ECOLOGICAL POTENTIAL OF SURFACE WATERS IN NATURAL SCIENTIFIC RESERVE "LOWER PRUT"

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Abstract. According to the Regulation on monitoring and systematic evidence of the surface and groundwater status, the Beleu Lake is included in the network of surface waters state monitoring in the Republic of Moldova. The research results have marked a low value of the self-purification capacity for Beleu Lake water, between 0.12 and 0.19, which is of 1.2-2 times lower than those from Prut River (0.25), correlating positively with the values of BOD_5, COD-Cr and the time of biochemical oxidation of ammonium ions. The oxidation of ammonium into nitrite ($NH_4^+(NH_3) \rightarrow NO_2^-$) in the nitrification process in lake water (collected in November 2014) takes place about 25 days and the process $NO_2^- \rightarrow NO_3^-$ being more than 35 days. The period of nitrification is about 2 times higher than in lake water collected in 2015 and 2.8-3.0 times higher than those of the model with water from Prut River.

Keywords: Lake Beleu, self-purification capacity, nitrification process, BOD_5, COD-Cr.

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Introduction

The Republic of Moldova has three Wetlands of International Importance with total area of 94705 ha and became a member of the Ramsar Convention in June 2000, when the "Lower Prut Lakes" (19152.5 ha) was included in the List of Wetlands of international importance.

Scientific reservation "Lower Prut" is located at the South of republic between Prut River and village Slobozia Mare, South of Cahul city. It covers 1691 ha, including 312 ha of forest and Beleu Lake (10 km^2). In that zone there were registered 39 species of mammals, 5 being included in the Red Book of Moldova (RBM), 203 bird species (27 included RBM), 5 species of reptiles (2 included RBM), 9 amphibians (one included RBM) and 41 species of fish (6 included RBM) [1].

Beleu Lake and Manta water body (Rotunda, Dracele and Badelnic Lakes) represent some unique ecosystems. Both water bodies can be considered natural, or at least close to natural as floods characteristic [2].

Medium area of Beleu Lake is of 9.5 km^2, being one of the largest natural lakes in the Republic of Moldova with water volume of 8.39 million m^3. The length of the lake is of 5 km, width - 2 km, the depth average – 0.5-1.5 m and maximum - of 2.5 m. About 1/3 of the scientific reservation surface constitutes waters of Beleu Lake. Water reaches in the Beleu Lake by two arms that come together in one. The water level in the lake overflows and floods depends on spring and summer of the Danube and Prut Rivers.

A problem in the reservation is that oil extraction is done from the wells that are close to the strictly protected area of the reservation, about 200 m from aquatic bird nesting. Oil is extracted on a platform with an area of 40 m^2 completely surrounded by water [3].

Article 26 of the Law on State Protected Natural Areas, no. 1538 of 25.02.1998 [4] provides that in the scientific reserve prohibited activities that could lead to disruption of the natural evolution of natural processes, in particular: b) exploration and extraction of natural resources, except those of national importance (oil, natural gas), provided the special environmental protection set by the central authority with natural resource management and environmental protection.

Since oil extraction in Moldova takes place from wells, located near the protected area of the reserve "Lower Prut" [4], it is necessary to study the state of its environmental compounds according to Decision of Republic of Moldova Government No. 932 of 20.11.2013 [5] and EU Water Framework Directive (WFD, 2000/60/EC [6]).

So, Beleu Lake, in conformity with the Republic of Moldova Regulation on monitoring and systematic record of the status of surface and groundwater monitoring network is included in no. 52: Beleu natural Lake, Slobozia Mare, Cahul, 45° 35' 12.88" North, 28° 09' 09.65" East, Alt. 5. Monitoring and systematic evidence of surface waters state in the Republic of Moldova lies by the State Hydrometeorological Service in Activity Program which provides 4 times on year the evaluating the physical and chemical parameters of water quality in Beleu Lake [5].

Status of surface water quality in Beleu and Manta Lakes is present in reports of State Hydrometeorological Service, being analyzed the content of macro compounds, dissolved O_2, BOD, COD, petroleum products, anionic surfactants, nitrogen and phosphorus compounds, some heavy metals, etc. In accordance with these reports, during of 2009-2013 years the water quality of Beleu Lake can be attributed to class II of quality (clean) in 2009 and class III (moderately polluted)

in 2012-2013 [2]. However the analyses do not include the investigation of lakes water self-purification and nitrification process of ammonium ions, as similar previously studies for surface and small rivers water [7-9].

