

# STUDY ON SURFACE WATER QUALITY OF CARSKA-BARA SPECIAL NATURE RESERVE AND DELTA (BALTA) NERA NATURE RESERVATION

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## Acknowledgment

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All project activities, outputs, photo gallery and visibility actions can be followed on project webpage: [www.aeps.upt.ro](http://www.aeps.upt.ro)

## 1. Special Nature Reserve “Carska bara”

### 1.1. Introduction

The Serbian Banat is spread over 9830km<sup>2</sup> which is almost half of the total area of AP Vojvodina and about 12% of total area in Serbia [1]. The total population is 623868 which is approximately 8.76% of the total population of Serbia and 32.5% of total population of AP Vojvodina [2]. Area of 85% of total administrative territory of Banat area is agricultural arable land which is over 16% of the total arable land of the Republic of Serbia.

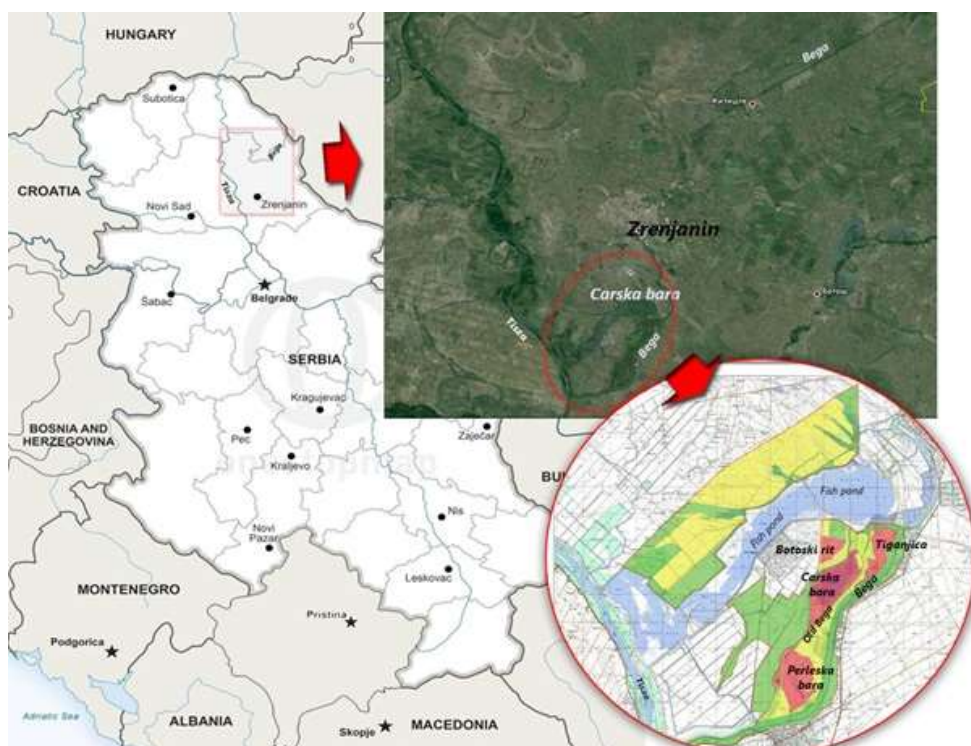
The Banat region is a plain with Deliblatska Pescara and Vrsac mountains (elevation 641 m) in the south. The most important natural waterways are certainly Danube and Tisa which are the borders of southern and western horizon of the region as well as numerous shorter rivers (Tamis, Karas, Nera, and Bega). Danube – Tisa – Danube Canal should also be mentioned.



Next to the Danube and the Tisza, Bega is the most important river in Banat and the largest tributary of the Tisza in our country. Bega River enters Republic of Serbia near settlement that is named Srpski Itebej and with its entire length, it flows through the Banat region, entering the Danube River

next to the Pancevo city at the very south of Banat region. Bega consists of two parts: the Old Bega and Bega canal (or navigable Bega). The two parts flow into one another at Klek, forming Bega which further flows through Zrenjanin, next to Ečka, Lukino Selo, Stajićevo and Perlez, to the confluence in the Tisza. From the source to the confluence length of the Bega is 244 km of which 67 km in Romania and 168 km in our country. Through the years Bega had changed directions, leaving the bayous along its course. One of the most famous bayous is Special Nature Reserve “Carska bara” that is located at the lower Bega course, occupying the area near Zrenjanin, between Tisza and Bega River.

