Assessment of surface water pollution indices from the urban ecosystem of Bălți

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DOI: 10.4316/GEOREVIEW.2023.01.02 **ABSTRACT:** At the current stage in the Republic of Moldova, surface waters are subject to anthropogenic pressures, with a high degree of pollution with organic substances, thus changing the chemical composition of the water. Regarding the administration of the sustainable management of water resources, the Republic of Moldova faces a series of challenges and long-term trends, both at the national and regional level. The present study aims to evaluate the state of surface water quality in the Bălți urban ecosystem, based on physical-chemical indicators, for which we used data from the third quarter, 2022. The proposed methodology includes taking water samples, chemical analysis under laboratory conditions, processing the results and classifying the quality status of water bodies according to the degree of pollution. The statistical data provided, confirmed a high degree of pollution with organic substances (chemical and biochemical oxygen demand, matters in suspension), the water bodies falling into quality class V (very polluted), except the Flămânda tributary, class I (very good). The highest degree of pollution with ammonium ions and nitrites was found in the Răut river, downstream from the sewage treatment plant. Thus, in 80% of the investigated water bodies, major deviations of the physical-chemical values from the natural fund of the water quality were found, the biological components, especially fish, are damaged and the water cannot be used for certain purposes. The present study reflects the current scenario of surface water quality in the Bălți urban area, thus helping policy planners and decision makers in the Republic of Moldova to adopt appropriate management and mitigation strategies for sustainable management of water resources.

KEY WORDS: water bodies, water quality class, urban ecosystem, degree of pollution, source of pollution, eutrophication.

1. Introduction

Under the conditions of urbanization and industrialization, contemporary civilization causes a worrying process of pollution of water resources and deterioration of the ecological balance. The

management of water resources is put in difficulty, both from the point of view of quantity and quality. The establishment of mechanisms for the protection of the state of waters is carried out through systematic monitoring, namely: supervision, forecasting, warning and intervention. In recent years, the organization of monitoring systems has required an integrated approach, where quality elements are correlated with quantity elements, at the hydrographic basin level, taking into account the cause-effect interdependencies, respectively point sources, diffuse sources of pollution, water quality in correlation with the pollution associated with sediments and suspended matter, the links of priority pollutants, target groups generating pollution. Not all pollutants pose the same risks to aquatic ecosystems, some being biodegradable. Water bodies are naturally able to transform and partially or completely remove biodegradable substances, thus ensuring the maintenance of ecological balance and water quality.

Flowing and standing waters are indispensable elements of nature that have determined the permanent formation and development of urban ecosystems. Today, waters shape the spatial planning of urban areas (Mateusz and Krzysztof, 2020). Historically, people preferred to live near rivers and lakes because of their safety, access to water for consumption, economic and agricultural purposes.

At present, water pollution is becoming more and more serious in cities has posed a threat to the safety of residents and has become a major obstacle to people's health and social development.

For the Republic of Moldova, environmental issues regarding water protection present a challenge and require policies and protection measures, the vulnerable situations of river waters being the subject of discussion at various national and international forums. The quality of water bodies in the Republic of Moldova, in general, is characterized by a high degree of class IV-V pollution, especially with organic substances, nutrients and a low oxygen content, which varies seasonally depending on the self-purification capacity, the source the main source of pollution being the discharge of untreated or insufficiently treated wastewater (Bulimaga et al, 2020; Raport anual, 2021). In the Republic of Moldova, standing water bodies located in urban areas correspond to quality class IV - V (polluted and very polluted). The process of eutrophication of water bodies is observed more and more frequently.

As an example of the excessive pollution of water resources, the Bâc River, which crosses the capital of the Republic of Moldova, Chișinău, is represented. The results of research by specialists in the field have shown that Bâc river water in the city of Chișinău maybe be characterized as polluted and very polluted (Raport anual, 2021). Insufficiently treated wastewater from the sewage treatment plant and meteoric water are the point sources of pollution of the water body with organic substances, nutrients. A total ecological disaster is attested, pollutant concentrations sometimes exceed 10 times the limit values for surface waters.

