

ACTUAL ASPECTS CONCERNING THE WATER QUALITY MONITORING ON THE SULINA CHANNEL FROM THE DANUBE DELTA - ROMANIA

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Abstract

This paper presents the evaluation of the ecological status of the Tulcea-Sulina Channel in the Danube Delta, using the water quality index (WQI) and some important monitoring points where the Danube is discharged in the Black Sea, respectively where the river is splitting into 3 arms. The Sulina Channel is a navigable channel for heavy ships and, in the same time, represents a source of local drinking water, while keeping specific features of unique biodiversity in Europe. Besides the navigation, other anthropogenic activities are present (e.g. agricultural and fish farms, tourism and fish poaching), which frequently involve discharges (e.g. detergents, domestic waste, agricultural fertilizer, animal manure, oil products) in the Sulina Channel. These inputs are responsible for the enrichment of the water with nutrients (e.g. nitrogen and phosphorus based) and organic substances that contribute to the growth of algae and other aquatic plants and ultimately to the water eutrophication, fact recognized as a major environmental issue for the management of water resources. This paper tackles the issue of general information on the Danube River, Danube Delta and historical information on water quality along the river. It describes the water quality monitoring procedure, as well as the main activities necessary to successfully carry out the water quality monitoring process, in the light of European legislation on water quality monitoring, focusing on The Water Framework Directive (WFD) and the Drinking Water Directive (DWD) of the European Union (EU). A series of aspects related to the water quality monitoring network in the Danube basin were detailed, followed by a list and description of quality indicators that were monitored in this study in order to calculate the value for the Water Quality Index (WQI) further used to estimate the water quality status and respectively to establish the possible uses of the available water resources along the Tulcea-Sulina Channel.

Key words: water management, surface water monitoring, Danube Delta, Tulcea-Sulina Channel, water quality index, water quality indicators

1. INTRODUCTION

Water quality and ecology of the lotic systems are affected by many anthropogenic activities, including farmland/agricultural/hydrotechnical works and wastewater discharge. Therefore, there is a need for action in terms of improving the water management, where the water monitoring plays an important role. Particularly, the Water Framework Directive is a legislative instrument for solving the water environmental issues, including those related to the European large wetland Danube Delta, where the water quality and biocenosis structure changed overtime. The Tulcea-Sulina Channel is one of the main arms derived from the Danube River, which is subject to variation in physical-chemical properties due to the many pollution sources, which affects the river and the Black Sea ecosystems.

The main objectives of this study consist in: collecting water samples from the Sulina branch; determining the main water quality indicators (physical-chemical indicators) from various measurement points distributed along the Tulcea-Sulina Channel; computing the water quality index (WQI); comparative analysis of the data obtained in 2021 with the historical data in order to develop a

forecast of possible future evolution of water quality, with serious consequences on the river and marine ecosystems.

1.1. The physical-geographical characteristics of the Danube River

The Danube is known as the second largest river in Europe, having a length of 2860 km and a river basin covering an area of about 817,000 km². It is thus a key international waterway in Europe, allowing a junction between the fluvial and marine transportation and being an international tourist attraction [1]. As can be seen in Fig. 1, the Danube originates in Germany, flows through 19 countries, and discharges into the Black Sea through the Danube Delta, which largely belongs to Romania [2].



Fig. 1. The Danube River Basin [3]

The Danube River Basin is divided into three sectors: Upper (from the Black Forest Mountain, Germany, to the Devin Gate of Vienna, Austria), Middle (from the Devin Gate, Austria, to the Iron Gate Dams of Drobeta Turnu Severin, Romania) and Lower Basin (from the Iron Gate Dams, Romania, to the Black Sea). The last one consists of the Romanian-Bulgarian plain and its plateaus. The important tributaries in this region are Timok, Iskar and Jantra from the South and Jiu, Olt, Arges, Ialomita, Siret, Prut from the North) [4]. The Lower Danube Basin has a dry continental climate with warm temperatures, as follows. The winter average temperature is ranged between -2 to -6 °C., while the minimum temperature ranged between -30 to -35 °C. The summer average temperature is ranged between +20 to +30 °C, while the maximum temperature ranged from +40 to +42 °C. The daily temperature changes can be significant, e.g. from + 15 to +20°C [5]. It can be mentioned that the mineral content of the river is higher in winter than in summer, while the organic content is relatively low, but it is strongly influenced by the industrial pollution. The average annual flowrate of the river is 6,047 m³ · s⁻¹, while the maximum values are recorded in the spring and (13,000-14,000 m³ · s⁻¹) [6]. From a hydrological and ecological point of view, there are three distinct regions in the Lower Danube Basin: the channel, the floodplain, the delta [5]. The map of the Danube Delta is shown in Fig. 2

It is known that the Danube Delta is the most important protected area of Romania and belongs to the UNESCO "Man and the Biosphere" Programme, being the World Heritage Site since 1990 and it is a Biosphere Reserve of The International Union for Conservation of Nature (IUCN) and Nature 2000 (SCI-Site of Community Importance, SPA- Special protected area). The Danube Delta is located in Tulcea County, being a low alluvial plain covered by wetlands and water. The area between the three branches (Chilia, Sulina and Sfantul Gheorghe (Saint George)) forms three main delta units (Letea, Caraorman and Dranov), which are linked by deltaic lakes, channels and streams. About 5,200 species of flora and fauna are subject of the biodiversity from the Danube Delta Biosphere Reserve, which

covers 580,000 hectares in Romania divided into: i) conservation priority area (8.7%); ii) buffer areas (38.5 %) and; iii) economic sectors (52.8 %) with almost 15000 inhabitants [8].



Fig. 2. The Danube Delta [7]

The formation of the Danube Delta started long time ago in the Black Sea Gulf and has been influenced by several factors, including the Black Sea wind waves (up to 7 m in height) and sediments transportation [9-11]. Sediment structure can include a mixture of quartz, feldspar, garnet and pyroxene, volcanic and metamorphic rocks. The organic sediments and nutrients follow the same trends as the inorganic ones. Overall, the delta is prone to nutrient accumulation (nitrogen and phosphorus). The chemistry of the Danube Delta, climate and hydrology are influenced by the course of the river and determine the characteristics of the marine habitat [12].