This is one of the most preserved nature areas of Tisza and Bega river flood areas. The whole area is unique entity consisting of the numerous, single, aquatic ecosystems. Because of its nature values and its biodiversity as well, it is protected by national legislation like Special Nature Reserve “Carska bara” having three different levels of protection (Map 1).



Map 1 – Special nature reserve „Carska bara“ location and areas of different levels of protection (I protection zone - red area, II I protection zone- yellow areas, III protection zone- green areas)

Since Special Nature reserve “Carska bara” was the flood area of two rivers, now it represents complex area of wetlands, forests, meadows and steppes ecosystems that are rich in biodiversity typical for Pannonia plane. Hence, there are more than 500 plants, 239 birds (e.g. all 8 European herons are nesting at this area), 20 fish and 30 mammals (otter, wild cat, Spermophilus, Microtus arvalis etc.) species [3].



*Photo 1 – Special nature reserve „Carska bara” - view*

## 1.2. National and international classification of Special Nature Reserve “Carska bara”

According to the Law on nature protection [4], Special Nature Reserve “Carska bara” is classified as I category - protected area of international, national and exceptional importance [5].

According to the classification of the International Union for Conservation of Nature (IUCN), Special Nature Reserve “Carska bara” is classified as „IUCN Category IV” - Habitat and species management area [6].



*Photo 2 – Special nature reserve „Carska bara“ – fauna view*

International status of Special Nature Reserve “Carska bara” is classified as follows [7]:

- Ramsar area - wetland of international importance (International Convention on wetlands -Ramsar Convention) [8].
- IBA area- Important Bird and Biodiversity Area (IBA) for Europe [9].
- IPA area -Indigenous Protected Areas important for Central and East Europe [10].
- Emerald Network of Areas of Special Conservation Interest-area of exceptional importance for nature protection [11].

### 1.3. Environmental pressures

Due the unfavourable climate conditions during past decades and lack of good management practice in water streams regulation, the Special Nature Reserve „Carska bara“ is dealing with the huge pressures that jeopardize its environment quality and natural values.

Thus, huge freshwater fish pond that deals with intensive fish production is located near the protected area of „Carska bara“. There are several separate fishponds speeding in total area of 1700ha. The vicinity and

intensive fish growing endanger protected area by different nutrients contained in fish food and chemicals for fish ponds maintenance as well. The company that manage the fishponds is also in charge of Special Nature Reserve „Carska bara“ management.



*Photo 3 – Special nature reserve „Carska bara“ – flora view*

Additionally, excavation of new reclamation canal system in this agricultural area represents huge environment pressure, contributing to the nature devastation, mainly due the pesticide and fertilizers transport from soil to the aquatic ecosystem. Also, due the rainy seasons, waters rich in nutrients goods surrounding area, contributing to intensive eutrophication process and consequently production of more bottom sludge. This leads to the reduction of water surface and transformation aquatic system to the wetland. In this area this processes are very progressive, representing the primary problem of the Special Nature Reserve „Carska bara“. According to the some research [12] the sludge depth is more than 3m, and the height of the water column is only 40cm [13]. The process of sludge generation is the most intensive at the 15th km of the protected area. Hence, strong and fast changes in the water regimes leads



to the extinction of some valuable nature values like characteristic species. In general it leads to the biodiversity reduction.

Also, a shipyard located near the protected area contribute in environment pollution especially in noise and light pollution that intensively disturbs birds.



*Photo 4 – Special nature reserve „Carska bara“ – “Starji Begej” canal view*

The focus of this Study was on raising the awareness of NGO's and public institutions responsible experts on the need of protecting cross-border nature reservations Djerdap / Iron Gate national park and Carska Bara special nature reserve and environment.

#### 1.4. Limit values of pollutants in surface waters, Serbia

Legislative concerning water management and limit values for pollutants in surface and underground waters and sediments, are harmonized with EU Directives (reference).