In European countries, the chemical pollution of surface waters is also a problem faced by the authorities in the field of environmental. Thus, at the European level, a case study was carried out by specialists in the field, which attests that 62% of water bodies would not be able to achieve a good chemical state of surface water quality (considering measured concentrations of 45 priority substances) (Posthuma et al, 2020). This is interpreted as a potential threat to aquatic ecosystems through direct exposures and/or exposures through secondary poisoning and/or a threat to human health.

According to national statistical office, Statistics Netherlands (CBS), in 2015, almost 40% of Dutch surface waters met the standards for good chemical status, compared to 2009 when this was still 70%. The decline was mainly caused by changes in the measurement programme and tightening of the standards. In 2015, standards were exceeded both for more substances and in more surface

waters. The most disturbing chemical substances in this compliance check are tributyltin, brominated diphenyl ethers, mercury, nickel and some polycyclic aromatic hydrocarbons (PAHs).

According to the report prepared by the specialists of the Environment Agency of Slovakia (Irena, 2016), in Slovenia, 98.7% of surface water bodies are in good chemical condition. The two water bodies are in poor chemical condition due to the excess of metals. In general, Slovenian surface waters are not loaded with priority substances in the water, but they are loaded with too high concentrations of mercury and brominated diphenylethers in fish. These are ubiquitous pollutants that are excessively present in biota both in Slovenia and in Europe. Compared to the previous assessment period (2009-2015), good ecological status is achieved by 9% fewer water bodies.

A stunning report released by the UK Environment Agency in 2022 (Fourth Report of Session, 2022), found that only 14% of English rivers were in good ecological status and no rivers were in good chemical status. From a chemical point of view, the phosphorus indicator remains the most important pollutant of water bodies. The UK Environment Agency shows that only 45% of rivers currently achieve good status for phosphorus. In the urban area, the sources of pollution are represented by sewage and wastewater (36%) and meteoric water (18%).

According to the Environmental Report developed by the Romanian National Water Administration, 2022, the chemical state of surface water bodies is mostly good, but there are also water bodies that do not reach good chemical state. By applying the evaluation criteria for the chemical state, in the period 2018 – 2020, a number of 622 monitored surface water bodies (rivers, natural and reservoir lakes, transitional waters, coastal waters) were evaluated. Thus, 95.82% of surface water bodies (596 water bodies) are in good chemical status and 4.18% in bad chemical status (A.N.A.R., 2020).

Under the pretext of anthropogenic pressures, Europe's waters are much cleaner than 25 years ago thanks to investments in waste water treatment systems. However, the WFD target for 2015 was met for only 53% of surface water bodies in Europe (Directive 2000/60/EC of the European Parliament). The others are still in a bad ecological state.

In conclusion, water resources are under increasing pressure, undergoing significant changes following centuries of human activity. They have caused environmental changes at the level of aquatic ecosystems, such as water pollution and eutrophication, loss of biodiversity, change in the natural flow regime, deterioration of the natural landscape. In order to continue to benefit from the vital services that aquatic ecosystems provide, we need to improve the way we use and manage water resources.

The necessary measures to be implemented in urban ecosystems consist first of all in improving the methods and technology of wastewater treatment. Very important attention must be paid to the management of urban rainwater, which during heavy rainfall or snowmelt, leads to the loading of water bodies with organic substances.

The main objective of this study is to determine the current state of the quality of water bodies in the Bălți urban ecosystem, by evaluating the physico-chemical parameters. Therefore, the main sources of chemical contamination of water bodies were highlighted. Determining the quality of water bodies according to the quality class is the key element for the prevention or elimination of chemical contamination and for the remediation of negative effects on aquatic ecosystems of local importance.

