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STUDIES ON THE QUALITY OF THE DANUBE IN GIURGIU AREA

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Abstract
The Danube river basin collects water from 19 continental European countries, covering an area of 801,463 km2 (according to ICPDR), and making it the most international river basin in the world. Giurgiu Environmental Protection Agency monitors water quality quarterly and the quality of sediment annually, taken from the sectors corresponding to kilometers 502, 511 and 520. The research in this paper is part of this monitoring program. The present work "Studies on the quality of the Danube in Giurgiu area", aims to achieve the following objectives: Determining the structure of phytoplankton biocenosis; Determining the dynamics of the seasonal variation of the physical-chemical parameters in the studied period; Correlation of the variation dynamics of phytoplankton density with the main physical-chemical parameters; Determining the ecological status of water quality in the studied sector. Both sampling areas are characterized by a good ecological status - the values of biological, hydro-morphological and physical-chemical elements have moderate deviations from the values characteristic of unaltered (reference) areas or minor anthropogenic alterations. In the future, it is recommended to monitor the Danube River in order to prevent possible sources of negative anthropogenic impact and to monitor it with an annual frequency in order to make sure that the ecological quality status is maintained at least at the current level.

Keywords: environmental quality, Danube, phyto and zoobenthic structure

1. INTRODUCTION

The European legal framework of waters is based on the Water Framework Directive (2000/60/EC) which is the fundamental European directive of waters. It promotes the concept of river basin management, and establishes a framework for water protection, mainly by preventing damage, the conservation and improvement of aquatic ecosystems, the promotion of the long-term sustainable use of water resources, as well as the gradual decrease of groundwater pollution and the prevention of pollution.

Romania has an area of 238,397 km^2, (approx. 6% of the UE area – ranking 9th) and a resident population of 19,328,838 inhabitants (January 1st, 2020, according to official National Institute of Statistics data), thus holding approx. 4% of the EU population, ranking 7th. It is mentioned that, out of the total surface of the country, there are 232,193 km^2 inside the Danube basin (representing 97.4% of the total country); according to the data mentioned above, Romania holds 29% of the surface and 21.7% of the population of the Danube basin.

The Danube river basin collects water from 19 continental European countries, covering an area of 801,463 km^2 (according to ICPDR), and making it the most international river basin in the world.

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Approximately one third of the surface of the river basin and one third of the length of the river are on the Romanian territory (fig.1.). Also, due to the influence of the Danube on the morphology of the shore and the state of the waters in the Danube river, the Romanian coastal waters as well as the tributary basins flowing into the Black Sea (with an area of about 5,198 km^2) were included thus forming the Danube River, in accordance with the provisions of the Water Framework Directive. In this regard, the entire Romanian territory is included in the Danube River Basin District.

Figure 1. Danube River Hydrographic District (https://www.usgs.gov/products/maps)

The Danube River, with a length of 2,857 km (of which 1,076 km on the Romanian territory, about 37.7% of the total length) and an average multi-annual flow at the entrance to the delta of approximately 6,500 m^3/s is the second river in Europe (after the Volga). It is the collector and emissary to the Black Sea of all discharges from upstream riparian countries, thus affecting both the water quality of the Danube Delta, and the coastal area of the Black Sea.

The Danube Delta, with a total area of 6,750 km^2 (of which 82% in Romania and 18% in Ukraine, according to ICPDR data), the youngest geographical unit in Romania and the second largest deltaic unit in Europe (after the Volga River Delta), is a unique complex of ecosystems (with over 5,200 species), consisting of 3 large deltaic units (Letea, Caraorman and Dranov) and 3 arms (Chilia, Sulina and Sf. Gheorghe) to which are added deltaic lakes, canals, brooks, backwaters and periboina (natural depressions produced by sea waves) that connect both the lakes and the lakes and the main arms or the sea.

The hydrographic network drains the relief divided into main units: mountains - 31%, hills and plateaus - 36% and plains - 33%. The climate is temperate-continental, the average multiannual air temperature varies between +11°C on the coast and -4°C in the Carpathian Mountains, and the average multiannual rainfall varies between 400 mm/year in Dobrogea and 1,400 mm/year on the high peaks of the Carpathians. The average specific runoff varies between less than 1 $l/s \times km^2$ in the Romanian Plain and 40 $l/s \times km^2$ on the ridges of the Southern Carpathians.

