Revista de Chimie
https://revistadechimie.ro
https://doi.org/10.37358/Rev.Chim.1949

Case Study Regarding the Variation of the Qualitative Parameters of Wastewater

ANDREI RADU IOVA, CECILIA VIOLETA NEAGU*, DANIELA CRETU
University of Agronomic Sciences and Veterinary Medicine of Bucharest, 59 Marasti Blvd, 011464, Bucharest, Romania

Abstract: *Romania is making efforts in order to enforce the Directive concerning urban waste water treatment and was left behind by other member states. Starting from the premise that the lack of a proper treatment of wastewater can negatively influence the quality of the emissary in which they are discharged., we proposed that in this paper we analyze the main indicators of wastewater quality, identifying also the causes of water pollution. For this purpose, we followed the variation of five representative indicators of wastewater from Călărași Wastewater Treatment Plan: chemical oxygen consumption, biochemical oxygen consumption, total nitrogen, total phosphorus, suspended solids. The best results in purification were observed regarding the biochemical oxygen consumption (over 95%). The low temperature of wastewater at the entrance to the Wastewater Treatment Plant during winter leads to a difficult exploitation of the biological step and implicitly to the increase of the phosphorus and total nitrogen concentration in the effluent, which means a weak process of eutrophication in the emissary.*

Keywords*: emitter, treated water, quality indicator, urban environment, wastewater*

1.Introduction

Sustainable development links in a coherent framework the environment, social and economic policies, thus contributing to the enforcement of environment legislation and policies. It is somewhat early to draw solid conclusions about the impact on the rural development and the environment. In many cases, the information about their impact is missing, partly because some countries have adopted these only recently and partly because monitoring is deficient [1]. Ensuring compliance with environment legislation consists in all activities undertaken by public authorities in order to ensure that industries, farmers and other categories fulfill their obligations to protect water, air and nature and manage waste [2]. The municipal wastewater treatment plants of medium and high size have a specific flow of sludge treatment and conditioning [3].

According to the Accession Treaty, the deadline granted to Romania for ensuring the compliance with the Directive was the end of 2018. Taking into consideration the low compliance rates, the Commission decided to initiate an infringement procedure against Romania, based on the interim terms in 2013 and 2015 established in the Accession Treaty, in respect of compliance with collection and treatment requirements for the agglomerations that exceed 10,000 equivalent inhabitants [4]. The required investment to ensure proper collection and treatment of wastewater from the remaining agglomerations is estimated at 12 billion EUR. This figure is still high, despite the significant number of EU-funded projects. Other ongoing studies indicate greater investment needs. According to the latest report, it is estimated that the last projects will be finalized by 2027-2030, well beyond the deadlines of 2015 and 2018, established in the Accession Treaty of Romania [5]. Romania must finalize as soon as possible the projects for agglomerations that breach the obligations stipulated in the directive. In order to comply with the obligations, Romania needs to improve the methodology for setting priorities concerning the proposed water projects for EU funding and to accelerate their elaboration and implementation. Furthermore, revenues generated by water companies should ensure the sustainability of newly built infrastructure [2]. Romania is compelled to implement and comply with the stipulations of Directive 91/271/EEC on wastewater treatment [6].

**email: cecilianeagu2005@yahoo.com*

According to recent reports, only 2.5% of wastewater in Romania have been collected (8 agglomerations) in accordance with the Directive, and 6 agglomerations have fulfilled the conditions for secundary treatment and only 1 agglomeration has fulfilled the conditions for a thorough treatment [7]. To maintain the ecosystems integrity, environment improvement and keeping the water quality is crucial so that the wastewater can be purified and efficiently managed. Through wastewater treatment the loading into organic and inorganic pollutants, as well as into bacteria is reduced, clean water is obtained, in different degrees of purification, as well as a mixture of minimum substances called sludge. Insufficiently treated wastewater that has reached the emissary affects its capacity of self-purification and natural recovery of the biogeochemical balance. Poor treatment of wastewater makes the water that results from insufficient treatment impossible to be used in households, industry or even agriculture.

