

## ASSESSMENT OF WATER QUALITY IN THE DANUBE RIVER (CĂLĂRAȘI BRĂILA SECTION, KM 375 - KM 175)

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### Abstract

*The use of water resources for the satisfaction of socio-economic needs depends on their quality. In the actual context of socio - economic development, the water resources of the planet are strongly affected so that their protection has become a major problem of humanity. The main purpose of this study is to assess the water quality of the Danube River, the Braila - Calarasi section (km 375 - km 175) in 2011, through physico - chemical parameters. In the same time, it was carried out and an analysis of similarities and differences in the composition of the physical - chemical river water between stations. The water samples were taken from three main points, the Bala arm and sandbar Caragheorghe (km 347 - km 343) (station 1 - S1), the Epurașu Island (km 342- km 341) (station 2 - S2), Caleea arm (km 197 - 195) (station 3 - S3). The physico - chemical parameters used in this study are: the regime of temperature, pH, dissolved oxygen (DO), nutrients N-NO<sub>3</sub>, N-NO<sub>2</sub>, N-NH<sub>4</sub>, P-PO<sub>4</sub> cations Ca<sup>2+</sup>, Mg<sup>2+</sup>, conductivity and turbidity. We conclude that in the Calarasi - Braila river waters fall into third quality class (moderate ecological status).*

*Keywords: the Danube River, physico-chemical parameters, water quality assessment.*

## 1. INTRODUCTION

The quality of the surface waters depends on all the environmental components participating in the resource composition as well as anthropogenic pressures exerted on the aquatic ecosystem. The surface water chemistry varies both due to natural causes, such as geology and morphology of the watercourse, but also, due to anthropogenic causes such as urbanization and agricultural intensification. The qualitative assessment of surface waters is a complex process that is dependent on several criteria. Because the water quality does not remain constant over time, but varies due to natural or artificial sources of contaminants (Truffles, 1975) it is required a permanent monitoring of the parameters defining the quality of the surface waters. The Danube water quality assessment is important both because it is a source of drinking water for riparian population and to identify and quantify the anthropogenic effects (Iticescu et al 2013).

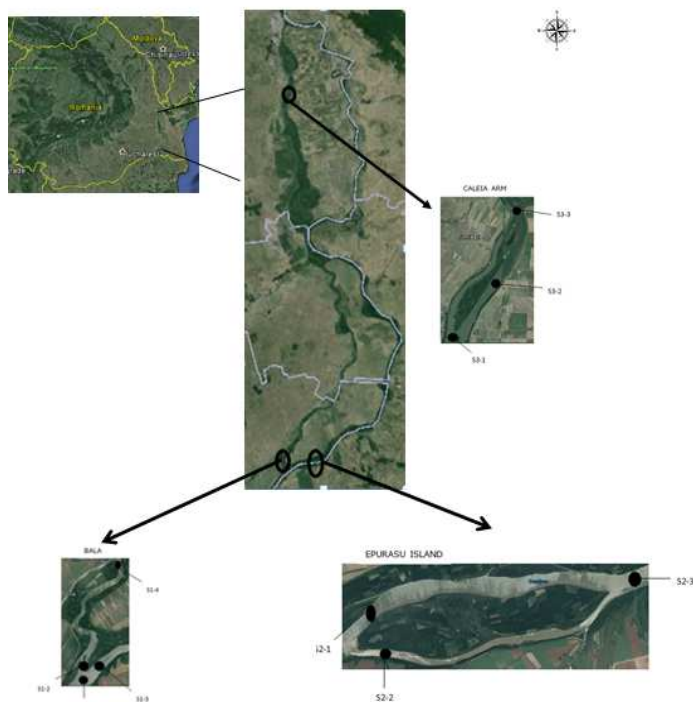
## 2. MATERIALS AND METHODS

### *Description of study site*

The Danube is one of the most important inland waterway of Europe, crossing the continent from west to east over a length of 2860 km. In Romania, the Danube stretches 1075 km. Our country holds approximately 31% of the total catchment area of the Danube. The importance of this river is

very high, both in terms of economic as well as ecological terms. From the economical point of view, the Danube waterway is the most important maritime way of Europe.