Water management in Romania has a long tradition starting with 1924, and the foundations of water management on river basins were laid in 1975, establishing the Water Directives for the following

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basins/hydrographic areas: Someş - Tisa, Crişuri, Mureş, Banat, Jiu, Olt, Argeş - Vedea, Buzău - Ialomiţa, Siret, Prut - Bârlad, Danube River, Danube Delta SH Dobrogea and coastal waters.

Water Law no. 107/1996 with its subsequent amendments and completions defined at national level the following river basins/ hydrographic areas and drew up the Management Plans for: Someș - Tisa; Crisuri; Mureș; Banat; Jiu; Olt; Argeș - Vedea; Buzau - Ialomita; Siret; Prut - Bârlad; Danube, Danube Delta, Dobrogea (including coastal waters).

The water resources in Giurgiu County are freshwater sources and consist of rivers, natural and artificial lakes, the Danube River and groundwater. The most important watercourse in Giurgiu County is the Danube River that crosses Giurgiu on a distance of 76 km, from Pietrişu - km 527 to Greaca - km 452.

Giurgiu is the county seat of the county with the same name, Muntenia, Romania. It is a river port and a border point with Bulgaria, with a total area of 5,388 hectares. Giurgiu is located on the southern edge of the country and the county, on the left bank of the Danube, in a swampy area 65 km south of the capital Bucharest, on the border with Ruse area in Bulgaria. The town is located both in the plain of Buraz and in the Danube Meadow and has a predominantly sandy soil.

The Danube in the area of Giurgiu County is part of the Lower Danube and the length of the Danube river basin of Giurgiu County is 122 km. The Port of Giurgiu is a medium-sized Danube port.

The national navigable water course, according to the Port of Giurgiu is:

• Danube - left bank, km 479 - km 482, on a width of 150 m.
• Danube - left bank, km 497 - km 502, on a width of 150 m.
• Ara arm
• Dunărica arm

The river provides the Port of Giurgiu connections with 8 riparian countries in Europe, but it is also an important link for traffic to the Balkan countries and the Middle East. It is one of the Danube ports that allows river cruise ships to dock, which is why, many tourists have stopped here lately.

Giurgiu Environmental Protection Agency monitors water quality quarterly and the quality of sediment annually, taken from the sectors corresponding to kilometers 502, 511 and 520. The research in this paper is part of this monitoring program.

The present work "Studies on the quality of the Danube in Giurgiu area", aims to achieve the following objectives:

- Determining the structure of phytoplankton biocenosis;
- Determining the dynamics of the seasonal variation of the physical-chemical parameters in the studied period;
- Correlation of the variation dynamics of phytoplankton density with the main physical-chemical parameters;
- Determining the ecological status of water quality in the studied sector.

2. MATERIALS AND METHODS

Water test involves a set of laboratory methods and techniques specific to physics, chemistry and biology. The parameters to be determined are established according to the purpose of the analysis. Getting the most accurate results is in compliance with rules on the collection, storage, transport and processing of samples.

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- For this paper, research was conducted twice a month between May 2019 and March 2020. Both the sampling and the physical-chemical and biological tests were carried out twice a month, within the current water quality monitoring program from two major points of the Danube in Giurgiu, namely: Km 502 - Slobozia and Km 511, each sample containing 1000 ml of water;

- Both the sampling and the performance of the actual tests were done in compliance with the official norms in force provided in: *"The General guide for sampling techniques SR-ISO 5667-1/1998" and "The Guide for sampling water from natural and artificial lakes SR-ISO 5667-4/2000"*, in the case of physical-chemical parameters; *STAS 6329-90*, for the study of the structure and dynamics of phytoplankton. The samples were transported to the laboratory in refrigerated boxes at a temperature of 4°C, thus avoiding their alteration.
- ***The laboratory tests for determining the values of chemical indicators*** did not require special preparation except for those necessary to determine the oxygen dissolved in water, which was previously fixed in the field and then determined in the laboratory by iodometric method (based on oxidation of divalent manganese hydroxide in trivalent manganese hydroxide, by molecular oxygen dissolved in water, in a highly alkaline environment).
- The rest of physical-chemical tests (water pH, biochemical oxygen consumption, chemical oxygen consumption, nutrient concentrations - total/mineral nitrogen and total phosphorus, concentrations of total suspended matter) were carried out in the laboratory, without the samples to require some processing.
- The following standardized working protocols were used for the laboratory tests: *SR ISO 7150-1* (to determine the concentration of ammonium ions), *SR EN 26777/2002* (to determine the concentration of nitrite ions), *SR ISO 7890-3/2003* (to determine the concentration of nitrogen ions concentration), *ISO 6878/2004* (to determine the concentration of total phosphorus), *SR ISO 10523-09/09* (electrometric method for pH determination) and STAS 6953-81 (method by which insoluble substances in wastewater could be separated by filtration, centrifugation or sedimentation; total solid matter with the two components - suspended solid matter and dissolved solid matter (<1 μm), have important characteristics to establish the efficiency of the treatment process, in different stages). Biochemical oxygen consumption (**BOC_5**) was calculated by the difference between dissolved oxygen concentrations in the samples tested at the beginning and end of the 5 day incubation period.