2. Study area

The bodies of water in the Bălți urban ecosystem are made up of permanent and intermittent watercourses. The waters are used for various purposes, irrigation, fish farming, recreation, etc. In the region, there is an advanced degradation of aquatic ecosystems, expressed by the reduction of flows, partial or total clogging, heavy pollution, drying during the warm period of the year, the drastic decrease or even the total disappearance of hydrobionts in rivers (Centrul Național de Mediu).

The Răut river represents the main body of water in the study area, being the largest tributary of the Dniester, and also the largest river that originates and flows entirely on the territory of Moldova. The Răut River has a length of 286 km, the surface of the basin is 7760 km². The Răut river basin occupies a considerable part of the Dniester Plateau and the Central Moldavian Plateau. The average flow in the study area is 1.46 m³/sec, the annual runoff volume is 46.2 million m³. In the Răut hydrographic basin, there are practically no natural lakes, and reservoirs occupy only 0.2 % of its total surface (Cazac et. al., 2007).

In the Bălți urban ecosystem, the Răut river crosses the city, with an average width of 3-5 m, an average depth of 0.4 m, abundantly populated with aquatic herbaceous plants, rushes and reeds. On the bottom of the river there are silt sediments and residues in the form of particles of organic origin, black in color, with a specific smell. Household waste is stored in some places in the protection area of the river, stormwater is discharged directly into the water body. This phenomenon can also be seen on the tributaries of the Răut river. The researched ponds are characterized by a high degree of eutrophication, a phenomenon that occurs during the summer, when nutrient concentrations increase at high temperatures.

The study area included 10 surface water quality control points located in the Bălți urban ecosystem:

- 1. Răuțel tributary;
- 2. Vânătorilor și Pescarilor pond;
- 3. Orășenesc pond;
- 4. Răut river, upstream of the city;
- 5. Copăceanca tributary;
- 6. Răut river, Locomotivelor street;
- 7. Flămânda tributary;
- 8. Dobruja tributary, Sorocii street;
- 9. Răut river, upstream of the sewage treatment plant (STP);
- 10. Răut river, downstream of the sewage treatment plant (STP).

The monitoring network was designed in such a way as to ensure a coherent and comprehensive general description of the chemical state of surface waters.

When selecting control points for surface water chemical monitoring, free, safe and permanent access was taken into account, as well as the ability to provide representative samples.

Scheme of the location of the water sampling points is represented in Figure 1.

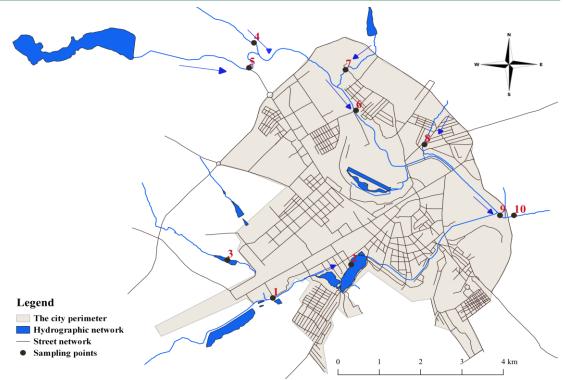


Figure 1 Scheme of water sampling points.

3. Methods

The water samples from water bodies located in the Bălți urban ecosystem, collected in the third quarter of 2022, served as the object of study. The monitoring period was characterized by a lack of atmospheric precipitation, the water level variation within the water bodies ranged from low to medium.

For each control point, 1500 – 5000 ml of water sample was sampling, depending on the analyzed quality parameter. Containers that do not produce losses through adsorption, volatilization or contamination with foreign substances were used. The beginning of the laboratory tests was carried out on the day of water sampling.

The general rules for taking surface water samples are contained in the standards SM SR ISO 5667-4:2007 (lakes) and SM EN ISO 5667-6:2017/A11:2020 (rivers), they describe and the techniques to be used so as not to alter the composition of the water during sampling.

During the sampling of the water, records are made regarding the observations related to the organoleptic properties: smell, turbidity and color. Water samples are preserved according to the type of analysis to be performed. The conservation method is provided in the water quality parameter analysis standard or in the ISO 5667-3:2018 guide. This procedure is performed when it is not possible to carry out laboratory tests within 24 hours.