This study includes the common estimating with State Hydrometeorological Service of the chemical status of lake water based on measured concentrations of monitored parameters, for the first time determining the capacity of water self-purification and nitrification.

Experimental part

Water sampling was done according to the Guidelines for taking water from natural and artificial lakes [10]. The analyses were performed in three replicates to yield average values. The concentrations of anions and cations were determined using national standards [11]. The amounts of nitrogen compounds, phosphorus, sulphate ions, iron, were determined photometrically. Titrimetrically there were estimated alkalinity, chloride content, the amount of calcium and magnesium. The pH of the water was determined by potentiometric method [12]. The value of BOD_5 and COD-Cr provide information about oxygen content required for oxidation the content of organic matter from water [13,14]. Using gas chromatography it was determined the content of oil in lake water [15].

In order to establish the environmental status, the classification of water quality in the lake was done according to Governmental Decision no. 890 of 12.11.2013, Annex 1 [16]. Self-purification capacity was calculated by the ratio BOD_5: COD-Cr [15, 17]. The study of ammonium ions biochemical transformation in natural water of Beleu Lake was performed using laboratory modelling [18]. Water solutions obtained after adding ammonium ions were exposed to light (which excluded direct sunlight). Daily there were determined the concentration of NH_4^+, NO_2^-, NO_3^- ions and value of pH, the modelling tests being done at 20-22°C.

The correlation between nitrification time and indices that characterize the level of organic pollution (CCO-Cr, BOD_5, days-nitrification) from natural surface waters was performed using double correlative analysis method that enables recording and evaluation of concentration dependence of 2 chemical components of water. Lower $K_{0.05}$ of calculated values was considered statistically unsignificant [19].

In this study there was evaluated the physical-chemical composition of water collected from various points of Beleu Lake on 14.11.2014, 28.05.2015 and 20.08.2015.

Results and discussion

The results of physicochemical analyses performed during of 2009-2013 years show that the water quality of Beleu Lake, village Slobozia Mare, according to Water Pollution Index (WPI) is attributed to class II of quality (WPI = 0.78 - pure) in 2009 and class III (WPI = 1.21 - moderately polluted) in 2012. During of 2013 year the mineralization (about 500 mg/dm^3 of dissolved solids, attributed to class I of quality) did not exceed maximum allowable concentration (MAC) values. The content of dissolved oxygen has been ranged from 9.44 to 10.17 mg/dm^3 (class I of quality). Nitrite concentration was between 0.022 and 0.11 mg/dm^3 (1.7 MAC, class I-II of quality), oil products content was between 0.23 mg/dm^3 in 2013 and 0.24 mg/dm^3 in 2012 (4.6-4.8 MAC, class II-III of quality) [2, 20].

In water samples from the lake, assessed in this study (2014-2015 years), the concentration of chlorine ions was ranged between 26-36 mg/dm^3, ammonium ions in the range of 0 - 0.14 mg/dm^3, nitrates from 0 to 0.77 mg/dm^3, anionic surface active substances - 0.01 mg/dm^3, BOD_5 value from 2.29 to 2.62 mg/dm^{3}O and mineralization in the range of 195-490 mg/dm^3 that correspond to I class of surface water quality (Table 1).

Table 1

Physical-chemical composition and quality class of Beleu Lake water.

No.	*Parameter*		*2012*	*14.11.2014*		*27.05.2015*			*Quality class*
				Brooks					
			Village Slobozia Mare	*Rotaru -Manolescu*	*Popovca -Rotaru*	*Popovca -Rotaru*	*Rotaru -Manolescu*	*Mano-lescu*	
1	pH		8.33-8.68	8.47	8.48	8.8	8.18	8.3	II
2	Hardness, me/dm^3		3.2-8.9	4.6	4.8	2.9	4.1	3.7	I-II
3	BOD_5, mg/dm^3 O		2.34-3.63	2.52	2.62	2.4	2.29	2.45	I
4	COD-Cr, mg/dm^3 O		-	20.2	17.0	12.7	13.3	15.3	II-V
5	Suspensions		50-303	50	105	57	63	267	V->V
6	SO_4^{2-}		71.8-132	146	153	32.8	85.2	89.8	I-II
7	Cl^-		31.9-111	35.4	35.4	36.1	26.9	26.2	I
8	Mineralization		377-842	460	475	195	309	326	I
9	NH_4^+	mg/dm^3	0.07-0.83	0.14	0.06	0	0	0	I-III
10	NO_2^-		0-0.061	0.007	0.007	0.005	0.018	0.009	I-II
11	NO_3^-		0-4	0.65	0.77	0	0.77	0.72	I
12	P_{tot}		0.104-0.26	0.098	0.108	0.048	0.094	0.096	I-II
13	Petroleum products		0.05-0.24	0.09	0.07	0.09	0.1	0.3	I-III
14	Surface active substances		0-0.02	0.01	<0.01	0.01	0.01	0.01	I