Wastewater treatment represents the physical, chemical, biological and bacteriological processes assembly, which reduces the loading in organic and inorganic pollutants as well as in bacteria, in order to protect the environment [8]. As a result of these procedures, clean water is obtained, in different degrees of purification, depending on the technologies and equipment used, as well as a mixture of substances called sludge [9]. The countless sources of water pollution and its limited ability to self-purify have led to the identification of the main pollutants becoming very important [10]. The real sources of pollution to be considered are those created by the activity of human beings.

Wastewater treatment plays a major role in protecting the environment [11], thus becoming a moral responsibility of each of us, and it plays a role in protecting public health, as poor sanitation of water discharged into the emitter is the main cause of surface water contamination, causing different types of diseases [12].

Worldwide, the most common problem related to the water quality is its pollution with nutrients, most often with nitrogen and phosphorus, coming mostly from the agricultural activities, industrial or human waste [13]. Nitrogen and phosphorus are essential nutrients for plants, but when their concentration exceeds a certain limit, they are considered pollutants and lead to excessive growth of aquatic plants, a process called eutrophication [14]. The elimination of phosphorus from wastewater is an environment necessity, as it stimulates the growth of aquatic plants and contributes to the eutrophication process in general [15]. Red mud proved to have positive influence on the removal of the phosphates from wastewater, to reduce the pollution potential [16].

The treatment enhancement post-physicochemical stage leads to the discharging of the biological stage of further loads, which means that the resulting treated water will have the necessary indicators that allow it to be used [17].

According to the Department for Sustainable Development of Romania, the current institutional structure is not suitable for implementing and monitoring of the Sustainable Development Goals (SDGs). A project to create special structures for the implementation of the SDGs must be designed and implemented. Romania national strategy for sustainable development is under review [11]. In 2018, a voluntary national evaluation on the implementation of the SDG was submitted to the UN [18].

The purpose of this paper is to analise the loading of wastewater with pollutants at their discharge into the emissary (Borcea branch) and into the Danube.

2.Materials and methods

The processed data found in this paper were provided by Călărași Environment Protection Agency, which monthly conducts analyzes of wastewater discharged into the emissary and by the Călărași Wastewater Treatment Plant, which daily collects samples and analyzes them in the laboratory. Călărași Wastewater Treatment Plant is an efficient one, upgraded after the implementation of the European project "Extension and rehabilitation of water supply and sewerage systems in Călărași County", from 2012, co-financed through the cohesion fund within the "Sectoral Operational Program" Environment "[19]. The Wastewater Treatment Plant belongs to ECOAQUA S.A. Călărași and includes the following components: mechanical filtration step, biological step, chemical treatment of wastewater, sludge treatment, installations for gas produced in the treatment plant. The published literature and the European

Commission Reports, the Directives on urban wastewater treatment respectively, Eurostat Reports, but also the locally drawn up Reports by the organizations where the study was conducted were used for description of technical processes, the requirements regarding the influence of environmental factors on the sustainable development, as well as the content of indicators that were determined following the data processing.

The main indicators of interest regarding waste water quality that have been analyzed in this work are: BOD_5 (biochemical oxygen consumption in water – determined by the electrochemical method, in mgO_2/L, according to SR EN 1899-22002), COD (chemical oxygen consumption – determined volumetrically, in mgO_2/L, according to SR ISO 6060-96), Ntot (total nitrogen – determined by combustion and IR spectroscopy, according to SR EN ISO 13395:2002), Ptot (total phosphorus – determined spectrophotometrically, according to SR EN 1189-2000), SS (suspended solids – determined gravimetrically, according to STAS 6953-81) [19]. They were compared with the maximum allowed value, according to NTPA001 [20].