According to the Regulation on Determining Water Bodies of Surface and Groundwater [14], Bega River is classified as Type 1-large, plain rivers.

Limit values for measured parameters are defined in the Regulation on limit values of pollutants in surface waters, underground waters and

sediments and deadlines for reaching the limit values [15] and Regulation on the parameters of ecological and chemical status of surface waters and parameters of chemical status and quantitative status of groundwater [16] (Table 1).



Photo 5 – Special nature reserve „Carska bara“ – view

Table 1. Limit values for parameters analysed in surface waters

Parameter	Unit	Limit values				
		I class*	II class*	III class*	IV class*	V class*
pH		6,5-8,5	6,5	8,5	6,5	>6,5 or >8,
Dissolved oxygen (DO)	mgO <sub>2</sub> /l	8,5	7	5	4	>4
Nitrates	mg/l	1	3	6	15	>15
Nitrites	mg/l	0,01	0,03	0,12	0,3	>0,3
Orto phosphate (PO <sub>4</sub> -P)	mg/l	0,05	0,2	0,4	1	>1
Sulphates	mg/l	50	100	200	300	>300
Biochemical oxygen demand (BOD)	mgO <sub>2</sub> /l	2	5	7	25	>25
Chemical oxygen demand (COD)	mgO <sub>2</sub> /l	10	25	50	125	>125
Conductivity	mS/cm	<1000	1000	1500	3000	>3000

\*I class – The class description corresponds to the high ecological status. Based on the limit values of quality elements, surface waters in this class provide conditions for the functioning of the ecosystem, existence and protection of fish (cyprinids and salmonids), and they can be used for the following purposes: drinking water supply with prior filtration and disinfection treatments, bathing and recreation, irrigation, and industrial use (process and cooling water).

II class – The class description corresponds to good ecological status. Based on the limit values of quality elements, surface waters in this class provide conditions for the functioning of the ecosystem, existence and protection of fish (cyprinids) and can be used for the same purposes and under the same conditions as surface waters in class I.

III class – The class description corresponds to moderate ecological status. Based on the limit values of quality elements, surface waters in this class provide living conditions and protection of cyprinids and can be used for the following purposes: drinking water supply with prior coagulation, flocculation, filtration, and disinfection treatment, bathing and recreation, irrigation, and industrial use (process and cooling water).

IV class – The class description corresponds to poor ecological status. Based on the limit values of quality elements, surface waters in this class can be used for the following purposes: drinking water supply with a combination of previously mentioned treatments and advanced treatment methods, irrigation, and industrial use (process and cooling water).

V class – The class description corresponds to bad ecological status. Surface waters in this class cannot be used for any purpose.

Limit values for metals are defined in Regulation on limit values of pollutants in surface waters, underground waters and sediments and deadlines for reaching limit values [15], and Regulation on limit values of priority and priority hazardous surface waters pollutants and deadlines for reaching limit values [17] (Table 2 and Table3).

Table 2. Limit values of pollutants in surface waters.

Parameter	Unit	Limit values <sup>(1)</sup>				
		Class I <sup>(2)</sup>	Class II <sup>(3)</sup>	Class III <sup>(4)</sup>	Class IV <sup>(5)</sup>	Class V <sup>(6)</sup>
Arsenic (As)	µg/l	<5 (or PN)	10	50	100	>100
Bor (B)	µg/l	300 (or PN)	1000	1000	2500	>2500
Copper (Cu)	µg/l	5 (T=10)	5 (T=10)	500	1000	>1000
		22 (T=50)	22 (T=50)			
		40 (T=100)	40 (T=100)			
		112 (T=300)	112 (T=300)			
Zinc (Zn)	µg/l	30 (T=10)	300 (T=10)	2000	5000	>5000
		200 (T=50)	700 (T=50)			
		300 (T=100)	1000 (T=100)			
		500 (T=500)	2000 (T=500)			
Chromium (total) (Cr)	µg/l	25 (or PN)	50	100	250	>250
Iron (total) (Fe)	µg/l	200	500	1000	2000	>2000
Manganese (total) (Mn)	µg/l	50	100	300	1000	>1000

(1) Unless otherwise stated, values are expressed as total concentrations in the sample

(2) The class description corresponds to the high ecological status based on the classification provided in the Regulation which prescribes parameters for ecological and chemical status of surface waters. Based on the limit values of quality elements, surface waters in this class provide conditions for the functioning of the ecosystem, existence and protection of fish (cyprinids and salmonids), and they can be used for the following purposes:

drinking water supply with prior filtration and disinfection treatments, bathing and recreation, irrigation, and industrial use (process and cooling water).