1.2. The hydrographic network of the Danube Delta

The first bifurcation of the Danube, called Ceatal Izmail, which marks the starting point of the Delta, consists in the Chilia (Kilia) branch to the north and the Tulcea Channel to the south. The Chilia branch (the largest one in the Danube Delta), has a length of 117 km and acts as the Romanian-Ukrainian border. Before discharging into the Black Sea, the Chilia branch forms a secondary delta of 24,400 ha. The Tulcea branch is shorter and is followed by a new bifurcation, at Ceatal Sfantu Gheorghe (St. George), where it is divided into two main Channels: Sulina on the left and St. George on the right [13]. The Sulina branch has a length of 71.7 km, including 8 km of dams at the discharge into the Black Sea, being the straightest and shortest branch of the Danube. The Sulina channel is an international waterway, with great economical implications [12]. In comparison, the St. George branch has a length of 108.8 km, until the discharge into the Black Sea [2]. The biodiversity of the Danube Delta is very diversified and is presented by several authors [9, 14], where the symbiosis between natural and anthropogenic ecosystems can be observed.

1.3. Water quality of the Danube and the Danube Delta

As it was previously mentioned, the aquatic ecosystem of the Danube River Basin has an important economic, social and ecological impact, taking into consideration that the water resources are used for the drinking water preparation and other purposes such as irrigation in agriculture, use as industrial water, electricity production, aquaculture, tourism, transportation by water, etc. [13].

Water quality in the Danube River, as well as in the Danube Delta area and the Black Sea coastal areas has become a problem due to the increasing of the total nitrogen and total phosphorus loads by 10 times than the natural background, leading to water eutrophication. Every year, over 500,000 tons of nitrogen and over 20,000 tons of phosphorus are discharged in the Black Sea from the Danube River. Moreover, high organic pollution (antibiotics, petroleum hydrocarbons, pesticides, personal care products, untreated wastewater, etc.) led to a significant risk for the aquatic habitats [15]. Microbiological contamination in the Danube river basin is caused by the discharge of municipal wastewater and rainwater, as well as runoff from agricultural activities.

In the Danube Basin, anthropogenic influence has demonstrated the need for water quality improvement. The 1986 Bucharest Declaration proposed standard monitoring methods to achieve this goal. In 1994, the Convention on the Protection of the Danube River, signed in Sofia, aims to improve the environment, economy and quality of human life in the Danube River Basin [15].

A "good ecological status" can be achieved by appropriate management of the water resources, including the development of new concepts in water monitoring, e.g. evaluation of the ecological status through an integrated physical, chemical, hydro-morphological and biological approaches [11].

Moreover, the program for continuous monitoring of the Danube Delta National Institute for Research and Development allows the evaluation of water quality of the Danube River and indicates the influence of the anthropogenic activities due to the toxic substances or wastewater discharges [15].

Based on water quality data (in terms of physical-chemical characteristics), pollution with nutrients and heavy metals was considered as one of the most critical water management issues in the Danube basin, with a particular impact on the Danube Delta and the Black Sea area [16].

The results of the Danube Delta National Institute for Research and Development (since 2007) in terms of nutrients show that the largest pollution of the Danube River occurred in the 1980s, fact that can explain the acceleration of the eutrophication process occurring in the Danube Delta. It is the period before the establishment of the Danube Delta Biosphere Reserve, where agriculture and fisheries have been applied extensively in the delta, accompanied by the accentuation of the hydrological deficit [17].

For the settlements along the Sulina branch, the water from the Danube River is the main source of drinking water. Surface water can only be used as drinking water after it has been treated in drinking water treatment plants. The raw water captured from the Danube is subjected to the drinking process through a series of successive processes such as: settling, flocculation, filtration and chlorination, followed by the temporary storage of drinking water and sending to consumers through distribution networks. Domestic wastewater must be taken from consumers through sewerage networks and pumped to the treatment plants where the physical and biological processes are involved in order to ensure the water quality before discharge into natural emissary represented by the Sulina Channel. Maintaining water quality in the Sulina Channel is closely linked to ensuring a sustainable management system for water resources in the Danube Delta localities, in accordance with the Integrated Strategy for Sustainable Development of the Danube Delta and the proper management of the Danube Delta Biosphere Reserve [9].

1.4. Water quality monitoring

Water quality monitoring process refers to the acquisition of the representative information (physical/chemical/biological characteristics of a water body) in time and space. The water quality is evaluated by the comparison of the acquired data with the baseline values, in the frame of the water quality monitoring network [18]. For example, a diagnosis in terms of eutrophication, acidification, heavy metal contamination etc. could be performed, by monitoring of relevant indicators for the respective purpose [19].

According to the Water Framework Directive (WFD), water quality assessment includes the evaluation of the water bodies in terms of chemical status and ecological status, as based on the water quality indicators, which are regularly monitored by national authorities and reported to the EU. The ecological status depends on both biological as well hydro-morphological and physical-chemical

elements, while the chemical status involves the priority substances. There are five water quality classes for the ecological status (very good, good, moderate, bad and very bad) and two classes for the chemical status (good chemical status; poor chemical condition) [20].

1.5. Water quality monitoring in the Danube Basin

Water quality monitoring in the Danube River basin is an important strategy to control the water pollution at the cross-border [21], with many opportunities and challenges (e.g. related to the obtaining of the valid data, calibration and standardization of sampling/analysis methods etc.). Particularly, modeling nutrient discharges into the Danube and international agreements and regulations have been adopted to reduce nutrient pollution [22]. The long-term evolution and interactions of the individual water quality indicators in the Danube River have been observed. To assist the authorities and stakeholders and to communicate information to the public, an overall assessment of water quality can be a very useful tool [22]. As earlier mentioned, both ecological as well chemical status are envisaged [23]. Particularly, the frequency of water quality monitoring and evaluation contributes to the development of the management strategies for controlling surface water pollution facing increasing urbanization and anthropogenic pressure on water resources [22].