For the laboratory analyzes, bidistilled water was used: Bidistilator Boeco Bidest 4 (Germany), Klab R 700CX refrigerator (Italy), was used for storage and preservation of water samples and chemical solutions.

In the water samples, 13 quality parameters were analyzed (Table 1).

Quality parameters		Unit	Analysis method	Used equipment
1.	Hydrogen ion concentration (pH)	unity pH	SM SR EN ISO 10523:2014 potentiometric method	Multiparameter Consort C3010 Belgium and Magnetic stirrer BOECO MSH 140, Germany
2.	Electrical conductivity	μS/cm	SM SR EN 27888:2005 potentiometric method	Multiparameter Consort C3010 Belgium and Magnetic stirrer BOECO MSH 140, Germany
2.	Mineralization (TDS)	mg/l	SM SR EN 27888:2005 potentiometric method	Multiparameter Consort C3010 Belgium and Magnetic stirrer BOECO MSH 140, Germany
3.	Matters in suspension (MS)	mg/l	SM STAS 6953:2007 gravimetric method	Oven electric SNOL 120/300, Lithuania and Balance ABJ 320- 4NM, Germany
4.	Chemical oxygen demand (COD-Cr)	mg/l	SM SR ISO 6060:2006 titrimetric method	WHM Witeg, Germany, 6-seat adjustable temperature mantle and reflow facility. Automatic burette, class A, 10 ml
5.	Biochemical oxygen demand after 5 days (BOD ₅)	mgO ₂ /I	SM EN ISO 5815-1:2020 titrimetric method	Incubator Selecta Prebatem 2000964, Spain. Automatic burette, class A, 25 ml
6.	Chloride (Cl ⁻)	mg/l	SM SR ISO 9297:2012 titrimetric method	Automatic burette, class A, 25 ml
7.	Ammoniacal nitrogen (N/NH₄⁺)	mg/l	GOST 4192-82 spectrometric method	Agilent Cary 60 spectrophotometer, USA
8.	Nitrite nitrogen (N/NO2 ⁻)	mg/l	SM SR EN 26777:2006/C91:2012 spectrometric method	Agilent Cary 60 spectrophotometer, USA
9.	Nitrate nitrogen (N/NO ₃ -)	mg/l	GOST 18826-73 spectrometric method	Agilent Cary 60 spectrophotometer, USA
10.	Total phosphorus (P _{total})	mg/l	SM SR EN ISO 6878:2011 spectrometric method	Agilent Cary 60 spectrophotometer, USA
11.	Total hardness	mmol/l	GOST 4151-72 titrimetric method	Automatic burette, class A, 25 ml
12.	Anionic Surfactants (MBAS)	mg/l	SM SR EN 903:2012 spectrometric method	Agilent Cary 60 spectrophotometer, USA
13.	Petroleum products (PP)	mg/l	PS-PP-01, ed.1/2021 gravimetric method	Adjustable temperature mantle (4) with distillation plant, ISOLAB, Germany

The laboratory tests were carried out by me personally within the accredited laboratory "Laboratorul Investigații de Mediu" S.R.L., which has the status of legal entities under private law,

and is legally responsible for its laboratory activities in accordance with the requirements of the reference document SM EN ISO/IEC 17025:2018.

Based on the results obtained, the assessment of surface water quality was carried out in accordance with the legislative framework regarding the characterization of surface waters in the Republic of Moldova. According to the Regulation on environmental quality requirements for surface appeal, approved by Government Decision no. 890 of 12.11.2013, environmental quality requirements for surface appeal and how to classify waters into five quality classes are established (Table 2).