Knowing the value of biochemical oxygen consumption at 5 days (BOD_5), it is extremely important to evaluate the degree of wastewater pollution, expressing the amount of biodegradable organic substances contained in that water. Dissolved oxygen is determined before and after 5 days of incubation at 20°C ± 1°C in complete darkness. A nitrification inhibitor is added [19].

Chemical oxygen consumption COD (potassium dichromate method) represents the mass concentration of oxygen equivalent to the amount of potassium dichromate consumed for the oxidation in acid medium of dissolved and suspended organic materials present in wastewater.

The method for determining the total nitrogen in wastewater is IR analysis - oxidative combustion. The gases in the combustion tube, after passing the detection in IR, for CO_2 analysis, are taken and introduced in a chemiluminescence detector, used for nitrogen analysis [19].

Phosphorus compounds are usually part of the composition of detergents and chemical fertilizers; as a result they can appear in wastewater resulting from household consumption, hotels, restaurants, laundries as well as in agricultural waters.

The suspended solids present in the wastewater are determined by filtering a determining volume of water through a fiber glass filter, followed by dissolving the salts present by washing the filter with distilled water. The filter solids are dried at a standard temperature of 100-105°C. The result obtained is the amount of dry material relative to the volume of water initially used [19].

3. Results and discussions

Although on national level progress has been made concerning the implementation of Directive 91/271/EEC regarding urban wastewater treatment, the increase of collection and treatment level was registered especially in urban areas in 2009-2015, so that the collection level has increased from approx. 51% in 2009 to 63.46% in 2015 and the treatment level has increased from approx. 37.5% in 2009 to 56.71% in 2015, in agglomerations greater than 2,000 equivalent inhabitants. However, in rural areas, the wastewater collection and treatment level is still very low. One of the causes is the low connection level of the population to the sewerage networks, having infrastructure without connected population [21]. In 2016, the population connected to the sewage systems represented 49.2% and the connection rate to the treatment plants was 47.8%, substantially below the level reached by other countries in the same area [7]. During 2009-2015 about 4.14 billion Euro was invested having different sources of financing (national and international) for the construction, rehabilitation and modernization of wastewater collection and treatment systems [18].

Although significant investments have been made regarding the sewerage network and the modernization of Călărași Wastewater Treatment Plant, wastewater is still a threat to public health and natural ecosystems, affecting the emitter capacity for self-purification and natural recovery of the biogeochemical balance [22, 23]. The weaknesses of wastewater collection and treatment system in Călărași county are represented by numerous damages in the sewerage system by break of collectors and collapses, and the population benefiting from the wastewater collection service represents 75% of the population of the municipality [19].

The main watercourse of Călărași county is the Danube river, Borcea branch - considered to be a special avifaunistic protection area [22]. The Danube and Borcea branch have now reached in Călărași municipality the limit of natural capacity for restoring the biogeochemical balance, therefore, a control and an efficient treatment of the discharged waters it is necessary. The spillage of wastewater, poorly purified, in surface waters, produces adverse effects on the natural phenomenon of self-purification [19].

For accurate assessment of wastewater discharge impact in Călărași municipality, both the influent of the wastewater and the resulting effluent from Călărași Wastewater Treatment Plant were chemically analyzed. During 2017-2018, the main indicators of wastewater quality and purified water presented the following values [19].

Table 1. Indicators of wastewater quality (influent and effluent) calarasi wastewater treatment plant during 2017-2018