(3) The class description corresponds to the good ecological status based on the classification provided in the Regulation which prescribes parameters for ecological and chemical status of surface waters. Based on the limit values of quality elements, surface waters in this class provide conditions for the functioning of the ecosystem, existence and protection of fish (cyprinids) and can be used for the same purposes and under the same conditions as surface waters in class I.

(4) The class description corresponds to the moderate ecological status based on the classification provided in the Regulation which prescribes parameters for ecological and chemical status of surface waters. Based on the limit values of quality elements, surface waters in this class provide living conditions and protection of cyprinids and can be used for the following purposes: drinking water supply with prior coagulation, flocculation, filtration, and disinfection treatment, bathing and recreation, irrigation, and industrial use (process and cooling water).

(5) The class description corresponds to the poor ecological status based on the classification provided in the Regulation which prescribes parameters for ecological and chemical status of surface waters. Based on the limit values of quality elements, surface waters in this class can be used for the following purposes: drinking water supply with a combination of previously mentioned treatments and advanced treatment methods, irrigation, and industrial use (process and cooling water).

(6) The class description corresponds to the bad ecological status based on the classification provided in the Regulation which prescribes parameters for ecological and chemical status of surface waters. Surface waters in this class cannot be used for any purpose.

Table 3. Environmental quality standards for the first and second group of priority substances.

Hazardous pollutant	CAS No.	Average annual concentration (µg/l)	Maximal allowed concentration (MAC) (µg/l)
Cadmium and cadmium compounds (depending on water hardness) <sup>1</sup> (Cd)	7440-43-9	<0,08 (class 1)	<0,45 (class 1)
		0,08 (class 2)	0,45 (class 2)
		0,09 (class 3)	0,6 (class 3)
		0,15 (class 4)	0,9 (class 4)
		0,25 (class 5)	1,5 (class 5)
Mercury and mercury compounds (Hg)	7439-97-6		0,07
Lead and lead compounds (Pb)	7439-92-1	1,2 <sup>3</sup>	14
Nickel and nickel compounds (Ni)	7440-02-0	4 <sup>3</sup>	34

<sup>1</sup>For cadmium and its compounds, the value of environmental quality standards varies depending on the water hardness, which is categorized into five classes (class 1: <40 mg CaCO<sub>3</sub>/l, class 2: 40 to <50 mg CaCO<sub>3</sub>/l, class 3: 50 to <100 mg CaCO<sub>3</sub>/l, class 4: 100 to <200 mg CaCO<sub>3</sub>/l, and class 5: ≥200 mg CaCO<sub>3</sub>/l). <sup>3</sup> These values of environmental quality standards indicate the concentrations of the substance that are bioavailable.

### 1.5. Sampling sites, Carska-Bara/Bega

Sampling was provided during three monitoring campaigns (in July, September and October) at 4 sampling sites located in I, II and III level of protection areas. Table 4 represents samplings names and coordinates (Map 2)

Table 4. Samplings names and coordinates.

Sample No	Samplig site name	Protection zone	Coordinates
SS13	Bega, before the dam	III	N45°14'58.96" E20°24' 06.70"
SS14	Bega , before „Tractor bara“	III	N45°16' 57.85" E20°26' 12.84'
SS15	„Carska bara“ (14km)	I	N45°15' 58.19" E20°24' 44.67'
SS16	„Carska bara“ (21km)	II	N45°13'01.8'3 E20°21' 57.43"

For sampling action, a license from Provincial Institute for Nature Conservation was provided (Annex 1). During the July, sampling was limited on SS13 and SS14, because of highs season for birds nesting (Table 5). During the sampling campaign in October, due the unfavourable weather (rainy days), sampling at SS15 was not abled and allowed because of road that could be damaged by terrain car.