1.6. Water quality index

Water quality index (WQI) is a score used to describe the status of the monitored surface water and to identify the most probable factor responsible for any deterioration in water quality. WQI is obtained by applying a specific weighting-based algorithm of some water quality indicators. Therefore WQI plays an important role in the water resources management [24-25].

In this study WQI was determined using the following water quality indicators:

Biochemical Oxygen Demand (BOD): reflects the content of the organic matter that can undergo aerobic oxidation by bacteria.

Chemical Oxygen Demand (COD): reflects the total amount of organic substances in the water that can be oxidized, if inorganic oxidable species are not present or these could be neglected.

Ammonium Nitrogen ($\text{NH}_4^+\text{-N}$): its presence is mainly due the discharge of industrial wastewaters that are rich in ammonium salts, but it can also form during the breakdown of protein substances or during the anaerobic conversion of the organic matter; it can be converted to the nitrates by the nitrifying bacteria; the presence of ammonium is one of the main causes of eutrophication [26-27].

Nitrates Nitrogen ($\text{NO}_3^-\text{-N}$): its concentration of nitrates in the surface water is normally low, but can reach high levels in the case of the agricultural discharges or contamination with leachate from household waste or with human or animal manure [28].

Total Phosphorus (TP): reflects the totality of organic and inorganic phosphorus compounds, which are dissolved or bound to particles; it is an important biogenic factor involved in metabolic processes of the living organisms, but its excess leads to negative consequences due to the water eutrophication [28].

Another water quality indicator, refers to the pH, which is known to plays an important role for aquatic life [29]. Due to its small level of variation, it was measured but was not considered in the calculus of WQI in this study.

2. MATERIALS AND METHODS

The monitoring area for this evaluation includes the Tulcea-Sulina Channel, part of the Danube Delta Biosphere Reserve, Tulcea, Romania. This study is based on the analysis of the water samples that were taken from the Tulcea-Sulina Channel, during May-July 2021, as well as data from three monitoring sampling points of the Danube River, which were derived from the database of The International Commission for the Protection of the Danube River - ICPDR, for the years 2000-2017. The use of this information in the actual study was with the consent of the ICPDR team that allowed

the access to the database for scientific purposes. Also, information on the physical-chemical indicators of the water in the Tulcea city area was provided by the Water Company, for the years 2013-2020.

Fig. 3 shows the water sampling points in Tulcea-Sulina Channel for the 2021 monitoring campaign, while Fig. 4 shows the location of the sampling points related to the historical data.

Water samples were collected and stored in 500 mL bottles, according to the typical methodology.

Standard methodology was applied for the measurement of the indicators; the BOD₅ was determined according to the SR EN 1899/2 2002 method, while the COD-Cr was determined according to the SR ISO 6060/96 method.

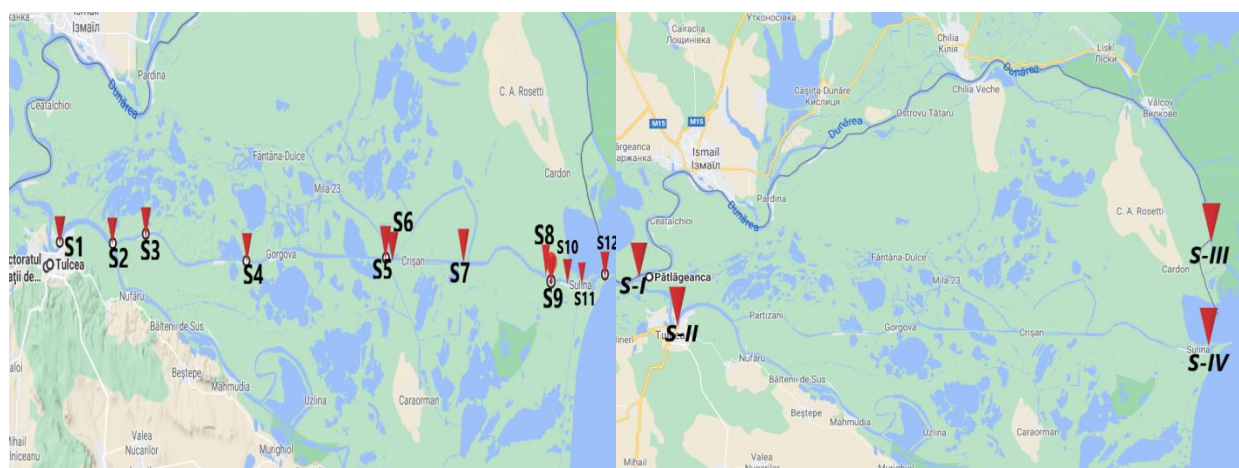


Fig. 3. Map of the sampling area: S1- Tulcea port; S2- Hydrological station; S3- Partizani; S4- Maliuc; S5- Crisan fire station (entrance to Crisan); S6- Camping Crişan; S7- Exit of Crisan; S8- Imputita Channel (intersection with Sulina channel); S9- Imputita Channel (belt channel); S10- Sulina drinking water treatment plant; S11- Sulina Port; S12- Sulina WWTP discharge tube.

Fig. 4. Location of water sampling points, for which was used information from the historical databases. S-I – Patlageanca; S-II – Tulcea; S-III – Chilia (Kilia); S-IV – Sulina.

Determination of Water Quality Index (WQI)

The methodology for the water quality assessment, based on the WQI determination, presented in this study, can be easily performed taking into consideration the limit values in national water quality standards. The method is based on weighted arithmetic mean using coefficients determined by the National Sanitation Foundation -Water Quality Index, which were successfully applied in various river basins.

The indicators analyzed for this study (BOD₅, COD-Cr, NH₄⁺-N, NO₃⁻-N, TP) are known as being the most frequently used and relevant for the chemical evaluation of water quality.

