seasonal ratio of the average organic substance content in the waters of the Dniester River in the Dubasari – Vadul lui Voda section during the period 2015–2024.

Table 4

Average values of organic substance concentrations in the waters of the Dniester River during the period 2015–2024.

Sampling point	*COD_{Cr}, mg O/L*	*C_{org}, mg/L*	*TOS, mg/L*	*BOD_5, mg O_2/L*	*BOD_5/COD_{Cr}*
Dniester (downstream Dubasari)	14.6	5.5	7.4	3.3	23%
Dniester (Criuleni)	19.3	7.2	9.7	3.1	16%
Dniester (Vadul lui Voda)	19.2	7.2	9.7	2.5	13%

Table 5

Multiannual seasonal dynamics of organic substance content in the waters of the Dniester River, Dubasari – Vadul lui Voda section (2015–2024).

Season	*Sampling point*								
	Dubasari			*Criuleni*			*Vadul lui Voda*		
	BOD_5 mg O_2/L	*COD_{Cr} mg O/L*	*BOD_5/COD_{Cr}*	*BOD_5 mg O_2/L*	*COD_{Cr} mg O/L*	*BOD_5/COD_{Cr}*	*BOD_5 mg O_2/L*	*COD_{Cr} mg O/L*	*BOD_5/COD_{Cr}*
Spring	3.3	14.4	23%	3.5	18.8	19%	2.3	19.9	12%
Summer	4.3	12.4	35%	4.0	19.0	21%	2.9	16.4	18%
Autumn	2.7	15.2	17%	2.4	18.1	13%	2.2	17.5	13%

The largest amount of substances measured by the BOD_5 parameter, compared to all organic substances measured by COD_{Cr}, is found in the Dubasari intake. This is because water from the Dubasari reservoir, which has a lot of biodegradable organic substances generated by natural processes, flows into the Dniester. During spring and summer, the amount of these substances goes up by 50% because of active natural processes and the buildup of new, biodegradable organic substances. During spring and summer, the amount of these substances increases by 50% due to active natural processes and the accumulation of new, biodegradable organic substances.

Then, it is noted that the amount of biodegradable organic substances compared to all organic substances, along the Dniester River water from Dubasari to Vadul lui Voda, decreased in every studied season. In spring, at the Criuleni intake, the amount of biodegradable organic substances decreased by about 20%, and at the Vadul lui Voda intake, it decreased by about 50% compared to the levels at Dubasari. In the spring period, at the Criuleni intake, the ratio of biodegradable organic substances decreased by about 20%, and at the Vadul lui Voda intake - by about 50% compared to the amount at the Dubasari. In the summer period, this decrease was about 40% at Criuleni and 50% at the Vadul lui Voda sampling point. In the autumn period, the BOD_5/COD_{Cr} ratio in Criuleni was 12%, and in Vadul lui Vodă - 18% lower than in the Dubasari intake. This trend indicates an increasing proportion of hard-to-degrade organic substances along the Dniester's course. Such substances are typically of anthropogenic origin, enter surface waters as a result of human activities, and contribute to water pollution and the reduction of their self-purification processes. Therefore, throughout the study period, continuous pollution was observed along the Dniester River from Dubasari to Vadul lui Voda, including input from the Raut and Ichel tributaries.

Natural water self-purification processes can be split into two main types based on how fast they happen: slow processes that mainly use dissolved oxygen and rapid processes that use hydrogen peroxide [33-35]. To establish the quality of natural waters, it is necessary to determine parameters that will reflect these two groups. Slow processes are checked using hydrochemical parameters like BOD_5 and COD_{Cr}, while rapid processes, called kinetic processes, are checked using parameters like hydrogen peroxide concentration, OH radical concentration, and inhibition capacity, among others.

To properly assess the ecological status of natural waters, it is necessary to conduct comprehensive water quality monitoring, which also includes parameters that characterize rapid self-purification processes. These include radical processes in which the principal oxidants are reactive oxygen species, especially hydroxyl radicals. The strength of these radical processes was tracked using a measurement called the inhibition capacity parameter ($\sum k_i S_i$)—the pseudo-first-order effective rate constant for the interruption of radical oxidation chains.