Table 5. Samplings dynamics.

Sampling Abb.	July	September	October
SS13	✓	✓	✓
SS14	✓	✓	✓
SS15	-	✓	✓
SS16	-	✓	-



Map 2 – Sampling sites location (I protection zone - red area, II I protection zone- yellow areas, III protection zone- green areas).

Water sampling was provided by the telescopic sampler with the sampling vessel. Samples were taken at the central part of the river water flow and from 50 cm of water surface depth. Air and water temperature, pH, dissolved oxygen (DO), conductivity and total dissolved solids (TDS) were measured at the site. For laboratory analysis water samples were transported to the laboratory in mobile freezer at the temperature of 4 °C.



*Photo 5 – First sampling campaigns (July 2020)*



Photo 6 – Second sampling campaign (September 2020)



*Photo 7 – Third sampling campaign (October 2020)*

### 1.6. In-situ and laboratory analysis, Carska-Bara/Bega

Using the multi-parameter handheld instrument (Lovibond® Water Testing Tintometer® Group SensoDirect 150 (Set 1) pH / Con / TDS / Oxi / Temp) the determination of dissolved oxygen (O<sub>2</sub>), oxygen concentration, conductivity, TDS, pH and ORP were provided at the sampling site (Photos 8 and 9). Measurements methods for terrain measurement are presented in Table 6.



Table 6. Measurement methods for terrain measurement.

Parameters	Measurement methods
Water temperature, pH dissolved oxygen, conductivity, TDS	User manual for multi-parameter handheld instrument (Lovibond® Water Testing Tintometer® Group SensoDirect 150 (Set 1) pH / Con / TDS / Oxi / Temp)
Air temperature	Thermometer



Photo 8 – Multi-parameter instrument



Photo 9 – In-situ measurements

In laboratory, the concentration of ammonia, nitrates, nitrites, sulphates, phosphates, chemical oxygen demand (COD), biological oxygen demand (BOD) and heavy metals were determined.

The laboratory analysis of the ammonia were provides in the same day as the sampling. Samples for nitrates, nitrites and phosphates were conserved with sulphuric acid and kept at the 4 °C prior the analysis. Samples for sulphates were stored at 4 °C prior the analysis.

Samples for metals analysts were conserved with nitrous acid and kept at the 4 °C prior the analysis. However, all the samples were analysed within the 7 days form sampling campaigns.

Methods for parameter analysis are presented in Table 7.

Table 7. Methods for parameter analysis in samples of Carska-Bara.

Parameters	Measurement methods
BOD	Manometry, equipment manufacturer's instructions
COD	Dichromatic method / Spectrophotometry
NH <sub>4</sub> -N	Spectrophotometry, User manual for Photometer HANNA HI 83200 (Adaptation of the ASTM Manual of Water and Environmental Technology, D1426-92, Nessler method )
NO <sub>3</sub> -N	Spectrophotometry, User manual for Photometer HANNA HI 83200 (Adaptation of the cadmium reduction method)
NO <sub>2</sub> -N	Spectrophotometry, Use manual for Photometer HANNA HI 83200 (Adaptation of the EPA Diazotization method 354.1)
(PO <sub>4</sub> -P)	Spectrophotometry, Use manual for Photometer HANNA HI 83200 (Adaptation of the Ascorbic acid method)
SO <sub>4</sub> <sup>2-</sup> [Sulphates]	Spectrophotometry, Use manual for Photometer HANNA HI 83200 (Sulphate is precipitated with barium chloride crystals)
Metals	ICP-OES equipment - Perkin Elmer Optima 8300 and version 5.0 WinLab software.



Photo 10 – Laboratory analysis

### 1.7. Physical-chemical parameters of Carska-Bara/Bega surface water

All samples in all sampling campaigns had a low turbidity. Samples had no odour.