Period	Parameters									
	BOD_5 (mg/L)		COD (mg/L)		N tot (mg/L)		P tot (mg/L)		SS (mg/L)	
	Infl.	Efl.	Infl.	Efl.	Infl.	Efl.	Infl.	Efl.	Infl.	Efl.
01.2017	103.93	11.24	252.84	32.00	39.17	8.04	2.99	1.08	179.61	28.03
02.2017	123.54	10.03	350.69	31.31	45.06	6.72	4.04	0.96	200.37	27.55
03.2017	147.98	9.24	361.94	30.58	49.93	5.21	4.44	0.98	193.81	30.32
04.2017	110.93	7.26	340.81	39.03	47.74	4.56	4.36	2.86	199.20	34.63
05.2017	132.89	6.43	328.76	38.93	47.52	4.98	5.08	1.46	204.16	28.16
06.2017	156.34	7.24	359.27	58.92	47.73	5.54	4.55	1.84	208.87	34.03
07.2017	102.33	6.34	313.86	33.44	47.88	5.16	4.75	1.75	194.68	26.90
08.2017	106.22	4.98	274.09	30.41	47.87	4.31	4.05	1.19	207.77	28.26
09.2017	112.08	5.15	287.87	34.00	44.52	3.94	4.22	0.59	200.53	22.87
10.2017	153.27	6.61	307.03	36.49	43.99	3.71	5.59	0.70	199.42	27.00
11.2017	155.73	4.78	252.20	38.60	39.19	5.30	4.24	0.59	193.30	25.33
12.2017	109.93	4.73	306.58	41.26	45.04	6.37	4.57	0.59	193.97	25.45
Annual average 2017	126.26	7.00	311.32	37.08	45.47	5.32	4.40	1.21	197.97	28.21
Purifying treatment degree 2017	**94.45%**		**88.08%**		**88.29%**		**72.5%**		**85.75%**	
	BOD_5 (mg/L)		COD (mg/L)		N tot (mg/L)		P tot (mg/L)		SS (mg/L)	
Period	Infl.	Efl.	Infl.	Efl.	Infl.	Efl.	Infl.	Efl.	Infl.	Efl.
01.2018	176.84	6.63	333.94	38.45	45.42	5.84	4.30	0.94	199.68	22.41
02.2018	178.98	10.12	326.36	47.76	43.06	16.45	4.10	1.13	187.04	27.29
03.2018	180.23	9.51	342.28	47.76	42.91	20.13	3.79	0.30	188.34	26.16
04.2018	169.44	6.62	279.24	36.62	38.20	7.26	4.30	0.32	201.31	30.66
05.2018	157.59	5.58	305.03	30.80	36.05	7.94	4.58	0.59	193.89	30.55
06.2018	148.70	5.37	307.31	43.51	41.80	9.00	4.50	0.46	197.45	26.96
07.2018	150.11	5.77	279.73	34.18	40.80	9.03	4.42	0.66	207.52	31.52
08.2018	139.81	3.22	320.52	38.06	50,01	10.60	5.12	2.55	205.78	25.79
09.2018	145.90	4.31	268.08	37.76	46.41	8.17	5.02	1.79	199.02	24.26
10.2018	161.35	5.03	277.32	40.18	39.88	9.95	4.97	1.93	222.25	23.19
11.2018	199.01	4.79	278.93	31.52	37.94	7.95	4.85	1.40	197.03	23.23
12.2018	182.56	4.55	241.96	26.50	32.09	6.34	4.79	1.82	195.77	22.77
Annual average 2018	125.05	5.95	296.72	37.75	41.21	9.88	4.56	1.15	199.59	26.23
Purifying treatment degree 2018	**95.24%**		**87.27%**		**76.02%**		**74.78%**		**86.85%**	

Source: Data from Călărași Wastewater Treatment Plant

We observe from Table 1 that during the two analyzed years, the efficiency of treatment plant in terms of purifying treatment degree of main indicators is placed between 72.5% (Ptot value in 2017) and 95.24% (BOD_5 value in 2017). In both years of study, the lowest level of purification is phosphorus (72.5%, respectively 74.78%), whilst the highest percentage is biochemical oxygen consumption (94.45% and 95.24% respectively).

The BOD_5 variation from water discharged into the emissary during 2017-2018 are presented in the Figure 1.