Quality parameters		Quality class									
		l very good	ll good	III moderately polluted	IV polluted	V very polluted					
1.	рН, unity pH	6.5 - 8.5	6.5 - 9.0	6.5 - 9.0	6.5 - 9.0	<6.5 or >9.0					
2.	Mineralization / TDS, mg/l	<500	700	1000	1500	>2000					
3.	Matters in suspension (MS), mg/l	<10	10	25	50	>50					
4.	Chemical oxygen demand (COD), mg/l	<10	15	30	90	>90					
5.	Biochemical oxygen demand BOD5, mgO2/l	3	5	6	7	>7					
6.	Chloride (Cl ⁻), mg/l	<80	150	250	300	>300					
7.	Ammoniacal nitrogen (N/NH₄⁺), mg/l	0.2	0.4	0.8	3.1	>3.1					
8.	Nitrite nitrogen (N/NO2 ⁻), mg/	0.01	0.06	0.12	0.3	>0.3					
9.	Nitrate nitrogen (N/NO₃⁻), mg/l	1	3	5.6	11.3	>11.3					
10.	Total phosphorus (P _{total}), mg/l	0.1	0.2	0.4	1	>1					
11.	Total hardness, mmol/l	<4	6	9	15	>15					
12.	Petroleum products (PP), mg/l	0.05	0.1	0.5	1	>1					

Table 2 Environmental quality requirements for surface waters (HG 890/2013).

4. Results and discussion

The elaboration of the synthesis of the surface water quality in the Bălți urban ecosystem was based on the processing of the primary data, resulting from the physical-chemical analyzes of the water samples. The concentrations of surface water quality parameters are represented in Table 3. The data obtained characterize the chemical state of the quality of water bodies that provide a general and consecutive synthesis of the ecological state of water, as well as allow their classification in one of the 5 quality classes.

Quality Quality parameters Aquatic bodies investigated	pH, unity pH	Electrical conductivity µS/cm	Mineralization / TDS, mg/l	Chemical oxygen demand (COD), mg/l	Biochemical oxygen demand (BOD ₅), mgO ₂ /I	Matters in suspension (MS), mg/l	Chloride (Ci), mg/l	Ammoniacal nitrogen (N/NH $_4^+$), mg/l	Nitrite nitrogen (N/NO ₂ ⁻), mg/l	Nitrate nitrogen (N/NO ₃ ⁻), mg/l	Total phosphorus (P _{total}), mg/l	Total hardness, mmol/l	Anionic Surfactants (MBAS), mg/l	Petroleum products (PP), mg/l
1. Răuțel tributary	8.21	2220	1200	73.5	14.7	44.4	93.1	0.70	0.03	0.25	0.27	11.2	< 0.05	< 0.3
2. Vânătorilor și Pescarilor pond	8.86	2310	1230	121.9	24.5	55.4	99.8	0.49	0.006	0.20	0.17	8.7	< 0.05	< 0.3
3. Orășenesc pond	8.91	2790	1490	133.5	26.7	64.8	133.3	0.42	0.006	0.29	0.10	11.0	< 0.05	< 0.3
4. Răut river, upstream of the city	8.29	2430	1270	116.1	23.2	42.2	68.4	0.32	0.006	0.35	0.30	12.0	< 0.05	< 0.3
5. Copăceanca tributary	8.63	2340	1250	124.5	24.9	75.0	89.6	0.58	0.01	0.26	0.44	10.0	< 0.05	< 0.3
6. Răut river, Locomotivelor street	8.16	2300	1220	134.8	27.0	64.2	76.9	0.36	0.01	1.13	0.36	10.8	< 0.05	< 0.3
7. Flămânda tributary	8.17	456	243	< 30	1.2	< 10	26.1	0.05	0.004	0.78	0.03	4.0	< 0.05	< 0.3
8. Dobruja tributary, Sorocii street	7.80	779	518	77.4	17.5	70.4	43.7	0.74	0.18	3.86	0.26	6.0	0.06	< 0.3
9. Răut river, upstream of the sewage treatment plant (STP)	8.23	2200	1160	80.2	10.8	53.8	75.4	0.43	0.02	1.47	0.24	10.0	0.06	0.4
10. Răut river, downstream of the sewage treatment plant (STP)	7.27	1867	994	87.4	11.4	67.8	96.5	8.20	1.55	0.20	0.15	8.8	0.07	0.5