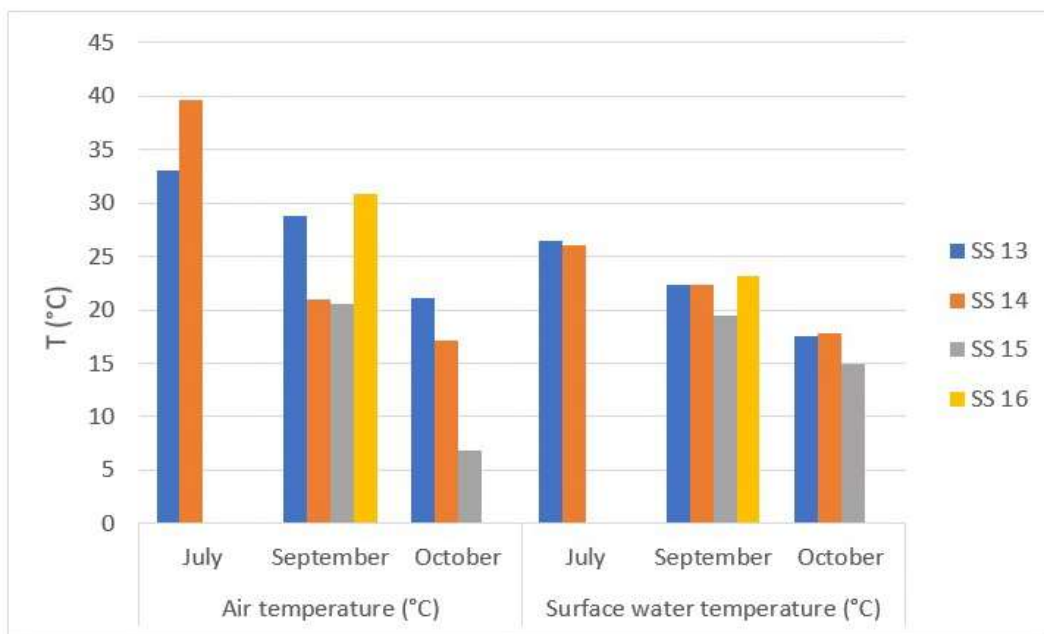


Fig. 1 – Air temperature and surface water temperature (°C)

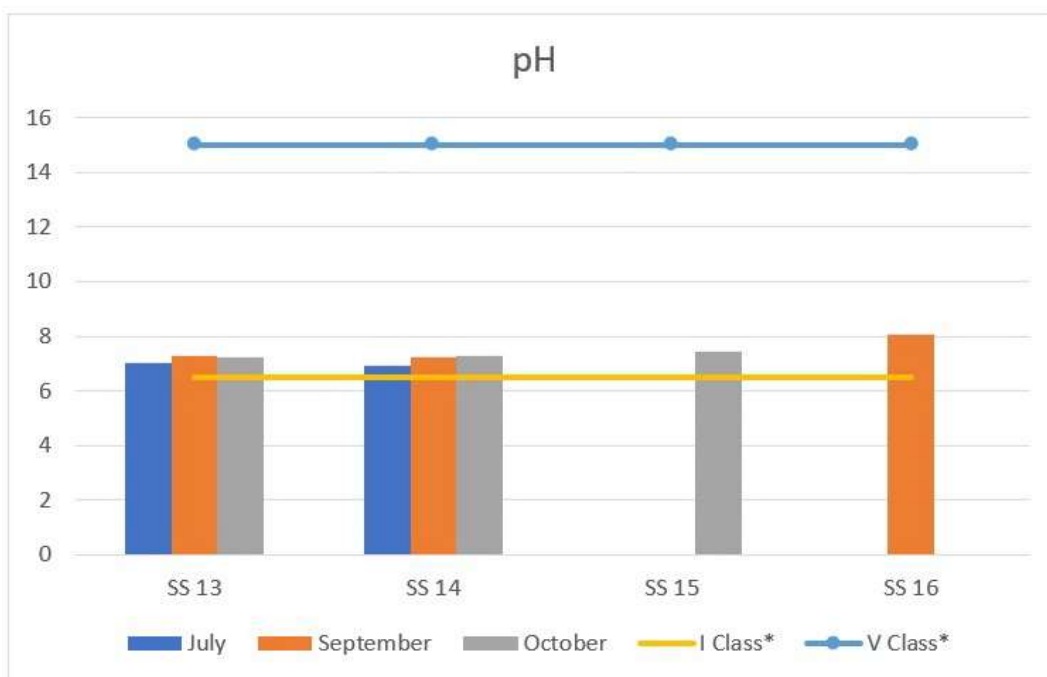


Fig. 2 – pH values

I, II, and III class have a same limit values for pH. All rivers that have  $6.5 > \text{pH} > 8.6$  are the rivers classified like IV and V class of quality. Samples in all three sampling season are classified into the I<sup>st</sup> class according to the pH value.