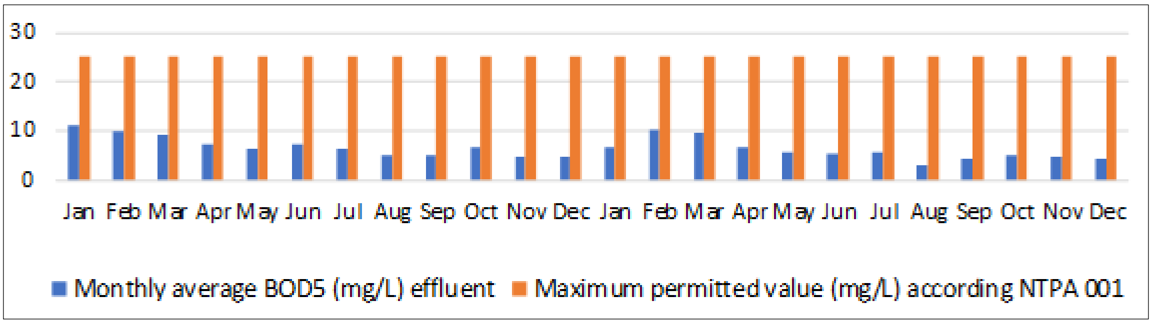

Figure 1. Variation of BOD_5 discharged in the emissary during 2017-2018, Calarasi Wastewater Treatment Plant. Source: elaborated by the authors

According to data in Figure 1, it can be observed that the highest amount of BOD_5 effluent was in January 2017 (11.24 mg/L), followed by February 2018 (10.12 mg/L). The variation of the biochemical oxygen consumption from one month to the other was due mainly to the climatic conditions or the recorded influential flow. However, throughout the studied period, we note that the values of the biochemical oxygen consumption of the purified water were much lower than the maximum value allowed by NTPA001, namely 25 mg/L [20].

In case of chemical consumption of effluent oxygen in the emissary (COD), as we observe in Figure 2, during 2017-2018 it`s values fluctuated, the highest value being registered in June 2017, that is 58, 92 mg/L, but this is well below the limit imposed by NTPA001 (125 mg/L) [20].

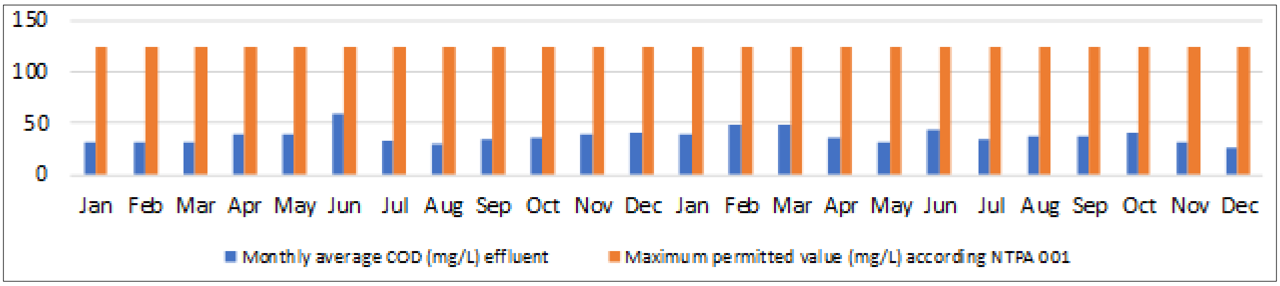

Figure 2. Variation of COD discharged in the emissary during 2017-2018, Calarasi Wastewater Treatment Plant. Source: elaborated by the authors

In Figure 3 we observe that during the studied period, the total nitrogen values discharged in the emissary exceeded the maximum allowed value according to NTPA001 (15 mg/L) [20] in February and March 2018 with 1.45 mg/L (9.66%) respectively 5.13 mg/L (34.2%). This fact is due to the low temperature of the waste water at the entrance to the treatment plant during the winter season (minimum temperature of 4^0C, average temperature of 7^0C) leading to a difficult exploitation of the biological step, the decrease of biological processes speed, the decrease of biodegradation efficiency of the organic compounds and implicitly by increasing the concentration of nitrogen and effluent compounds.