According to pH values (8.18 to 8.8), hardness (2.9 to 4.8 me/dm^3), content of sulphates (32.8 to 153 mg/dm^3), concentration of nitrite (0.005 to 0.018 mg/dm^3) and of total phosphorus (0.048 to 0.108 mg/dm^3) in all sections, the lake water is attributed to class I-II of quality. The research results are indicated that the content of particles in suspension is varied from 50 mg/dm^3 (brook Rotaru-Manolescu) to 267 mg/dm^3 (brook Manolescu) which differ significantly between the majority of lake brooks and the Beleu Lake (brook Manolescu), where class of quality is V->V. According to the petroleum products concentration, the lake water in the brook Manolescu is attributed to class III, while in the other sampling points it is attributed to class of quality I-II.

The content of ammonium ions in lake water (section village Slobozia Mare) varied significantly in 2012 (from 0.07 to 0.83 mg/dm^3) with seasonal character, lower values being reported during April-September when nitrification process occurs intensively. In May of 2015 the concentration of nitrates and ammonium ions did not exceed MAC. According to concentrations of pollutants, the Beleu Lake water is attributed to class III-V of quality.

Analyzing chemical parameters of Beleu and Rotunda Lakes water (village Manta, May of 2015) it was found that the concentration of organic substances (COD-Cr) ranged from 10.6 (Rotunda Lake) to 28.4 mg/dm^{3}O, BOD_5 has been maximum – 3.17 mg/dm^{3}O (Beleu Lake). Water collected in different seasons, according to values of BOD_5 and COD-Cr, falling within class I-II of quality except Beleu Lake sample taken in spring, around oil drilling activity (class I-III of quality). Self-purification capacity of water, which is depending on the season, is also different in studied waters. Self-purification capacity of Prut River water is medium (0.26), being 1.2 to 4 times more than for Beleu Lake, which is worth between 0.04 (practically absence) and 0.24 (Table 2 and Figure 1).

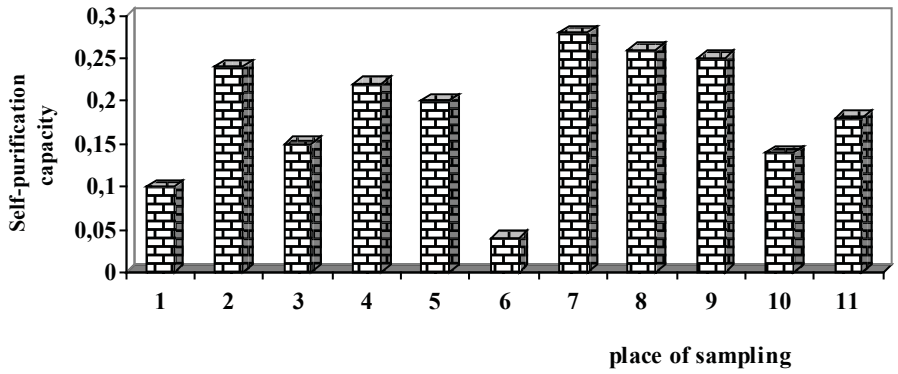


Figure 1. Self-purification capacity of water from Beleu and Rotunda Lakes compared to the Prut River (winter, spring, summer, 2015).
***Beleu Lake*: brooks Rotaru and Manolescu, near oil extraction taken in winter (1), spring (2), summer (3); brooks Popovca and Rotaru taken in winter (4), spring (5); brook Manolescu taken in spring (6), summer (7); village Slobozia Mare (8); Rounda Lake, village Manta (9).**
***Prut River*: village Valeni taken in spring (10), summer (11).**

Table 2

The concentration of organic matter and water quality class according to chemical and biochemical oxygen demand, 2015.