The water quality index (WQI) was calculated using the equation [20]:

$$WQI = \frac{\sum Q_i W_i}{\sum W_i} \quad (1)$$

where: **Q_i** is the quality rating scale of the indicator **i**; **W_i** is the weight corresponding to the indicator **i**; **Q_i** and **W_i** were calculated according to the following equations [20]:

$$Q_i = 100 \frac{V_i - V_0}{S_i - V_0} \quad (2)$$

$$W_i = \frac{K}{S_i} \quad (3)$$

where: V_i is the annual mean of the indicator i ; V_0 is the ideal value of the indicator; S_i is the standard limit value for the indicator i ; in this study, S_i values are Romanian standard values for the quality class II, because the Danube water quality is generally considered to belong to this class; $V_0=0$ for all indicators; K is a proportionality constant, which was determined using the equation [20]:

$$K = \frac{1}{\sum \left(\frac{1}{S_i} \right)} \quad (4)$$

The limit values S_i , as well as the calculated values $1/S_i$, $\sum 1/S_i$, K , W_i are shown in Table 1:

Table 1. Limit values S_i , calculated values $1/S_i$, $\sum 1/S_i$, K , W_i

Parameter	Unit	S_i	$1/S_i$	$\sum 1/S_i$	$K=1/(\sum 1/S_i)$	$W_i=K/S_i$
Biochemical oxygen demand (BOD_5)	mg O ₂ /L	5	0.2	3.073	0.325	0.065
Chemical oxygen demand (COD-Cr)	mg O ₂ /L	25	0.04	3.073	0.325	0.013
Ammonium nitrogen (NH_4^+-N)	mg N/L	0.8	1.25	3.073	0.325	0.406
Nitrate nitrogen ($NO_3^- -N$)	mg N/L	3	0.33	3.073	0.325	0.108
Total phosphorus (TP)	mg P/L	0.8	1.25	3.073	0.325	0.406
	$\sum$		3.073			1

The water quality status corresponds to the WQI values provided in Table 2.

Table 2. WQI values and the corresponding water quality status [20]

WQI	Water quality status
0-25	Excellent
26-50	Good
51-75	Poor
76-100	Very poor
Over 100	Critical

3. RESULTS

The water samples were collected and analyzed in May-July 2021 in the 12 monitoring points located on the Tulcea-Sulina Channel. The obtained average values are centralized in Table 3, while the graphical representation of each indicator is presented in Figs. 5-10.

Table 3. Average values obtained for the indicators, in the 12 collection points, along the Tulcea-Sulina channel.

Year	Location	BOD ₅ mg O ₂ /L	COD-Cr mg O ₂ /L	NH ₄ ⁺ -N mg N/L	NO ₃ ⁻ -N mg N/L	TP mg P/L
2021	S1- Tulcea port	1.42	11.9	0.09	2.75	0.18
2021	S2- Hydrological station	1.64	13.7	0.07	2.64	0.16
2021	S3- Partizani	1.51	12.6	0.14	2.20	0.14
2021	S4- Maliuc	1.62	13.5	0.07	1.10	0.12
2021	S5- Crisan fire station (entrance to Crisan)	1.78	14.9	0.1	1.10	0.17
2021	S6- Camping Crişan	1.81	15.1	0.07	1.06	0.19
2021	S7- Leaving the Crisan town	2.14	14.3	0.11	1.31	0.15
2021	S8- Imputita Channel (intersection with Sulina channel)	1.74	14.5	0.13	1.32	0.16
2021	S9- Imputita Channel (Belt channel)	1.84	14.2	0.03	1.22	0.21
2021	S10- Sulina drinking water treatment plant	2.33	14.6	0.07	1.32	0.15
2021	S11- Sulina Port	1.58	14.4	0.1	1.21	0.14
2021	S12- Sulina WWTP discharge tube.	2.32	15.5	0.09	1.17	0.20

The values of BOD₅ range between 1.4 and 2.4 mg O₂/L, the highest values being observed in points S10 and S12, while the lowest value is recorded in point S1 (Fig.5). These values are in the usual BOD₅ interval for the surface water, which varies from 0.5 to 5.0 mg O₂/L. This indicator is subject to seasonal and diurnal changes, which mainly depends on the temperature changes and the physiological and biochemical activity of microorganisms.

The monitored COD-Cr values are in the range of 11-15.5 mg O₂/L (Fig. 6), which are below the maximum allowable concentration of 25 mg O₂/L that was recorded for this indicator.

The results obtained from the analysis of the water samples in terms of NH₄⁺-N (Fig.7) fluctuate from the value of 0.03 mg N/L corresponding to the point S9, to the value of 0.14 mg N/L recorded for the point S3. The limit value for this indicator is 0.8 mg N/L, therefore the all 5 sampling points (S3, S5, S7, S8, S11) are in the frame of the threshold values.

Also, the maximum allowed concentration for the NO₃⁻-N is 3 mg N/L. Thus, analyzing the graph in Fig. 8, it can be noticed that the value of the NO₃⁻-N indicator does not exceed the limit value at any of the 12 sampling points.

Small values were also obtained for the TP, which varied between 0.12 for the point S4 and 0.21 for the point S9 (Fig. 9). All these values are below the limit value of 0.8 mg P/L.

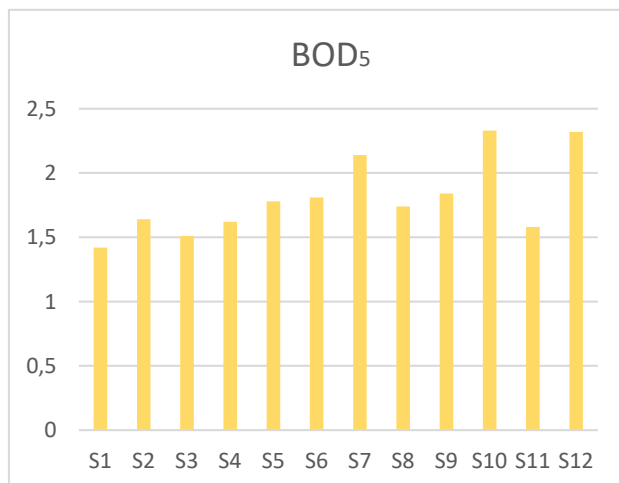


Fig. 5. Values for BOD₅, for the sampling points S1-S12 of Tulcea Sulina Channel, in the summer of 2021