In ecological terms, the flora and fauna is very diverse because of the varied relief conditions that the river runs through them.



*Figure 1. The study area*

The section Braila - Calarasi (km 375 - km 175) is characterized by splitting the Danube by two arms (merged into a single course between Giurgeni - Vadu Oii), which enclose in the interior precincts with ponds, swamps, lakes, forests, far dammed, drained and converted into agricultural areas ("Great Island of Braila" and "Ialomita Pond"). In this sector the erosion and sedimentation are very active. This sector represents an important route for migrating fish species and places of spawning by sturgeon due to habitat characteristics (rocky substrate) but also a navigation route linking the Danube river and the sea.

#### *Materials and methods*

The physico - chemical parameters analyzed were: temperature, dissolved oxygen (DO), pH, the nutrients (N-NH<sub>4</sub><sup>+</sup>, N-NO<sub>2</sub><sup>-</sup>, N-NO<sub>3</sub><sup>-</sup>, P-PO<sub>4</sub><sup>3+</sup>), cations Ca<sup>2+</sup>, Mg<sup>2+</sup>, conductivity, turbidity.

The samples were collected monthly in four campaigns conducted during May - July 2011. The samples were taken in three main stations: the Bala area and the Caragheorghe sandbar (km 347 - km 343) (S1), Epurașu Island area (km 342- km 341) (S2), the Caleia arm (km 197-195) (S3). The stations were established both on the main arms and the side arms of the river to capture the variety of conditions. In every main station were established more stations which was done the sampling from. Each sub - station sampling was done in three sections: the left shore, sailing line right shore. The water samples for the determination of the chemical parameters were collected in clean plastic bottles of 500 ml from the surface of the water horizon (0.5 m to 1 m). They were introduced in special devices in which the temperature was maintained constant (about 4°C.). The water sampling, transport and preservation were made according to the minimum recommendations included in SR

ISO 5667/2007. During the period of the study were performed over 1000 analysis of physio-chemical parameters (1053).

pH, conductivity, temperature, dissolved oxygen content were measured immediately using multiparameter sensors Portable Digital Electrochemistry electrodes with HQD meters and Intellical. The nutrients (N-NH<sub>4</sub><sup>+</sup>, N-NO<sub>2</sub><sup>-</sup>, N-NO<sub>3</sub><sup>-</sup>, P-PO<sub>4</sub><sup>3+</sup>) and Ca<sup>2+</sup> and Mg<sup>2+</sup> cations have been determined in the laboratory by spectrophotometric method using Spectroquant Nova 400 and Merck kits. The turbidity was determined with TB1 portable turbidimeter.

The water quality assessment has been carried out according to the Minister of Environment and Water No.161/2006 norms concerning classification of surface water in order to determine the ecological status of the water bodies. Also, it was used information from Annex 6.1 of the National Management Plan of the Danube River basin (2008) prepared in accordance with the requirements of the Water Framework Directive.

### 3. RESULTS AND DISCUSSIONS

Descriptive statistics of the parameters measured in the sampling stations is shown in Table 1.

*Table 1. Descriptive statistics of the variables determined in water samples from the Danube River.*