3. RESULTS AND DISCUSSIONS

Determining factors and pressures affecting water quality are represented by pollutants discharged into surface waters and by discharges of wastewater from economic operators and sewerage networks. The wastewater discharged in Giurgiu County consists of domestic and industrial wastewater.

Wastewater quality is monitored by S.G.A. Giurgiu by taking samples and physical-chemical tests from the following sources of contamination in the county.

The total volume of wastewater discharged through activities (thousand m^3) in Giurgiu County during May 2019-March 2020 is shown in table 1 and table 2.

The state of the water was monitored through microbiological and physical-chemical tests by SC Apa Service SA Giurgiu, the results being shown in table 3.

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Table 1. Amounts of pollutants discharged into surface waters

No	Emissary	Pollutants (t/year)					
		MTS	CBO_5	CCOCr	P_T	Cl^-	N_T
1.	Dunărea	23.27	10.84	103.36	3.94	220.56	21.64
2.	Sabar	3.56	4.34	13.72	0.18	11.57	5.80
3.	Argeş	4.52	5.14	12.55	0.18	10.29	5.11
4.	Gârla Pasărea	0.04	0.07	0.80	0.04	1.42	0.69

Table 2. Total volume of wastewater discharged

No.	Pollution sources/locality	Treatment station/Purification stage	Volume of treated wastewater m^3/year	Emissary	Specific pollutants
1	SC APA SERVICE SA / Giurgiu	biologică	1,796,865	Dunăre	MTS, CBO_5, CCOCr, Cloruri,P_T, N_T
2	SC APA SERVICE SA / Mihăileşti	biologică	79,476	Argeş	MTS, CBO_5, CCOCr, Cloruri,P_T, N_T
3	SC APA SERVICE SA / Bolintin Vale	biologică	106,364	Sabar	MTS, CBO_5, CCOCr, Cloruri,P_T, N_T
4	Comuna Malu	biologică	12,409	Gârla Pasărea	MTS, CBO_5, CCOCr, Cloruri,P_T, N_T

The tests carried out in 2019 met the quality standards provided for the first class, according to Order 161/2006 for the approval of the Norm on the classification of surface water quality in order to establish ecological water bodies.
The results of the physical - chemical tests are shown in table 4.
The values of the physical-chemical parameters showed that in most months, the Danube water in Giurgiu area was within the limits of **quality classes I – II**, according to Order 161/2006 for the approval of the Norm on the classification of surface water quality in order to establish ecological bodies of water.
As regards free dissolved oxygen (FDO) the Danube water in Giurgiu area falls into **quality class I**, as well as in the case of PO_3^{2+} ion. The values for NO_3^- are within the limits of **quality class II.**

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Table 3. Indicators analyzed

No.	Area	Analyzed indicators	Value obtained	Limit imposed
1.	Km 502	pH	7.54 unit de pH	>/= 6.5; </=9.5
		nitrite	0.004 mg/l	0.1 mg/l
		nitrate	21.33 mg/l	50 mg/l
		Ammonium	0.10 mg/l	0.5 mg/l
		chloride	42.55 mg/l	250 mg/l
		Total hardness	20.86^0G	min. 5^0G
		oxidisability	0.79 mgO_2/l	5 mgO_2/l
		Turbidity	0.42 U.N.T.	<5 U.N.T.
2.	Km 511	nitrite	0.004 mg/l	0.1 mg/l
		pH	7.20 unit de pH	>/= 6.5; </=9.5
		Ammonium	0.15 mg/l	0.5 mg/l
		chloride	49.64 mg/l	250 mg/l
		Total hardness	29.84^0G	min. 5^0G
		Turbidity	0.60 U.N.T.	<5 U.N.T.
		oxidisability	0.79 mg/l	5 mgO_2/l