Water samples		*Season*	*COD-Cr*	*BOD_5*	*Quality class*
			mg/dm^3 O		
Beleu Lake	brooks Rotaru and Manolescu, near oil extraction	winter	17.26	1.77	I-II
		spring	28.4	1.31	I-III
		summer	22.0	3.01	I-II
	brooks Popovca and Rotaru	winter	12.2	3.02	I-II
		spring	16.08	2.44	I-II
	brook Manolescu	spring	13.8	3.02	I-II
		summer	14.9	2.66	I-II
	village Slobozia Mare	spring	15.7	3.17	I-II
Rotunda Lake	village Manta	spring	10.6	3.01	I-II
Prut River	village Valeni	spring	12.06	3.08	I-II
		summer	8.65	2.15	I

Nitrification of NH_4^+ ions in Beleu Lake water

Ions of nitrite (NO_2^-) and ammonium (NH_4^+) are present in the case of pollution of aquatic medium and are toxic to living organisms. For this reason in the laboratory conditions was modelled the biochemical oxidation of NH_4^+ ions in Beleu Lake water during the cold and warm period of years (2014 and 2015).

Inorganic compounds with nitrogen (NH_4^+, NH_3, NO_2^-, NO_3^-) are present actually in all natural waters. Their amount varies depending on the degree of pollution [7]. Ammonia and ammonium ions in natural waters are oxidized biochemically by 2 steps:

$$NH_4^+ (NH_3) + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O + 54.9 \text{ kcal } (\textit{Nitrosomonas}) \quad (1)$$

$$NO_2^- + O_2 \rightarrow 2\,NO_3^- + 18 \text{ kcal } (\textit{Nitrobacter}) \quad (2)$$

A lot of chemicals present in the water hinder biochemical processes in the environment. Previously, it was studied the influence of phenol, copper ions and of some pesticides and surfactants on the oxidation of ammonium ions in surface waters [8, 9].

The oxidation of ammonium into nitrite ($NH_4^+(NH_3) \rightarrow NO_2^-$) in Beleu Lake water (collected in November of 2014) takes place in 25 days (Figure 2a) and in 2015 – in 9-15 days (Figure 3a). The transformation of nitrite into nitrate (process $NO_2^- \rightarrow NO_3^-$) takes place more than 35 days (Figure 2b), being by 2 times higher than the period in lake water sampled in 2015 and by 2.8-3.0 times higher than those for model with water from the Prut River (Figure 3b).

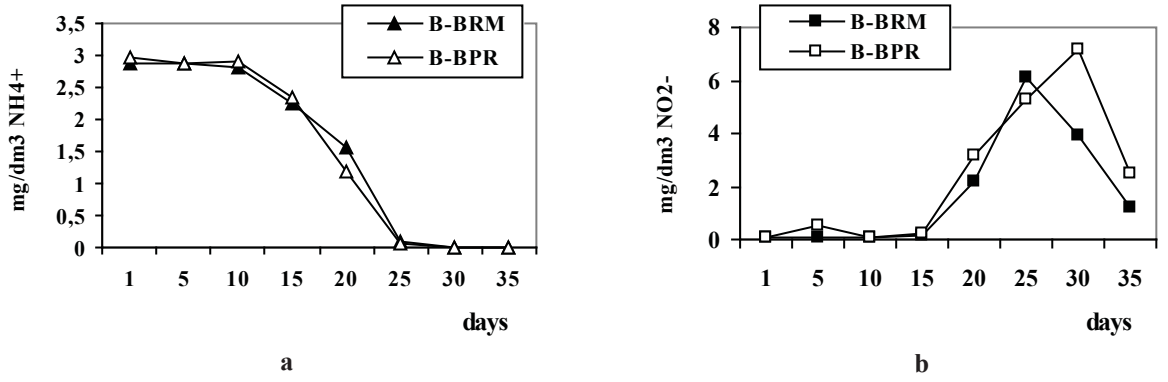


Figure 2. Dynamics of NH_4^+ ions concentration in the oxidation $NH_4^+ \rightarrow NO_2^-$ process (a) and of NO_2^- ions content in the oxidation step $NO_2^- \rightarrow NO_3^-$(b) in water samples taken from the Beleu Lake in autumn of 2014. B-BPR: brooks Popovca – Rotaru; B-BRM: brooks Rotaru – Manolescu.