	S1		S2		S3		P
	x (min – max)	SD	x (min – max)	SD	x (min – max)	SD	
T <sup>0</sup> C	<b>23,17</b> (17,3 -27,1)	2,94	<b>23,16</b> (16,3 – 28,3)	3,81	<b>22,3</b> (14,8-27,9)	4,49	p>0,05
O <sub>2</sub> (mg/l)	<b>11,6</b> (8,2-13,23)	1,43	<b>11,9</b> (9,28 -15,12)	1,7	<b>8,57</b> 6,14 – 11,45)	1,6	p<0,05
pH	<b>8,23</b> (7,08 –9,84)	0,55	<b>8,27</b> (6,97 –9,68)	0,59	<b>8,23</b> (7,76 – 8,7)	0,3	p>0,05
N-NH <sub>4</sub> <sup>+</sup> (mg/l)	<b>0,119</b> (0,015 - 0,3)	0,073	<b>0,143</b> (0,01 - 0,37)	0,10	<b>0,127</b> (0,01 - 0,56)	0,12	p<0,05
N-NO <sub>2</sub> <sup>-</sup> (mg/l)	<b>0,02</b> (0 - 0,06)	0,0125	<b>0,0074</b> (0 - 0,03)	0,0066	<b>0,019</b> (0 - 0,13)	0,025	p<0,05
N-NO <sub>3</sub> <sup>-</sup> (mg/l)	<b>3,78</b> (1,1 - 8)	1,53	<b>4,86</b> (2,5 - 9,4)	1,83	<b>6,87</b> (1,9 - 15,5)	3,46	p<0,05
P-PO <sub>4</sub> <sup>3+</sup> (mg/l)	<b>0,088</b> (0 - 0,8)	0,17	<b>0,167</b> (0 - 0,4)	0,097	<b>0,3</b> (0 - 1)	0,27	p<0,05
Ca <sup>2+</sup> (mg/l)	<b>64,34</b> (22 - 158)	29,67	<b>52,67</b> (2 - 140)	35,98	<b>58,92</b> (16 - 116)	25,55	p>0,05
Mg <sup>2+</sup> (mg/l)	<b>19,09</b> (9,3 - 38,1)	8,29	<b>17,046</b> (9,5 - 29,5)	5,61	<b>26</b> (3,3 - 116)	29,93	p>0,05
Conduc tivity (μS/cm)	<b>438,37</b> (399 – 496)	32,33	<b>431,7</b> (380 - 502)	36,93	<b>450,52</b> (418 - 508)	33,03	p>0,05
Turbi dity (mg/l)	<b>27,38</b> (7,3 - 92,9)	14,68	<b>28,19</b> (12,5 - 42,8)	8,73	<b>37</b> (12,5 - 74,6)	14,51	p<0,05

The *pH* is one of the important parameters of water that determines its reactivity capacity. The aquatic organisms life is possible at a pH between 5 to 8.5. Large variations in this parameter are stressful for aquatic organisms, especially for the fish fauna. (Florea, 2008). In the 3 stations monitored, the pH variation is small, between 8.23 ÷ 8.27, with 6.97 min (May, Station 2) and maximum 9.84 (July, Station 1). As shown in Figure 2 values of this parameter in the monitored

stations exceed the reference value for very good condition (optimum interval 6.5 to 8.5), so in terms of pH indicator, the water quality falls within Class III a- moderate ecological status. The pH can vary due to discharge of industrial and domestic waste of water or due to the increased photosynthesis process.

*DO*. The amount of dissolved oxygen concentration represents the concentration of the chemical or biological compounds that can be oxidized and that might have pollution potential, can affect a sum of processes that include re-aeration, transport, photosynthesis, respiration, nitrification, and decay of organic matter (Cox, 2003).

The mean concentrations of dissolved oxygen measured in the three stations ranged from 8.57 mg/l (station 3) and 11.9 mg/l (station 2). The maximum recorded was 15.12 mg/l in July (station S2) and the minimum 6.14 mg/l in July (station S3).

The amount of dissolved oxygen is very good at stations 1 and 2 but the third station is below the reference value for the first class water quality (figure 3), which is why the river water for this indicator is classified in the second quality class, which represents a good ecological status.