From a trophic point of view, the lake falls into the category of **β-mesosaprob**, in terms of nutrient concentration (nitrogen and phosphorus). The monthly average values for the four main physical parameters (pH, FDO, temperature, TH – Total Hardness) and the two main chemicals (NO_3^- și PO_4^{3+}) were followed and analyzed in terms of their variation dynamics, during the research period (fig. 2.and 3.). The temperature and concentration of FDO vary inversely proportional; the lower the temperature, the higher the concentration of dissolved oxygen, and the situation is reversed as the temperature increases.

The concentration of phosphates is low during July-September, increases significantly in October, and doubles the values throughout the cold season, with a slight decrease in January.

The average monthly values for nitrates are low during the summer period (July-October), but increase regularly in winter, reaching their maximum in December, after which the reverse phenomenon of proportional decrease occurs towards spring, as temperatures get higher.

As regards the biological tests, 11 taxa belonging to 6 classes were identified in the phytoplankton.

Class CYANOPHCEAE
Oscillatoria sp.
Nostoc commune
Aphanizomenon flos-aquae
Class DINOPHYCEAE
Psediastrum sp.
Class CLOROPHYACEAE
Volvax aureus
Cladophora sp.
Class BACILLARIOPHYCEAE
Melosira granulata
Fragilaria sp.
Class FLAGELLATA

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Mastigamoeba aspera
Class SARCODIA
Amoeba proteus
Actinosphaerium eichorni

Table 4. The values of the main physical-chemical parameters during May 2019 - March 2020 for the water of the Danube River, Giurgiu area

Date/ Parameter	Ph (mg/l)	T°C	DT	OLD mg/l	PO_3^{3-} mg/l	NO_3^- mg/l
04.05.2019	6.9	14.0	4.35	10.20	0.029	1.405
18.05.2019	6.9	13.0	4.15	10.17	0.031	1.380
average	6.9	13.5	4.20	9.45	0.030	1.395
01.06.2019	6.8	17.0	3.80	10.08	0.018	1.380
15.06.2019	6.9	18.0	3.55	8.80	0.016	1.377
29.06.2019	6.9	18.0	3.25	8.90	0.012	1.365
Average	6.9	17.5	3.45	8.85	0.014	1.369
13.07.2019	7.0	19.0	3.14	8.30	0.010	1.350
27.07.2019	7.0	20.0	3.03	7.65	0.011	1.430
Average	7.0	19.5	3.8	7.80	0.011	1.460
10.08.2019	6.9	21.0	2.47	7.66	0.013	1.420
24.08.2019	6.9	21.0	2.80	7.22	0.014	1.300
Average	6.9	21.0	2.66	7.45	0.013	1.380
07.09.2019	6.8	19.0	3.37	7.80	0.020	1.330
21.09.2019	6.8	18.0	4.38	8.23	0.019	1.280
Average	6.8	18.5	3.70	8.44	0.019	1.315
05.10.2019	6.9	16.0	4.25	8.60	0.016	0.910
19.10.2019	6.8	14.0	4.57	10.22	0.020	0.950
Average	6.8	15.0	4.33	9.39	0.018	0.930
02.11.2019	6.8	12.0	4.78	9.68	0.078	1.300
16.11.2019	6.9	10.0	4.26	10.29	0.035	1.480
30.11.2019	7.0	8.0	4.50	10.71	0.047	1.445
Average	6.9	9.0	4.45	10.10	0.062	1.465
14.12.2019	7.0	6.0	5.22	11.10	0.040	2.130
28.12.2019	7.0	6.0	5.70	11.33	0.050	2.110
Average	7.0	6.0	5.55	11.21	0.045	2.225
11.01.2020	6.9	3.0	4.80	11.68	0.029	2.240
25.01.2020	7.0	2.0	5.20	11.99	0.037	2.290
Average	7.0	2.5	5.05	11.75	0.032	2.108
08.02.2020	7.0	3.0	4.95	12.57	0.023	2.450
22.02.2020	7.0	3.0	5.10	12.35	0.032	2.300
Average	7.0	3.0	5.05	12.36	0.030	2.380
07.03.2020	6.9	6.0	4.60	11.33	0.027	1.350
21.03.2020	7.0	8.0	4.60	11.45	0.027	1.210
Average	7.0	7.0	4.20	11.34	0.019	1.280