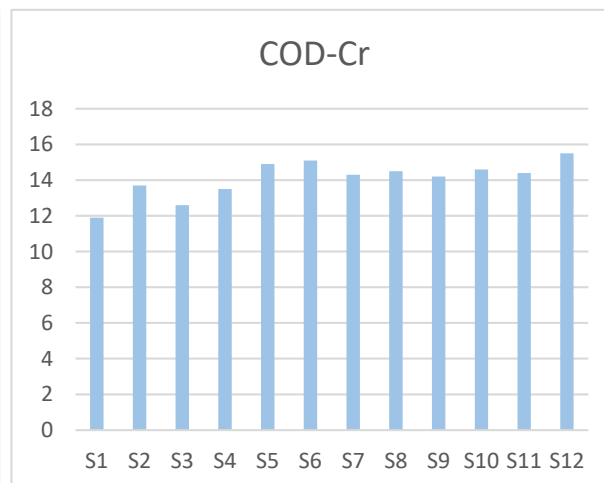


Fig. 6. Values for COD-Cr, for the sampling points S1-S12 of Tulcea Sulina Channel, in the summer of 2021

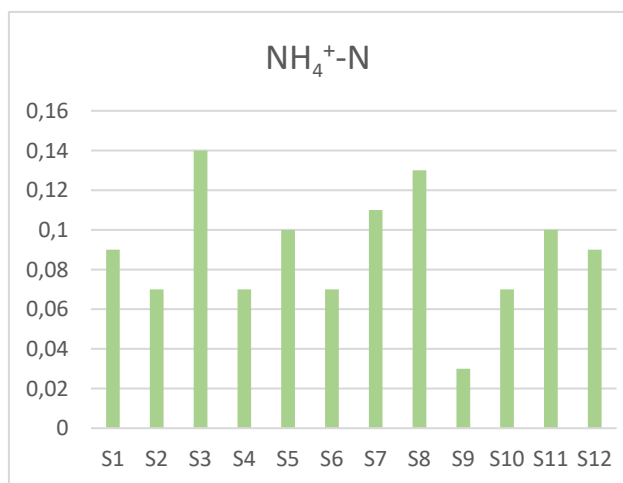


Fig. 7. Values for NH₄⁺-N, for the sampling points S1-S12 of Tulcea Sulina Channel, in the summer of 2021

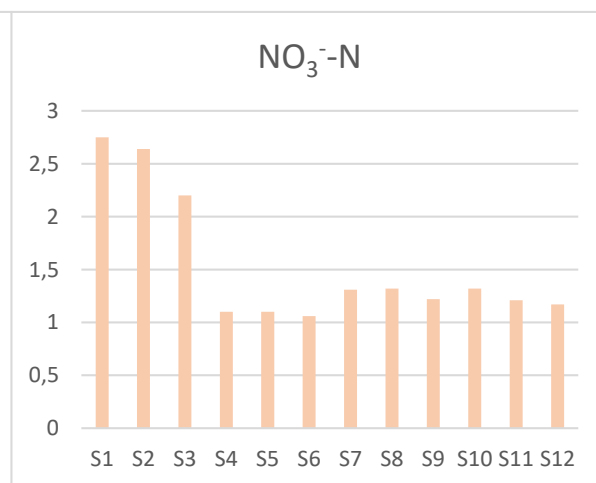


Fig. 8. Values for NO₃⁻-N, for the sampling points S1-S12 of Tulcea Sulina Channel, in the summer of 2021

As earlier mentioned, the pH was also measured (Fig. 10), but it was not used to calculate the WQI, as no significant changes in this indicator values were noticed. The determined pH ranged from 7.4 to 8.1, with the highest value of 8.1 recorded at the point S12- Sulina WWTP discharge tube, and the lowest value recorded at S10- Sulina drinking water treatment plant. The most common value was 7.5, which was recorded at 4 sampling points out of 12. These values are in the range of the usual pH values for the surface waters, which are between 6.5 and 8.2. Most aquatic organisms are adapted to a specific pH level and can die if the pH changes in a very short time. The pH can be affected by industrial waters or accidental discharge of pollutants.

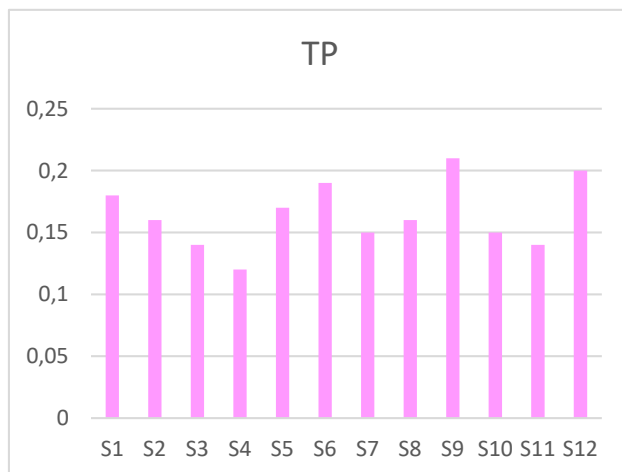


Fig. 9. Values for TP, for the sampling points S1-S12 of Tulcea Sulina Channel, in the summer of 2021

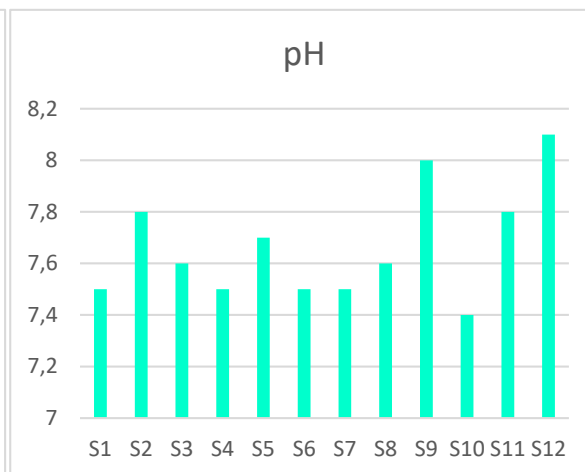


Fig. 10. Values for pH, for the sampling points S1-S12 of Tulcea Sulina Channel, in the summer of 2021

4. DISCUSSION

The water quality on the Tulcea-Sulina Channel was evaluated by monitoring these water quality indicators (by processing the results using the water quality index methodology, allowing the use of results and interpretations in surface water management, in accordance with national and European Union legislation).