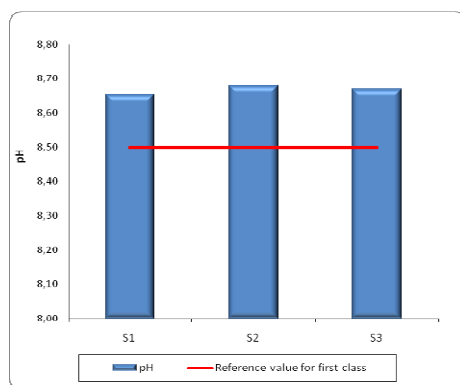


Figure 2. pH variation

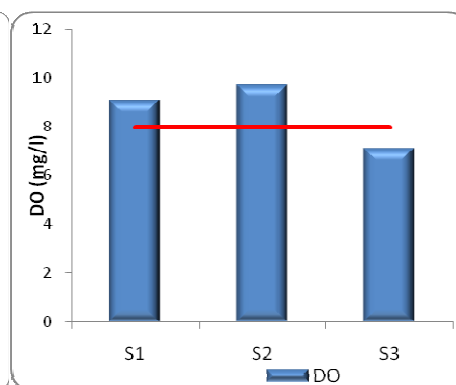


Figure 3. DO variation

*Ammonium* ( $N-NH_4^+$ ) *nitrite* ( $N-NO_2^-$ ) and *nitrate* ( $N-NO_3^-$ ). Nutrients or biogenic substances are represented by compounds of nitrogen and phosphorus. Their variation in surface freshwaters varies very large: from trace amounts up to 10 mg/l (Florea, 2008) and is due to precipitation, discharge of wastewater from industry or the domestic fertilizer use agriculture.

*Ammonium ion* ( $NH_4^+$ ) appears in the surface waters due to the decomposition of the organic matter under anaerobic conditions and the presence of bacteria or a result of reduced of nitrite ions. The values of this parameter are strongly influenced by the pH value. Thus, a pH value of about 7 ammonium ions predominate; above this value it appears as free  $NH_3$ , very toxic to aquatic organisms.

In the monitored stations, the average of this parameter ranged from 0.119 mg/l (S1) and 0.143 mg/l in S2. The minimum value recorded in the monitored period was 0.01 mg/l in stations S1 and S2 (June, July) and the maximum value was 0.56 mg/l in station S3 (June).

The average figures recorded in the three stations is below the reference value for this indicator (figure 4), the ecological state of water is considered very good, falling in the first class quality.

*Nitrites* ( $NO_2^-$ ) are found in the surface waters as a result of either the processes of nitrification, through ammonium ion is converted to nitrite ion or as a reduction of nitrate ions or anaerobic fecal pollution.

The mean variation is in the range 0.0074 mg/l in S2 and 0.02 mg/l 0.01 S1. The minimum values have been recorded in all the stations monitored. In some stations nitrites were not found. The maximum recorded was 0.06 mg/l in S1 (May).

The environmental status for this indicator is very good, water falls in the first class quality.

The concentrations of *nitrates* ( $\text{NO}_3^-$ ) varies depending on the season, so in the warm periods due to intense processes of photosynthesis are very diminished (sometimes may even disappear) and they grow in colder periods.

Also, large quantities are found in the surface waters in cases where near the watercourse are agricultural lands where are used fertilizers based on nitrogen or discharge of animal waste (Young, 1980).

The average change in the three stations of nitrate is comprised between 3.78 mg/l (station 1) and 6.87 mg/l (station 3) with at least 1.1 mg/l recorded in S1 (July), and not more than 15 5 mg/l recorded in S3 (May). As shown in figure 6 the concentrations of nitrates in the three stations exceeded the reference value for the second quality class, which is why the Danube waters for this indicator fall in the third quality Class, equivalent to the moderate ecological status.

Station 3 that registers the highest concentrations represents the sector located between Gropeni and Braila (KmD 194 - 186 KmD). The high concentrations of nitrate can have agriculture as the main source of contamination which is carried intensively in Big Island of Braila.