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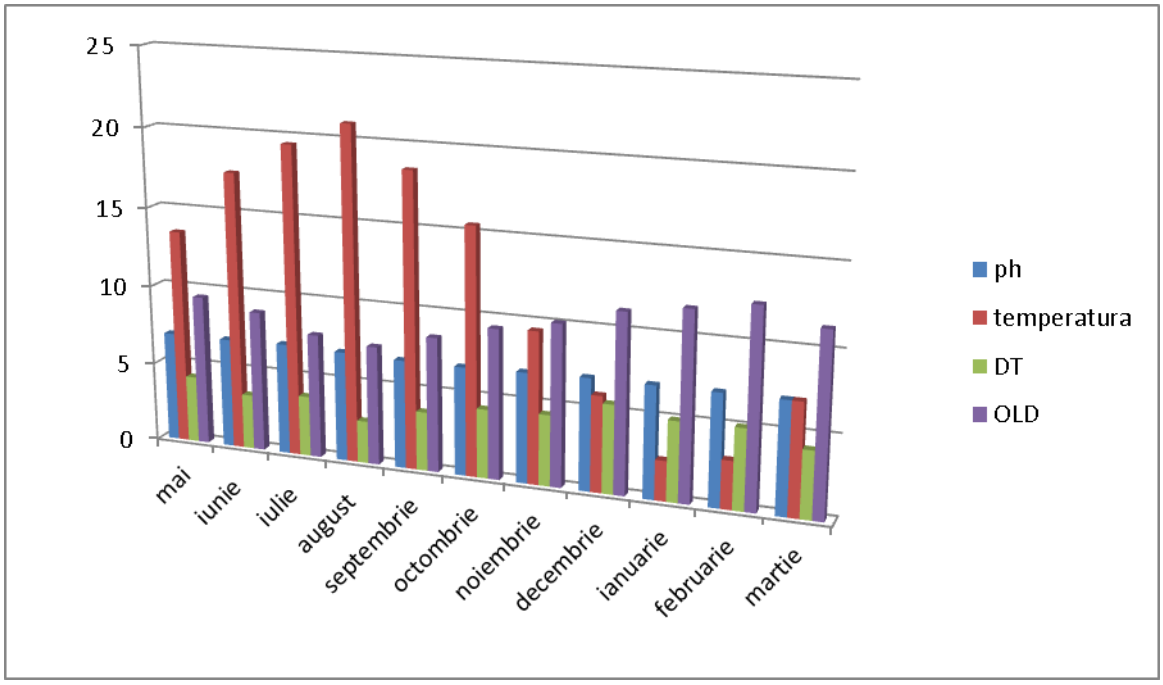

Figure 2. The variation dynamics of the main physical parameters (monthly averages) and the correlation between them during May 2019 - March 2020 for the water of the Danube River, Giurgiu area