The results obtained after using the water quality index (WQI) methodology, for the samples collected from the 12 monitoring points located on the Tulcea-Sulina Channel, during May-July 2021, are represented in Fig. 11.

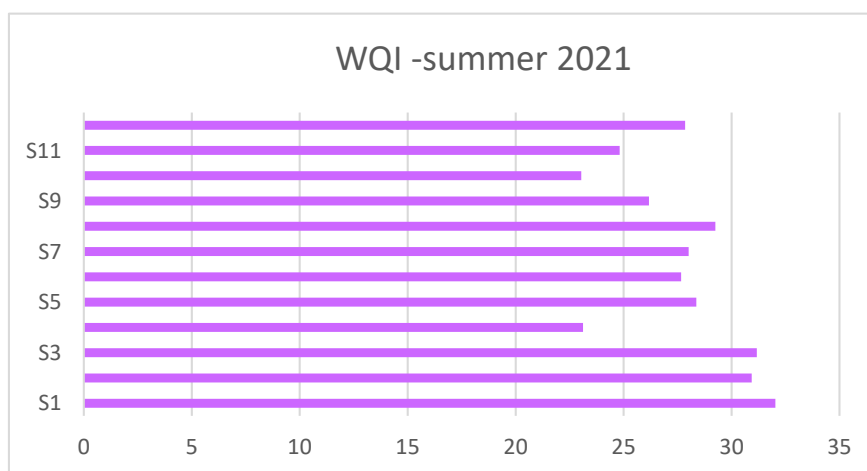


Fig. 11. WQI values for water sampling points S1-S12, in summer 2021

As can be seen in Fig. 11, the values obtained for the 12 monitoring points of the water samples fluctuate between a minimum of 23.12 for the S4-Maliuc station, and a maximum of 32.03 for the S1-Port Tulcea station. The sampling points that correspond to the values lower than 25 are part of the first category of water quality, which is the excellent category that allows the drinking water preparation, these points being S4, S10 and S11. The results obtained for the other locations were in

the range of 25-50, and therefore these values correspond to the second category of water quality - good ecological status.

Thus, following the monitoring of water quality on the Tulcea-Sulina canal for the period May-July 2021, promising results were obtained in terms of water quality at all 12 locations investigated in this study. However, in several locations the phenomenon of eutrophication has been observed, which might be due to the rich content of the nutrients in water (such as phosphorus or nitrogen), as results of the uncontrolled algae development (highlighted by the dark green color, visually observed). Therefore, this phenomenon was noticed near Sulina WWTP discharge tube -S12, where partially or insufficiently treated wastewater was discharged. Also, a higher level of eutrophication was observed in the smaller channels that flow into the Sulina branch, for example on the Old Danube channel, near Crişan.

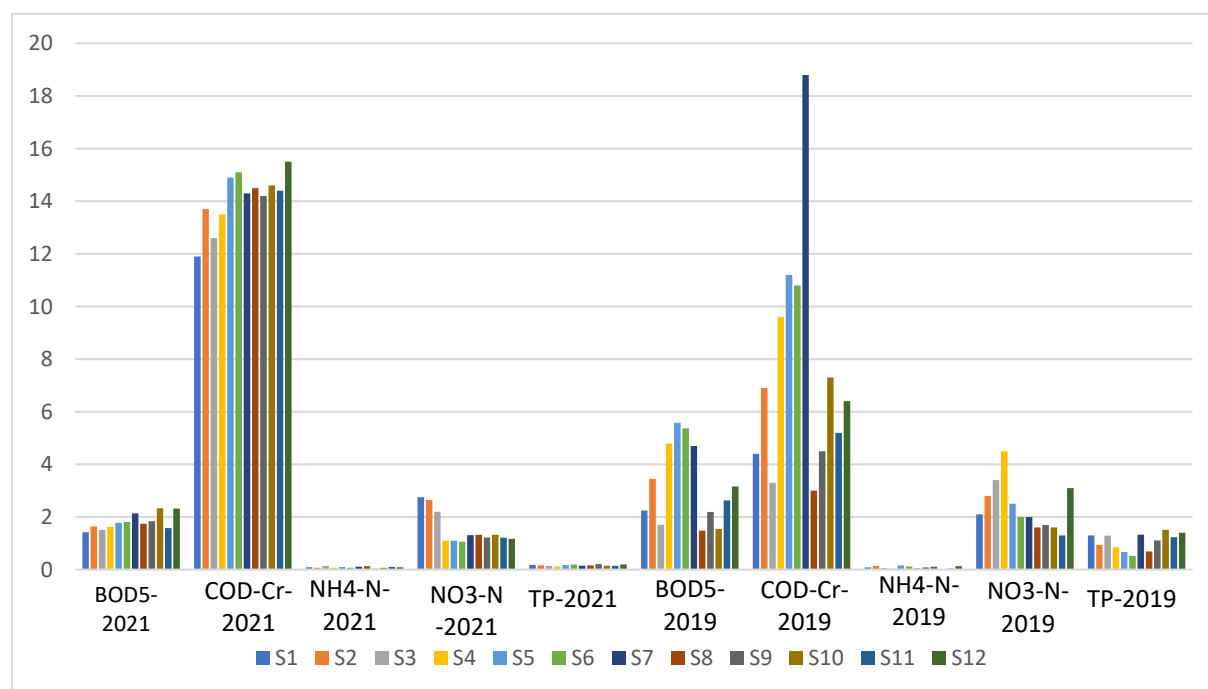


Fig. 12. Graphical representation of the values of indicators BOD₅, COD-Cr, NH₄⁺-N, NO₃⁻-N, TP, for the summer of 2019 and the summer of 2021

According to Fig. 12, it can be noticed that some of the BOD₅ values in 2019 exceed the limit value of 5 mg O₂/L, for the sampling points S5 and S6, while the BOD₅ values for 2021 did not exceed 2.4. The values of COD fall within the limits of the maximum allowed concentration of 25 mg O₂/L, both for 2019 and for 2021. The values of NH₄⁺-N are very similar, they remained approximately the same in 2021, in comparison with the year 2019.