The concentration of hydrogen ions in natural waters has a major importance on chemical and biochemical processes. The *pH* values in natural waters depend on the process of dissociation and hydrolysis of some compounds which essentially depends on the concentration ratio of carbonic acid and its ions, upon the dissociation of which hydrogen ions are formed. The *pH* value of the investigated water bodies varies between 7.8 - 8.91, classifying them as medium basic waters. In the Răut river point, downstream of the Bălți wastewater treatment plant, the pH was found to be 7.27, the reason for the decrease in the value towards the neutral environment is the impact of the treated wastewater discharges.

According to the *electrical conductivity* quality parameter, a complex and indirect indicator of water quality, which indicates the totality of salts dissolved in water, increased concentrations were found in 8 control points, the Dobruja and Flămânda tributaries – medium *conductivity*. This parameter is not regulated in Government Decision no. 890/2013. In the bodies of water, an essential change in the chemical composition of the water can be seen, depending on the concentration and nature of the ions present. Water *mineralization* which is dependent on water conductivity, indicates the total concentration of the main ions (sum of anions and cations). According to the laboratory results, it can be seen in the table, in 8 control points - the water quality is class IV (polluted), the tributary Dobruja and Flămânda - class I (very good).

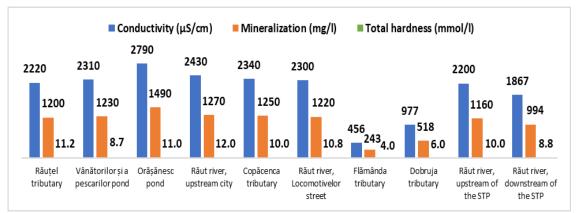


Figure 2 Conductivity and mineralization values.

A pollution with calcium and magnesium ions is found, the *total hardness* of the water being high in all control points (quality class IV), except for the Flămanda and Dobruja tributaries (quality class I). The *total hardness* of the waters depends on the degree of mineralization that can form insoluble salts (CaCO₃, CaSO₄), substances that present a significant risk of pollution of the aquatic environment.

The organic substances expressed by *chemical oxygen demand (COD)* and *biochemical oxygen demand (BOD₅)* of the investigated water bodies in the Bălți urban ecosystem, oscillated within the limits of 73.5 - 134.8mg/l, quality class IV- V (polluted and highly polluted), with the exception of the Flămânda tributary, where the lowest degree of pollution with organic substances was detected (*COD* < 30mg/l and *BOD*₅ 1.2mgO₂/l), quality class I (very good) and II (good). A correlation is observed between *COD* values which represent the amount of oxygen provided by an oxidizing chemical substance to break down biodegradable organic matter in water and *BOD*₅ which in turn expresses the amount of oxygen needed by microorganisms in biochemical processes, these two indexes being dependent on each other by another (Figure 3).

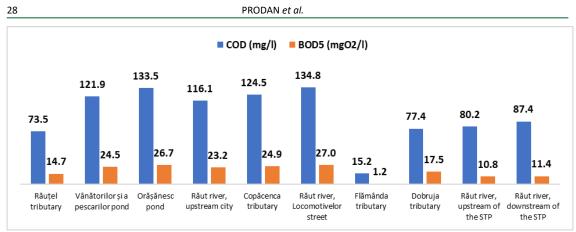


Figure 3 Concentrations of chemical and biochemical oxygen demand.

The high values of *COD* and *BOD*₅ in water bodies indicate the presence of a large amount of hard to degradable organic substances that produce functional changes in aquatic ecosystems. Considering also the fact that allochthonous microflora do not survive long in such conditions, it is difficult to predict the efficiency of self-purification processes.

The main polluting substances are dissolved or in suspension, these being inorganic (mineral salts) or organic (various organic substances), which can be toxic, inhibiting natural processes, favoring some natural processes causing unwanted effects for waters of surface. According to the *matters in suspension* quality parameter, the water bodies fall into the IV-V quality class (42.2 – 70.4 mg/l), with the exception of the Flămânda tributary, quality class I (< 10 mg/l) (Figure 4).