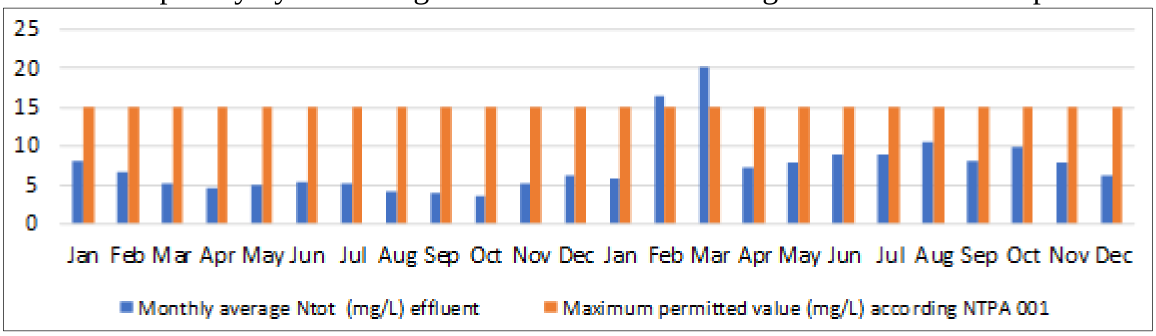

Figure 3. Variation of Ntot disharged in the emissary during 2017-2018, Calarasi Wastewater Treatment Plant. Source: elaborated by the authors

According to Figure 4 the amount of total phosphorus discharged into the emissary during the analyzed period exceeds the maximum allowed value according to NTPA001 of 2mg/L [20] in April 2017, with 0.86mg/L (43%) and August 2018, with 0.55mg/L (27.5%). The increased values dated April 2017 are due to climatic conditions (heavy rains and temperature fluctuations, the sudden passage from unusually high temperatures in February and in the first decade of March with maximum up to 15-23 degrees, during cold period, caused the activity of the microorganisms to be disturbed and no denitrification) or the recorded influential flow. The increased values dated August 2018 are due to water consumption increase, implicitly to influential flow increase, but concentration of wastewater was lower, thus the microorganisms did not have enough consumption matter, therefore the biological process of phosphorus removal was negatively influenced.

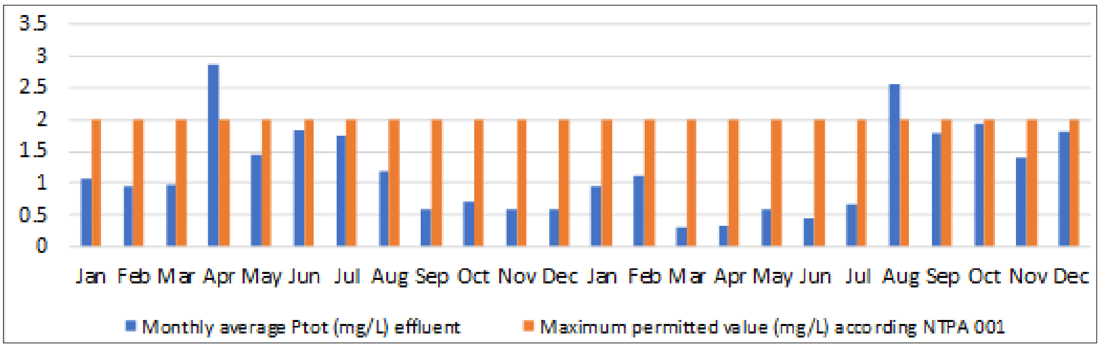

Figure 4. Variation of Ptot discharged in the emissary during 2017-2018, Calarasi Wastewater Treatment Plant. Source: elaborated by the authors

The suspended solids released in the emissary during 2017-2018 have oscillating values, the highest level being registered in April 2017 (34.63 mg/L), (Figure 5), but it falls within the maximum allowed value according to NTPA001 - of 35 mg/L [20].