During the monitoring period, inhibition capacity values varied slightly, ranging between $(1.03–4.76)\cdot10^5$ s^{-1} (Table 6). These data confirm that radical self-purification processes proceeded with approximately equal intensity across the monitored river section, keeping the water quality at levels considered slightly to moderately polluted.

Table 6

Inhibition capacity and degree of pollution by OH radical scavengers in the Dniester waters in the Dubasari – Vadul lui Voda section during the period 2015–2024.

Year	*Sampling point*		
	Dniester (downstream Dubasari)	*Dniester (Criuleni)*	*Dniester (Vadul lui Voda)*
	Inhibition capacity ($\sum k_i S_i \cdot 10^{-5}$, s^{-1}); Degree of pollution		
2015	1.55; s.p.	1.35; s.p.	1.66; s.p.
2016	1.64; s.p.	1.72; s.p.	1.54; s.p.
2017	4.76; m.p.	3.60; m.p.	3.52; m.p.
2018	4.25; m.p.	3.33; m.p.	1.53; s.p.
2019	3.35; m.p.	2.93; s.p.	2.53; s.p.
2020	1.10; s.p.	1.03; s.p.	1.33; s.p.
2021	2.73; s.p.	3.07; m.p.	3.07; m.p.
2022	1.68; s.p.	1.50; s.p.	1.30; s.p.
2023	3.83; m.p.	4.23; m.p.	3.50; m.p.
2024	1.97; s.p.	2.63; s.p.	1.75; s.p.

*s.p. - slightly polluted; m.p. - moderately polluted.

According to the findings, there is a modest level of OH radical scavenger pollution in the waterways, which disrupts the chain of OH radical regeneration. Thus, the process of radical self-purification of the Dniester waters is unaffected.

During the study, the content of organic compounds of a peroxidase nature, such as thiols, was also determined. According to our research, thiols can be considered one of the main classes of reducing equivalents, which maintain the dynamic redox balance in natural waters [24]. At the same time, the thiol content may also indicate pollution with biodegradable substances, usually of protein origin.

Over the 10-year monitoring period, the content of these compounds in the Dniester waters varied within the order of 10^{-6} M (Table 7).

The average thiol levels measured over several years at different points in the river are quite similar, suggesting that they come from natural biochemical processes in the water rather than from industrial or household wastewaters.

Seasonal variations in thiol concentrations were analysed to support this assumption. According to the obtained data (Figure 5), the thiol content in the waters of the Dniester River exhibits seasonal variation, with maximum concentrations observed during the summer, when temperatures in aquatic systems are optimal for the hydrobionts' development.

The linear correlation coefficients show a strong, almost perfect relationship between the thiol content and the BOD_5 values (Table 8). Thus, as the thiol content in the water increases, the BOD_5 values also rise, confirming that the thiols present in the waters of the Dniester are predominantly of natural origin, they are formed in the aquatic environment as a result of the metabolic processes of hydrobionts, especially microorganisms.

Also, it was calculated the linear correlation coefficient for the thiol content and inhibition capacity variables. At the Dubasari dam sampling point, the relationship between the variables shows a strong negative correlation (–0.71), which may suggest that the thiol concentration decreases to a greater extent due to biological self-purification processes, and thiols practically do not consume free radicals.

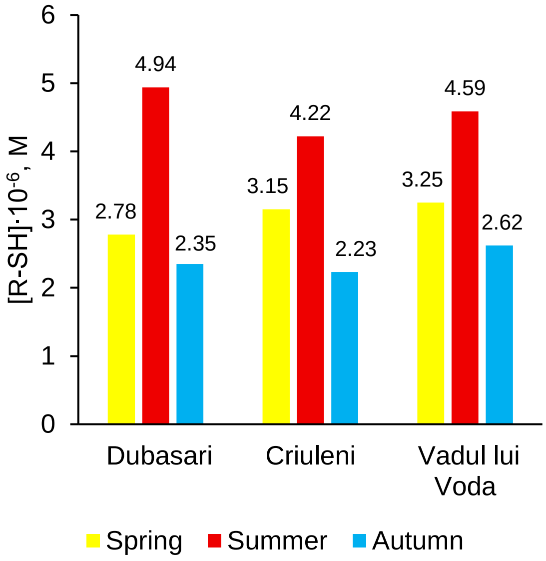

Figure 5. Seasonal variations of thiol values at the three sampling points along the Dniester River during the period 2015–2024.