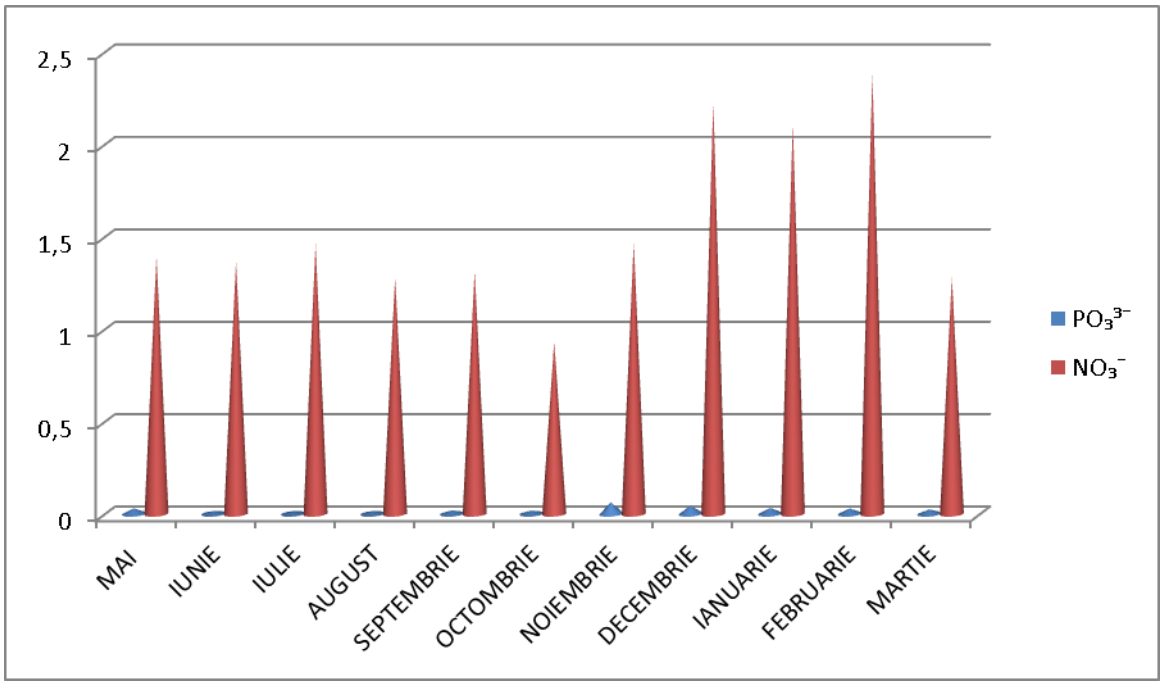

Figure 3. The variation dynamics of the main chemical parameters (monthly averages) and the correlation between them during May 2019 - March 2020 for the water of the Danube River, Giurgiu area (mg/l)

For the study period at Km 502 station, the bacillariophyceae (38%) has the highest proportion in the ecological spectrum (fig. 4), followed by chlorophyceae (26%), and the least represented

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flagellate (3%). The ecological spectrum is similar to Km 501 station (fig. 5), but with a higher percentage of bacillariophytes (41%) and a lower proportion of chlorophytes (21%).

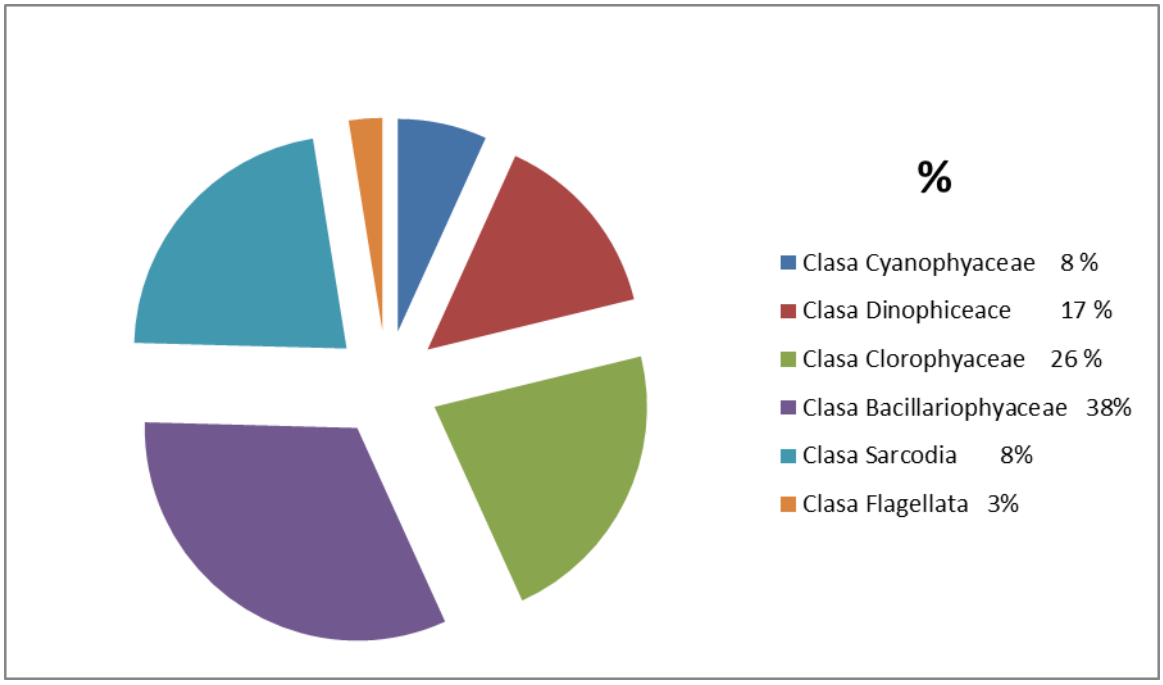

Figure 4. Ecological class spectrum of plankton in the Danube River, Giurgiu area, Km 502