In order to point out the similarities and differences of current water quality by comparison with the previous years, the results from the 2019 database were used as well (Cretescu et al, 2021). The comparison of historical data and the actual data is provided in Fig. 12, and finally the results in terms of WQI are provided in Fig. 13.

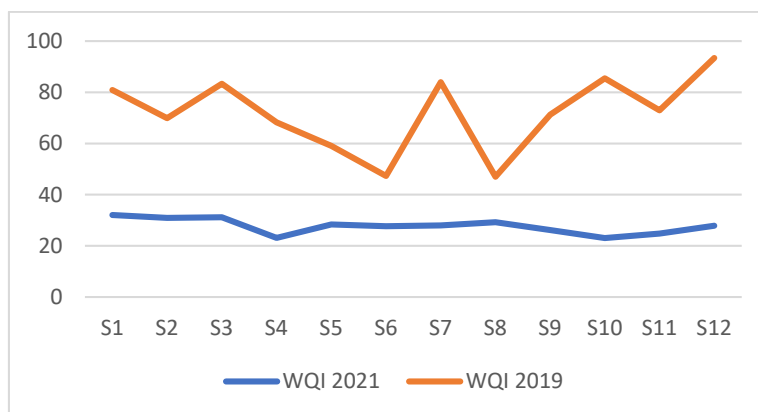


Fig. 13. Results of WQI values for summer 2019 and summer 2021, at the 12 monitoring locations

However, there are changes for the values of the NO_3^- -N, which are lower in 2021. In 2019, the values of this parameter exceeded the threshold of the limit value of 3 mg N/L only for 3 monitoring points, S3 – 3.4 mg N/L, S4 – 4.5 mg N/L and S12 – 3.1 mg N/L (Fig.12). Also, there are very high values in 2019 for the TP, which exceeded the limit value of 0.8 mg P/L in 9 sampling points out of 12. The highest value of the TP was observed in the sampling point S10 - 1.51, while the minimum value was observed in the sampling point S6 - 0.52.

The values of the WQI for 2019 fall into water quality classes II, III and IV, and the water quality corresponding to these classes is good, poor and very poor. Only for 2 sampling points the value of the WQI indicated that the water quality is good, these being the S6 and S8. The maximum value of 93.43 was identified for the S12, here the water quality is very poor, as well as in the S1, S3, S7 and S10. In the sampling points S2, S9 and S11 the quality of the water is poor. The water quality in 2021 appears at good or even excellent. This difference in WQI values is due to the TP indicator, which had high values for 2019.

By means of the databases provided by the Water Company from Tulcea (including the Wastewater Treatment Plant in Tulcea) and the International Commission for the Protection of the Danube River - ICPDR, the WQI was calculated for several monitoring locations, for previous years, namely: Patlageanca, Tulcea, Sulina and Kilia. These calculations were performed in order to form a general image of the water quality in the Danube Delta and to examine simultaneously and successively the changes that have taken place over the last years on the Tulcea-Sulina Channel.

Thus, the graphical representation of the WQI values in the water quality monitoring points Tulcea and Sulina for the years 2013-2020 is presented (Fig. 14).

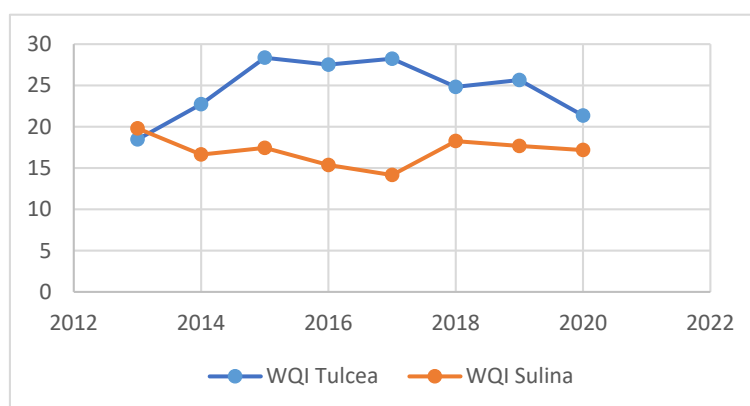


Fig. 14. Graphical representation of WQI values in Tulcea and Sulina monitoring points for the years 2013-2020

Analyzing the image above, it is found that the values obtained for the WQI in the Tulcea monitoring point are between 18 and 32, and those determined for the Sulina monitoring point are between 14 and 27. The values that are up to the limit of 25 suggest the fact that the water quality is excellent, while the values set in the range 26-50 indicate that the water quality is good. Also, the values acquired for Tulcea station are highlighted, which are higher than in Sulina station, from 2014 to 2021. Likewise, both in Tulcea and Sulina, the value of the WQI is higher in 2021, compared to the values obtained for the year 2020.

The comparative presentation of the WQI values in the Patlageanca (where the Danube is bifurcated in the two arms), Kilia and Sulina (where the Danube is discharged into the Black Sea) monitoring points for the years 2000-2017 is presented in Fig. 15.