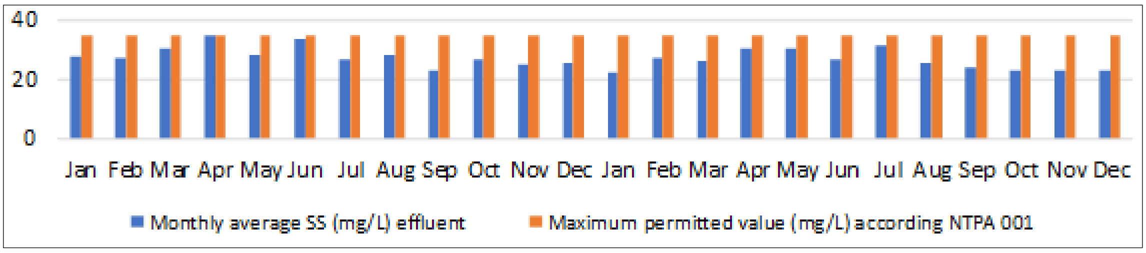

Figure 5. Variation of suspended solid discharged in the emissary during 2017-2018, Calarasi Wastewater Treatment Plant**.** Source: elaborated by the authors

4. Conclusions

Urban environment actvities are sources of pollution for all environment factors, so these activities must be controlled and managed in order to minimize the impact on the environment. The environment factors air, water, soil, flora, fauna continue to suffer under the impact of human activity and important quantitative and qualitative changes.

Based on the analyzes conducted on the main indicators of water quality discharged in the emissary from Călărași Wastewater Treatment Plant, the following can be concluded:

In 2017, the actual load of the station influencer is lower than the projected one, as follows:

-BOD_5 with 54%;
-COD with 24%;
-Total nitrogen (Ntot) with 1%;
-Total phosphorus (Ptot) with 37%;
-Suspended solid substances (SS) with 38%.

In 2018, the actual load of the station influencer is lower than the projected one, as follows:

-BOD_5 with 55%;
-COD with 28%;
-Total nitrogen (Ntot) with 10%;
-Total phosphorus (Ptot) by 35%;
-Suspended solid substances (SS) with 38%.

In winter, the low temperatures lead to the decrease of efficiency of organic compounds bio-degradation, meaning an increase in the concentration of nitrogen in the water discharged in Borcea branch.

The difficult exploitation of the biological step during cold periods results in a lower efficiency in removing phosphorus and total nitrogen, this bringing nutrients into the emissary and causing a process of eutrophication, much smaller than the previous period (the quantities reached in the emissary they are big).

From the evolution of the main analyzed indicators, it is observed the decrease of the content of organic substances and of the water eutrophication agents (total phosphorus and total nitrogen), their values being closer and closer to the norms required by the legislation in force.

The quality indicators of wastewater when entering the plant fall within the limits imposed regarding the quality of the wastewater discharged into the sewage network or directly in the treatment plant.

The quality indicators of wastewater discharged into the natural stream fall within the limits imposed by the regulations in force, NTPA 001 - suspensions respectively, BOD_5, COD, total phosphorus, total nitrogen.

The efficiency of treatment plant, analyzed for the 5 indicators is good, varying between 72-95%.

In order to solve the problems identified within Calarasi Wastewater Treatment Plant, we propose: ensuring optimal operating conditions during cold periods; ensuring the energy needed to raise the water temperature, to be done with the help of heating installations using unconventional energy sources: heat pumps, solar energy.