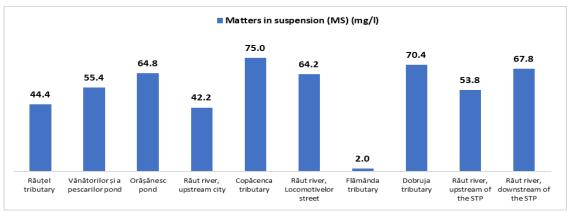


Figure 4 Concentrations of matters in suspension.

Matters in suspension prevents the absorption of oxygen at the surface of the water, causing habitat destruction for aquatic organisms. At the same time, oxygen is also necessary for the performance of aerobic self-purification processes, namely aerobic bacteria that oxidize organic substances, and which ultimately lead to self-purification of water.

Among the biogenic indicators (nutrients) *ammonia nitrogen* (N/NH₄⁺), *nitrite nitrogen* (N/NO₂⁻), *nitrate nitrogen* (N/NO₃⁻) and *total phosphorus* (P_{tot}), were determined in the water samples. The highest degree of nutrient pollution, especially N/NH₄⁺ and N/NO₂⁻ (class V, highly polluted) was found downstream of the Bălți wastewater treatment plant (8.2 mg/l and 1.55 mg/l) (Figure 5), the

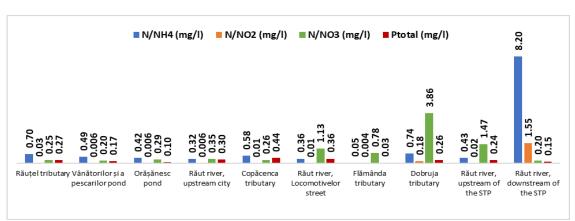


Figure 5 The nutrients concentrations.

Nutrient pollution in the urban environment also occurs in the case of heavy rains, the direct discharge of meteoric waters into water bodies, causes nutrient enrichment, especially with N/NH_4^+ .

The excess of nutrients in the studied ponds manifests itself most noticeably, through an abundant growth of aquatic plants, a process called eutrophication. The effect is very rapid on standing water quality, aquatic plants will continue to grow and multiply far beyond the amount needed to support the food web compared to flowing watercourses. The most harmful aquatic organisms are cyanobacteria (Şalaru et al, 2011), responsible for the production and release of toxins following extensive blooms.

Small concentrations of *anionic surfactants* and *petroleum products* were detected in the water of the Răut river, the control points downstream and upstream of the Bălți wastewater treatment plant.

5. Conclusion

points.

The quality status of the investigated surface water bodies in the Bălți urban ecosystem is subject to a significant risk of pollution with organic substances. Direct wastewater discharge and increased pollutant concentrations are among the most critical stressors that negatively affect the normal functioning of aquatic ecosystem services.

As a result, it can be concluded that the obtained experimental data indicate a high degree of surface water pollution (quality class IV - V) practically for all water bodies located in the Bălți urban ecosystem. The high degree of water pollution with organic substances (*COD* and *BOD*₅) is caused by the operation of industrial enterprises and anthropic communal household activities. For the waters of the Răut River, apart from the Bălți urban ecosystem, the main source of contamination with organic substances is meteoric waters and insufficiently treated waters from

the Bălți treatment plant. Especially during floods, meteoric waters is an uncontrolled source of nutrient pollution, especially in urbanized areas.

The quantity and quality of nutrient input to a body of water can have profound effects on the processes and structure of an ecosystem, ultimately altering water quality and influencing its biodiversity.

In the researched ponds, a high degree of eutrophication of the aquatic environment was found, which is one of the most serious consequences of human activities.

The existing activities and measures for managing the use of water resources and ecological management in the Bălți urban ecosystem, require new, reasoned and increased efforts in the context of the international requirements of sustainable development.

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