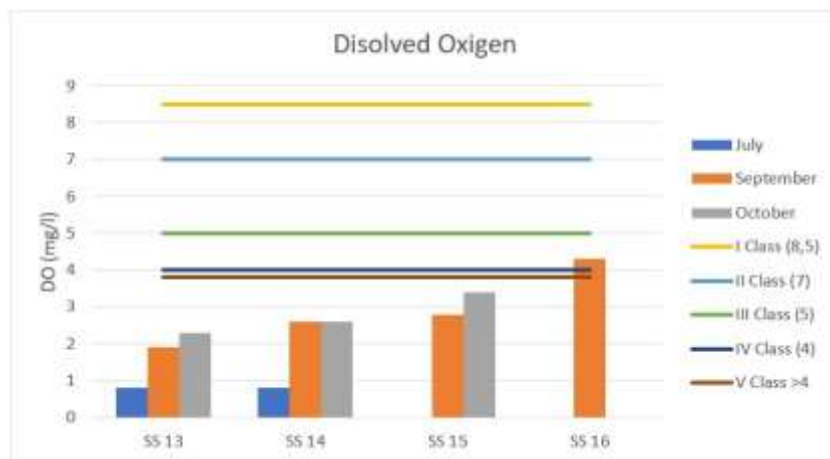


Fig. 3 – Dissolved oxygen (DO) (mg/l)

According to the concentration of dissolved oxygen almost all the samples were in V class for surface water quality that means that concentration was below 4 mg/l. However, only sample taken at sampling site No16 during September had a slightly higher dissolved oxygen concentration that classified it as an IV class of surface water quality.

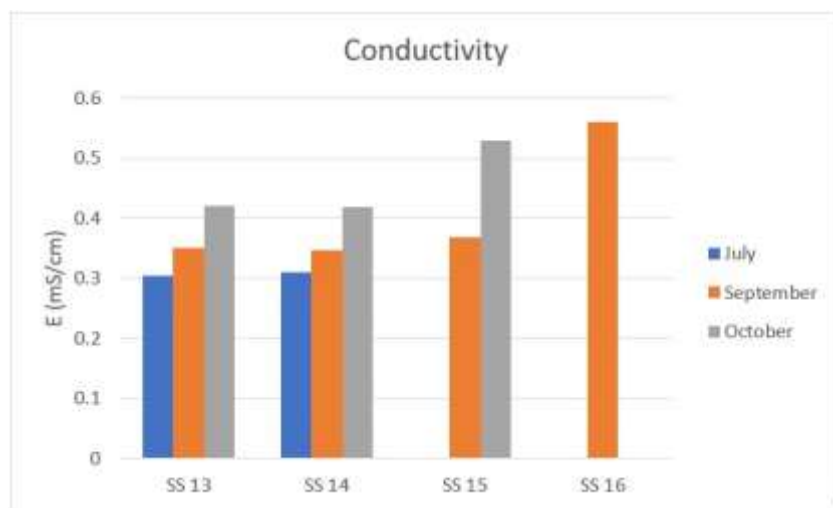


Fig. 4 – Conductivity (mS/cm)

Value less than 1000 mS/cm or natural level is defined for the I<sup>st</sup> water quality class. From the monitoring campaigns during the three seasons we can conclude that there slightly increasing trend in conductivity. The

minimum values of 0.30 mS/cm were measured at SS13 in July, maximal value of 0.56mS/cm were measured at SS16 during the September. Average value were 0.43 mS/cm. All the values were below LV for the I<sup>st</sup> class of surface water quality.