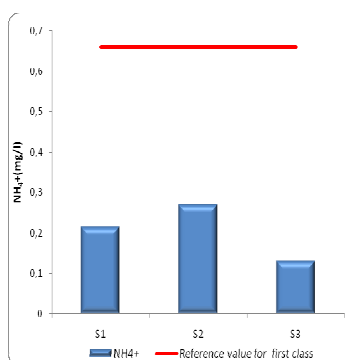


Figure 4.  $\text{NH}_4^+$  variation

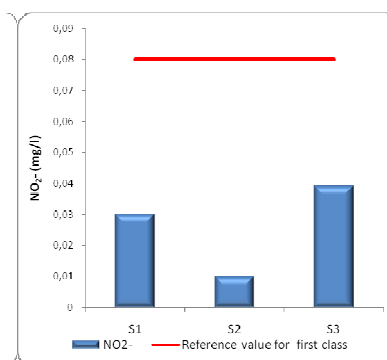


Figure 5.  $\text{NO}_2^-$  variation

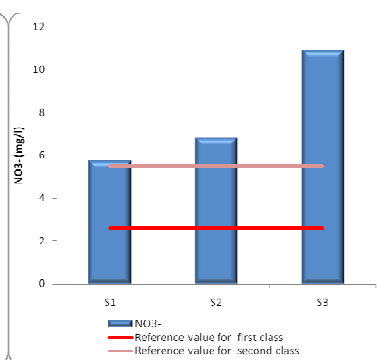


Figure 6.  $\text{NO}_3^-$  variation

The phosphates ( $\text{PO}_4^{3+}$ ) together with the nitrogen play an important role in the development of the aquatic life, however, larger amounts may act as a inhibitor of the development of some species. High concentrations occur in case of pollution sources (detergents industry, washing neighboring farmland which used fertilizers based on phosphate, sewage, etc).

Its presence in high quantities (together with nitrates) in watercourses lead to the eutrophication of it. For our study we mention that the phosphates were absent in many sampling points.

The average concentration of phosphates in the monitored stations ranged from 0.088 mg/l (S1) and 0.3 mg/l (S3). The minimum recorded value was 0.1 mg/l was found in all stations and throughout the study period, the maximum value of 1 mg/l was recorded in May, S3.

From this indicator point of view the water quality falls into the third class equivalent to moderate ecological status (figure 7).

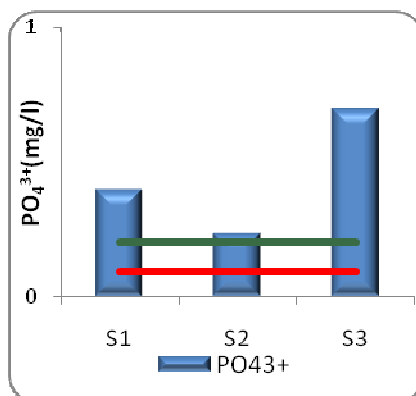


Figure 7. PO<sub>4</sub><sup>3+</sup> variation

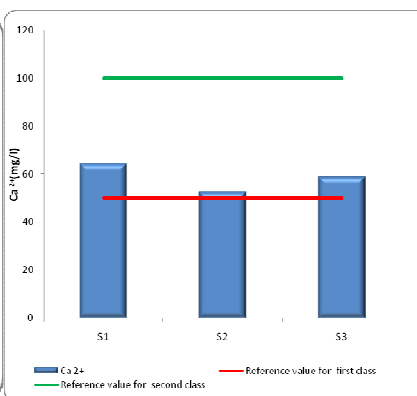


Figure 8. Variation of Ca<sup>2+</sup>

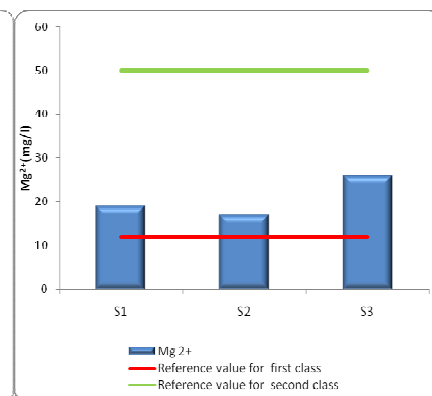


Figure 9. Variation of Mg<sup>2+</sup>

**Hardness.** The presence of different metal ions in the water, especially Ca<sup>2+</sup> and Mg<sup>2+</sup> indicates the hardness of the water. These elements are of natural origin and does not indicate water pollution. But, still according to Order 161/2006 it can be made a framing in quality classes of water after these indicators, too.