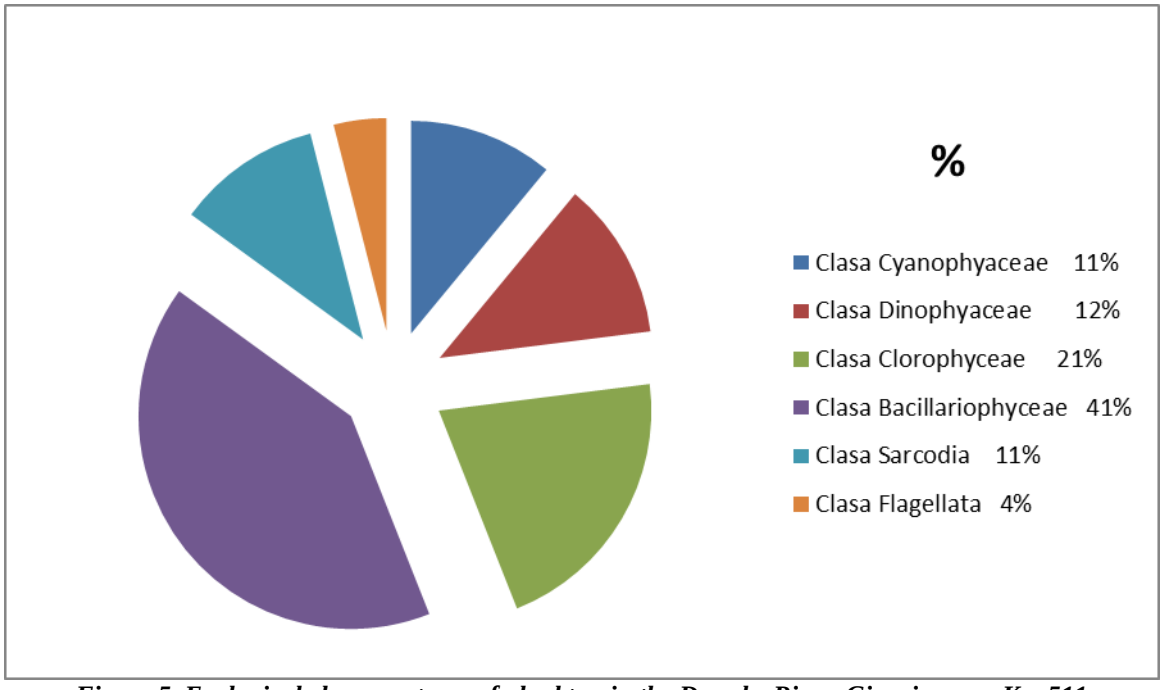

Figure 5. Ecological class spectrum of plankton in the Danube River, Giurgiu area, Km 511

4. CONCLUSIONS

Based on the data in the field, the following conclusions can be drawn:

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❖ The main plankton groups in the Danube River, Giurgiu area, are part of the classes: DINOPHYCEAE, CLOROPHYACEAE, BACILLARIOPHYCEAE, FLAGELLATA and SARCODIA.

❖ Bacillariophyceae and chlorophyceae are well represented in the studied area, both at Km 502 and 511.

❖ Flagellates have the lowest proportion in both sampling points (Km 502 and 511).

❖ The number of cyanophyceae and sarcodines is approximately constant in the two areas studied, with low values.

❖ Anthropogenic influence is present in the Danube, Giurgiu area, with the main sources of pollution: accidental spillage of residue from factories in the area, natural organic matter from animals in households, salt sprinkled on the roads during winter which is carried into the soil by rainwater and melted snow. There are seven water treatment plants in Giurgiu County that purify domestic wastewater and industrial wastewater, which are discharged into the Danube.

❖ Depending on the seasons researched, the values were comparable in the same area and in different months. Also they did not register high variations.

❖ Both sampling areas are characterized by a good ecological status - the values of biological, hydro-morphological and physical-chemical elements have moderate deviations from the values characteristic of unaltered (reference) areas or minor anthropogenic alterations.

In the future, it is recommended to monitor the Danube River in order to prevent possible sources of negative anthropogenic impact and to monitor it with an annual frequency in order to make sure that the ecological quality status is maintained at least at the current level.

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