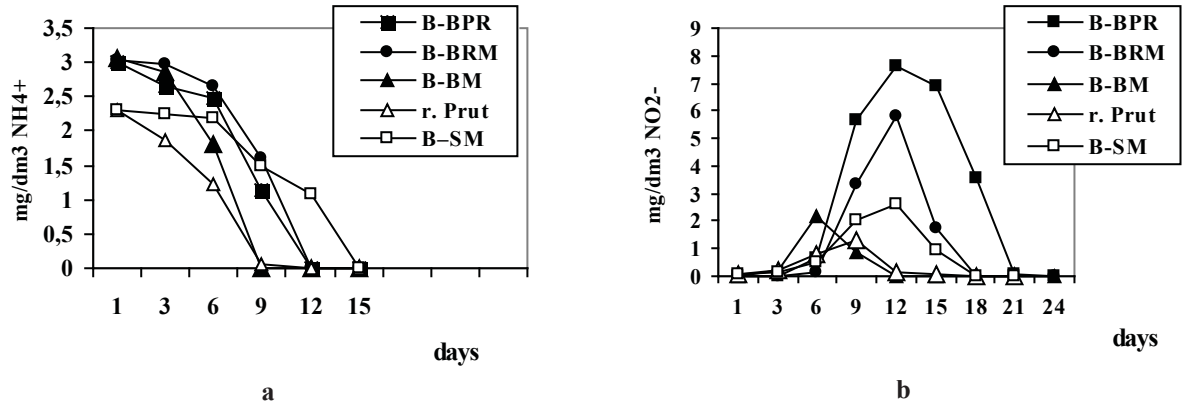
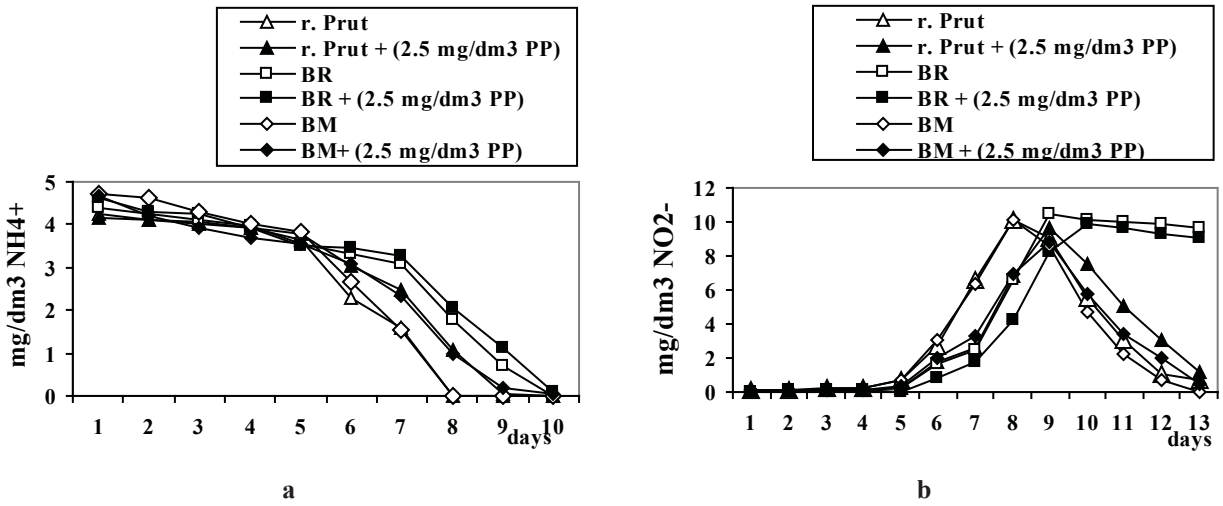


Figure 3. Dynamics of NH_4^+ ions concentration in the oxidation $NH_4^+ \rightarrow NO_2^-$ process (a) and of NO_2^- ions content in the oxidation step $NO_2^- \rightarrow NO_3^-$(b) in water samples taken from the Beleu Lake and Prut River (village Valeni) in summer of 2015.
***Beleu Lake*: B-BPR: brooks Popovca - Rotaru; B-BRM: brooks Rotaru - Manolescu; B-BM: brook Manolescu; B-SM: village Slobozia Mare.**

It is known that many chemicals affect the biochemical processes in natural waters [8,9,18]. Taking into account that oil extraction is done from the wells that are close to the protected area which include Beleu Lake, in laboratory conditions there was carried out the influence of petroleum products (PP) on nitrification of ammonium ions in water of Beleu Lake and Prut River (for comparison), samples collected in 20.08.2015. The amount of PP added was of 2.5 mg/dm^3, the permissible content discharged into natural water bodies [21].