References

1. TUDOR, V., MARIN, A., ZAMFIR-VÂȘCĂ, D., MICU, M.M., SMEDESCU, D.I., The Influence of the Plastic Bags on the Environment, *Mater. Plast.*, **55**(4), 2018, 595-599. https://www.revmaterialeplastice.ro/Articles.asp?ID=5081
2.***The National Strategy for Sustainable Development of Romania 2030- https://www.edu.ro/sites/default/files/Strategia-nationala-pentru-dezvoltarea-durabila-a-Rom%C3%A2niei-2030.pdf (accessed on 12.01.2020)
3. ȘTEFĂNESCU, M., DINU, L.M., BUMBAC, C., Ultrasonic Alkaline Pretreatment of Biological Activated Sludge from Wastewater Treatment Plants, *Rev. Chim.*, **70**(1), 2019, 301-303. https://revistadechimie.ro/Articles.asp?ID=6904
4. ***https://ec.europa.eu/romania/news/2016_2211_planul_ue_dezvoltare_durabila_ro (accessed on 11.01.2020)
5. *** Law no. 292/2018 on the evaluation of the impact of certain public and private projects on the environment, adopted and published on 10.12.2018 in the Official Gazette of Romania (The Official Gazette no. 1043, Part I)
6. ***Directive 91/271/EEC, http://eurlex.europa.eu/LexUriServ/ LexUriServ.do?uri= CELEX:32000L0059:EN:HTML (accessed on 12.01.2021)
7. ***Report Eurostat, May 2017, Current state of achievement of sustainable development objectives by EU and member states
8. DIMA, M. – Urban wastewater treatment, 2005, Tehnopress Publishing, p.65.
9. MANOLACHE, L., Poison in water, The Scientific and Encyclopedic Publishing, Bucharest, 2003, p.17

10. ***The European Commission - The evaluation of application of environment policies. COUNTRY REPORT. ROMÂNIA, Brussels, 4.4.2019 SWD (2019)
11. ***The European Commission - The ninth report on the state of application programmes foreseen by the Directive on urban residual water treatment (COM(2017) 749 and the working document of the Commission services accompanying the report (SWD(2017) 445.
12. OPREAN, L., Water – Fundamental source of sustainable development, vol. I, Bucharest, The Romanian Academy Publishing, 2012, p.67
13. POPA, D., Water – fundamental resource of sustainable development. Unconventional methods and techniques for water treatment and purification; Water resources protection within the concept of sustainable development, the Academy Publishing, 2011, p.56.
14. ŞCHIOPU, D. et al., Ecology and environment protection, „Ion Ionescu de la Brad" Publishing, 2002, p.164.
15. NEGREA, A., PODE V., NEGREA, P., IOVI, A., LUPA, L., CIOPEC, M., MOȘOARCĂ, G. – Studies on the elimination process by precipitation-coagulation of phosphate ion. Process modeling, *Rev. Chim.*, **58**(10), 2007, 999.
https://www.revistadechimie.ro/pdf/NEGREA.pdf
16. CUCIUREANU, A., CERNICA, G., STANESCU, B. A., IONESCU, I. A., Approaches Regarding Red Mud Valorization for a Green Future and Sustainable Environment, *Rev. Chim.*, **71**(1), 2020, 56.
https://revistadechimie.ro/pdf/7%20CUCIUREANU%201%2020.pdf
17. PANAITESCU C., STOICA M. E., Enhancing of COD Treatment in the Physico-chemical Stage of Refinery Wastewater Treatment Plants, *Rev. Chim.*, **66**(5), 2015, p.731.
https://revistadechimie.ro/pdf/PANAITESCU%20C.pdf%205%2015.pdf
18. ***The European Commission-„EU actions in order to improve the compliance with the environment legislation and environment governance", COM (2018)10, as well as in the working document of the Commission services, SWD (2018)10.
19. ***Călărași Wastewater Treatment Plant (database).
20. ***NTPA 001/2005, GD 188/ 20.03.2002 for the approval of some norms on the discharge conditions in the aquatic area of wastewater, modified and completed by GD 352/11.05.2005 (M.O. nr. 398, part I, 11.05.2005)
21. *** The updated National Management Plan related to the National Part of International Danube river Basin, A.N.A.R., 2016
22. ***Report on the state of the environment factors in Călăraşi in 2017. www.apmcl.ro – Călăraşi Environment Protection Agency.
23. *** Report on the state of the environment factors in Călăraşi in 2018. www.apmcl.ro – Călăraşi Environment Protection Agency.

Manuscript received: 22.09.2020