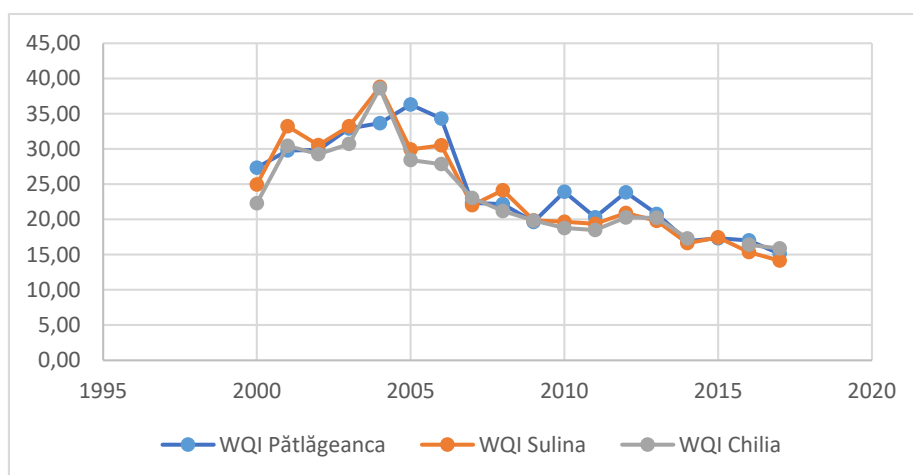


Fig. 15. The WQI values in the Patlageanca, Kilia and Sulina monitoring points for the years 2000-2017

There is a very good correlation between the values measured at the entrance (Patlageanca) and those at the exit (discharge into the Black Sea through the Chilia and Sulina branches). The values obtained for WQI are included in the first and second water quality classes, respectively the water quality was good and excellent.

In order to better highlight the contribution of each branch to the pollution of the Black Sea, Fig. 16 shows the annual values of the water quality index for a period between 2000 and 2017.

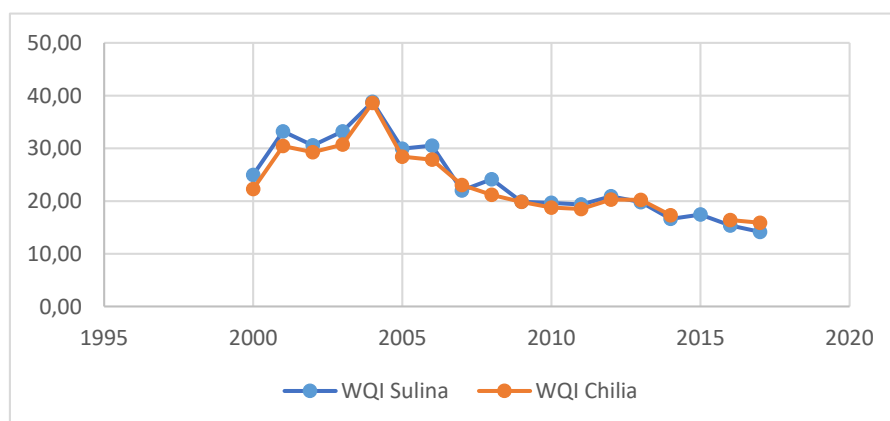


Fig. 16. Graphical representation of WQI values in Kilia and Sulina monitoring stations for the years 2000-2017

The same trend is observed in terms of water quality in both discharge points throughout the monitored period, although in recent years there has been a significant improvement in water quality compared to 2001-2006. In the period 2007-2017 the values of the water quality index is in the range of 0-25, which proves that the water flowing into the Black Sea was included in the first quality class.

5. CONCLUSIONS

The Danube Delta is part of the lower sector of the Danube River and is one of the most beautiful and special places in the world, being the UNESCO World Heritage Site. The hydrographic network of the Danube Delta consists mainly of the Chilia branch (Kilia) and the Tulcea branch, which splits into the Sulina branch and the St. George branch.

The industrialization process (intensified in the middle of the twentieth century) had a negative impact on the water quality in the Danube Delta. During the period of centralized planning systems, European countries did not develop comprehensive environmental protection policies that respond to the degradation of the river environment. Legal standards for environmental quality have often been neglected. The main tool for water body management is the installation of a water quality monitoring network.

In order to ensure a high level of water quality monitoring network, the European Union has implemented the necessary legislative acts, namely the Water Framework Directive and the Drinking Water Directive. As a result of these legislative acts, in Romania it was implemented a monitoring system that collects water quality data in order to determine the pollution sources in accordance with the water management plan.

This study was focused on the water quality monitoring in 12 points distributed along the Tulcea-Sulina Channel (S1- Tulcea port; S2- Hydrological station; S3- Partizani; S4- Maliuc; S5- Crisan fire station (entrance to Crisan); S6- Camping Crişan; S7- Leaving the Crisan town; S8- Imputita Channel (intersection with Sulina channel); S9- Imputita Channel (Belt channel); S10- Sulina drinking water treatment plant; S11- Sulina Port; S12- Sulina WWTP discharge tube), in May-July 2021 and the use of the information from the databases provided by the International Commission for the Protection of the Danube River (ICPDR) and the Water Company in Tulcea, respectively from scientific literature.

In order to avoid the risks regarding the deterioration of the ecological state of the water on the Tulcea-Sulina Channel, the following indicators were analyzed in this study: biochemical oxygen demand (BOD_5), chemical oxygen demand (COD-Cr), ammonium nitrogen (NH_4^+-N), nitrates nitrogen (NO_3^--N), total phosphorus (TP), pH.

The values of the above listed indicators (except the pH) were used to calculate the WQI (water quality index). Thus, the WQI in the 12 monitoring points generally showed a good ecological state of water quality in the Tulcea-Sulina Channel.

The comparative analysis of the values obtained for WQI in the 12 water monitoring points in the summer of 2021 with those recorded for the summer of 2019, showed that the water from the Tulcea-Sulina Channel in 2019 fell mainly into the third and fourth category, compared to the improved water quality in 2021. This difference in water quality is mainly determined by the total phosphorus indicator, which showed very high values in the summer of 2019.

Through the information provided by the databases previously mentioned, WQI was calculated in the monitoring points from Tulcea and Sulina for the years 2013-2020; the obtained values show that during these years the water quality, both in Tulcea as well as in Sulina, was included especially in the second category, but the WQI values for Tulcea from 2014 to 2020 were permanently higher than the values obtained in Sulina, which can be explained by the dilution caused by the discharge of channels adjacent to the navigable channel.

Following the comparative analysis of the values obtained for the water quality index for the years 2000-2017, in the monitoring points Patlageanca, Chilia and Sulina, it was found that, during this period, the water from these channels was classified in quality classes I and II. In the years 2001-2006,

the water quality was good for these three locations. In the years 2007-2017 there is a tendency to improve the water quality (due to the diminishing of the industrial activity), this being classified in the first category.

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