The results of study show that in the water samples taken from Prut River and Beleu Lake, brook Manolescu (water entering from Prut into the lake) the oxidation of ammonium into nitrite ($NH_4^+ \rightarrow NO_2^-$) takes place 8 days. With 2 days longer it take place the process in the water out of the lake (brook Rotaru), including in the presence of the normative content of petroleum products (Figure 4a). Step II of nitrification ($NO_2^- \rightarrow NO_3^-$) in the samples from Prut River and Beleu Lake, brook Manolescu, including in the presence of PP, takes place 13 days. More obvious it is the influence of water composition (not PP) of Beleu Lake, brook Rotaru - out of the lake, on the process $NO_2^- \rightarrow NO_3^-$, which in 13 days only about 10% of NO_2^- have oxidized (Figure 4b). So, in the water out of Beleu Lake there are substances which determine a low self-purification capacity and diminish the nitrification process in water (Table 3).



a **b**

Figure 4. Dynamics of NH_4^+ ions concentration in $NH_4^+ \rightarrow NO_2^-$ step (a) and NO_2^- ions content in $NO_2^- \rightarrow NO_3^-$ step (b) in ammonium ions oxidation process in water samples taken from Prut River (village Valeni) and Beleu Lake in August of 2015.
***Beleu Lake*: BM - brook Manolescu; BR - brook Rotaru, out of the lake.**

Self-purification capacity has positive correlation trends for following values: BOD_5 ($y = 0.085x + 2.2833$, $r^2 = 0.2653$), COD-Cr ($y = 0.85x + 15.8$, $r^2 = 0.1167$) and period of NH_4^+ ion nitrification: $NH_4^+ \rightarrow NO_2^-$ step ($y = 1.5x + 8$, $r^2 = 0.75$) and $NO_2^- \rightarrow NO_3^-$ ($y = 4.5x + 8$, $r^2 = 0.9643$) (Figure 5).

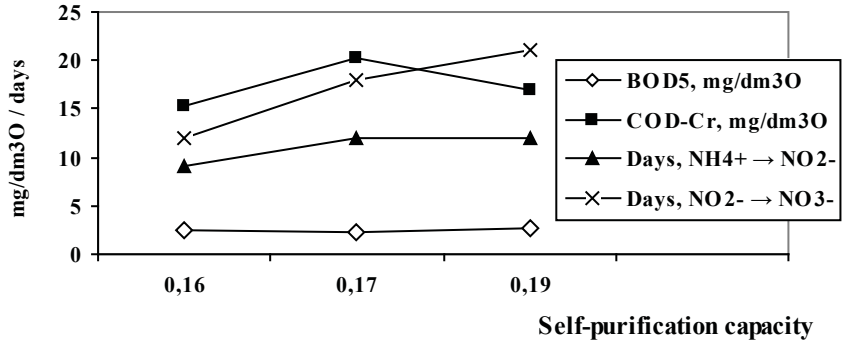


Figure 5. Correlation of self-purification capacity values to BOD_5 ($r^2 = 0.2653$), COD-Cr ($r^2 = 0.1167$) and period of NH_4^+ ion nitrification: $NH_4^+ \rightarrow NO_2^-$ stage ($r^2 = 0.75$) and $NO_2^- \rightarrow NO_3^-$ ($r^2 = 0.9643$).

So, it is outlines the influence of persistent organic pollutants and those degrading biochemical on the self-purification and nitrification of ammonium ions process in the water of Beleu Lake.

Based on information regarding the water quality of Beleu Lake, it is concluded that is necessary to create conditions to increase the self-purification capacity, given the multitude of biotic and abiotic factors, which determine the effectiveness of polluted natural waters improvements.

Conclusions

Values of self-purification capacity of the lake water are between 0.12 and 0.19 for Beleu Lake, which are by 1.2-2 times lower than the one for Prut River (0.25).

The values of BOD_5, COD-Cr and the time for biochemical oxidation of ammonium ions are positively correlated with self-purification capacity of water from Beleu Lake, confirming the existence of organic matter pollution.

Study shows that in water from Prut River and Beleu Lake, brook Manolescu (water entering from Prut River into the lake) the nitrification of ammonium ions, inclusive in the presence of petroleum products, took place 13 days, while in water sampled out of lake (brook Rotaru), in the absence and presence of PP, about 90% of NO_2^- were still unoxidized.

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