Thus, the mean variation of Ca<sup>2+</sup> in the monitored stations ranged from 52.67 mg/l in S2 and 64.34 mg/l in S1. The minimum, 2 mg/l was recorded in S2 (May) and the maximum, 158 mg/l was recorded in S1, May.

The average concentration of Mg<sup>2+</sup> ions varied from 17.05 mg/l (S2) and 26 mg/l (S3). The minimum recorded was 3.3 mg / l S3 (May) and a maximum of 116 mg / l S3 (May).

For both indicators (Figures 8 and 9) the water falls into the second quality class.

**The conductivity** is one of the most used indicators in assessing the degree of mineralization of the waters depending on the concentration of dissolved ions. The mean values for this indicator ranged between 431.7 mS/cm in S2 and 450.52 mS/cm in S3 (with a minimum of 399 mS/cm in S1 and maximum 508 mS/cm in S3).

The **turbidity** is due to the presence of solid particles (such as organic or inorganic matter) in the form of suspensions or colloidal. The turbidity is an important factor influencing directly and indirectly the life of the aquatic organisms. Large amounts of suspended particulate matter (SPM) exported by turbid rivers directly affect phytoplankton productivity, nutrient dynamics and the transport of pollutants in coastal zones (Doxaran et al., 2009). The three stations average turbidity values ranged from 27.38 mg/l in S1 and 37 mg/l in S3. The lowest value recorded was 7 mg/l in June, S3 and the highest 92.9 mg/l in May, S1.

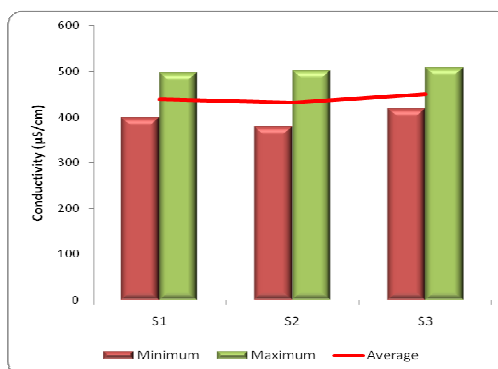


Figure 10. The variation of conductivity

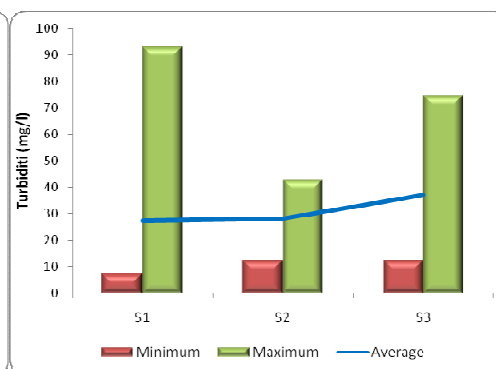


Figure 11. The variation of turbidity

#### 4. CONCLUSIONS

1. The quality of the water in the Danube Braila - Calarasi sector(km 375 - km 175) assessed by physico - chemical indicators falls for:

First class equivalent to high ecological status for ammonia and nitrates;

Class II equivalent of good ecological status for oxygen indicator;

Class III equivalent of moderate ecological status for indicators: pH, nitrates, phosphates.

The final ecological status is represented by the worst situation resulting from the evaluation of the elements quality. In this study the ecological state for Braila - Calarasi sector is the state of moderate (grade III) quality.

2. The high values of the nitrates and phosphates concentrations in the station S3 may be due to intensive agriculture practiced in the Big Island of Braila. Increases of these nutrients lead to an increase mass of phytoplankton and photosynthesis process,too. This explains the low pH values in this station. The lower concentration of dissolved oxygen which occurs in S3 can be explained by the intense breathing process and other processes of decomposition of organic matter. Although, normally,the ions nitrate toxicity is considered irrelevant (Russo, 1985; Camargo et al., 2005) the studies have revealed that if the concentration exceeds 10 mg/l may affect the aquatic organisms exposed on long term. Also, the sensitivity is higher in freshwater bodies than in saltwater bodies (Camargo et. al., 2006).

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