Table 7

Annual and multiannual average of thiol content in the Dubasari – Vadul lui Voda section during the period 2015–2024.

Sampling point	*[R-SH]·10⁻⁶, M*										
	2015	*2016*	*2017*	*2018*	*2019*	*2020*	*2021*	*2022*	*2023*	*2024*	*Multiannual average*
Dniester (downstream Dubasari)	7.78	2.88	4.50	3.26	5.15	2.58	1.27	0.31	0.83	1.11	3.12
Dniester (Criuleni)	5.50	2.29	5.88	4.65	3.09	2.38	1.52	1.08	1.04	1.30	3.01
Dniester (Vadul lui Voda)	5.88	1.91	5.19	4.32	6.15	1.73	1.19	1.63	0.98	1.92	3.32

Table 8

Pearson linear correlation coefficient values between thiol content, BOD_5, and inhibition capacity (Σk_iS_i).

Correlation components	*Pearson linear correlation coefficient, R*		
	Dniester (downstream Dubasari)	*Dniester (Criuleni)*	*Dniester (Vadul lui Voda)*
R-SH – BOD_5	0.97	0.97	0.99
R-SH – $\sum k_iS_i$	−0.71	0.66	0.33

At the next sampling point, the correlation is moderately direct (0.66), indicating an additional input of reducing compounds into the Dniester waters as a result of the discharge of the Raut River waters. This leads to a slowing down of biological self-purification processes and the overcoming of chemical self-purification processes, especially radical ones. In other words, the consumption of active forms of oxygen occurs, which also confirms the positive value of the linear correlation between thiol content and inhibition capacity.

After the Ichel River waters flow into the river, at the third sampling point, a decrease in the relationship between thiol content and inhibition capacity (0.33) is observed. The decrease indicates a tendency to restore the initial properties of the aquatic environment and a slow transition from the dominance of chemical self-purification processes, especially radical ones, to biological processes.

Conclusions

The analysis of the dynamics of the Dniester waters self-purification processes in the Dubasari - Vadul lui Voda section, of biodegradable organic substances, especially thiols (which are one of the main reducing equivalents classes), showed that, during the monitoring period from 2015 to 2024, in the Dniester waters in the Dubasari area, self-purification occurs mainly through biological processes. Further downstream, in the Criuleni area, the intensity of chemical self-purification processes involving free radicals increases. The increase may be the result of the discharge of the Raut River into the Dniester, which introduces an additional amount of polluting organic substances to the Dniester waters. This, in turn, increases the pressure on biological self-purification processes and raises the proportion of chemical self-purification processes.

At the third sampling point in the Vadul lui Voda area, was observed a tendency towards restoring the initial properties of the aquatic environment, with a decrease in the intensity of chemical self-purification processes and an increase in biological processes.

The study found that over 10 years of monitoring the Dniester from Dubasari to Vadul lui Voda, the water quality was rated as classes II (Good) and I (High) based on the BOD_5 parameter. This evidence indicates that there were no significant physico-chemical or biological changes in water quality, and the concentrations of biodegradable pollutants did not impact the functioning of the aquatic ecosystem. The biodegradable compounds present in the water are native, as confirmed by the seasonal variations in BOD_5 and thiol values.

Furthermore, according to the BOD_5 and COD_{Cr} parameters, it was established that along the Dniester from Dubasari to Vadul lui Voda, the proportion of biodegradable substances in the total organic substances decreases from 23% to 13%. This indicates that the Dniester tributaries, Raut and Ichel rivers, predominantly bring non-biodegradable substances into the Dniester. These non-biodegradable compounds may be persistent, but determining their origin and assessing their impact on self-purification processes requires further research.

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