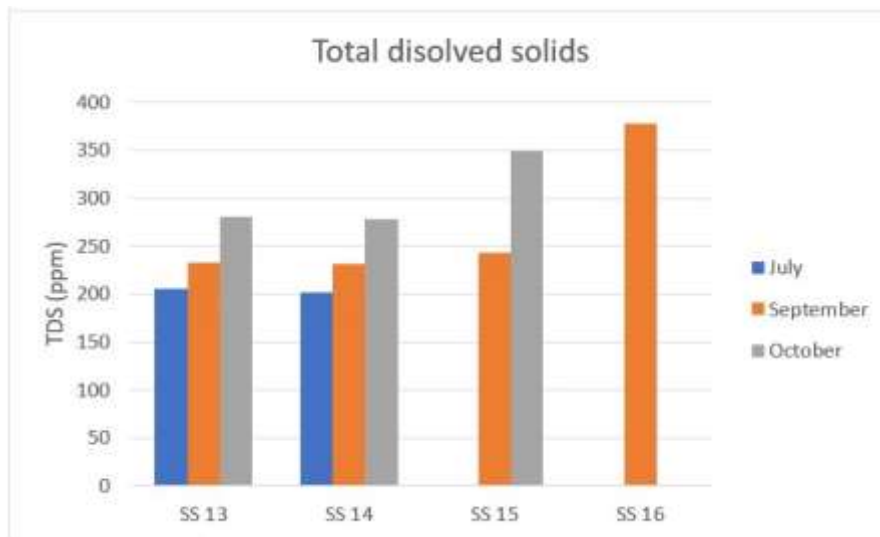


Fig. 5 – Total dissolved solids (ppm)

Limit value is not defined for this parameter. From the monitoring campaigns during the three seasons we can conclude that there slightly increasing trend in conductivity. The minimum values of 202 ppm were measured at SS14 in July and maximal value of 378 ppm were measured at SS16 during the September.

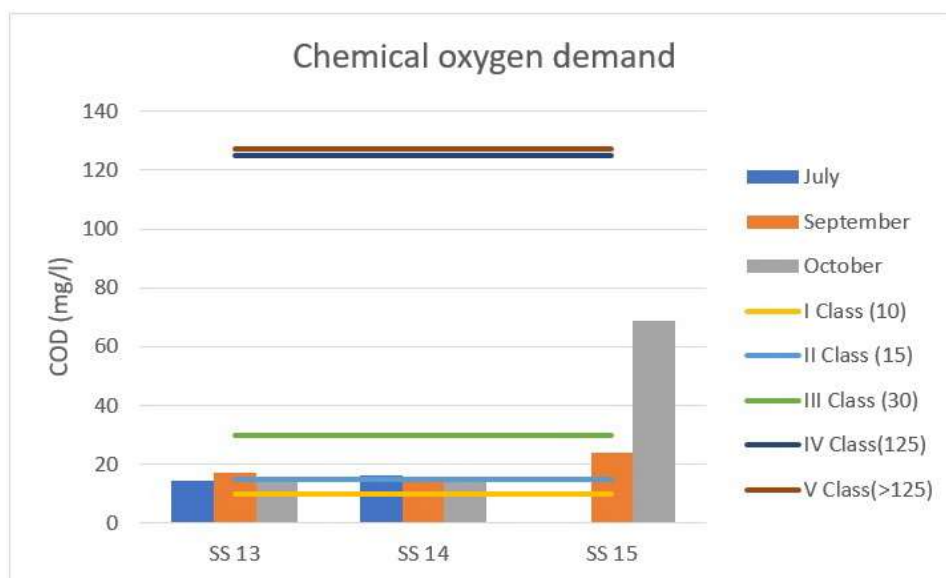


Fig. 6 – Chemical Oxygen demand (mgO<sub>2</sub>/l)

According to the results of all three monitoring campaign we can concluded that COD were mostly in the range of II<sup>nd</sup> class. Extremely high value of 69 mgO<sub>2</sub>/l were measured in October at SS15 that classifies that sample in III class. Minimum COD of 14.3 mgO<sub>2</sub>/l was measured in July at SS13. Average COD value were 21.32mgO<sub>2</sub>/l.

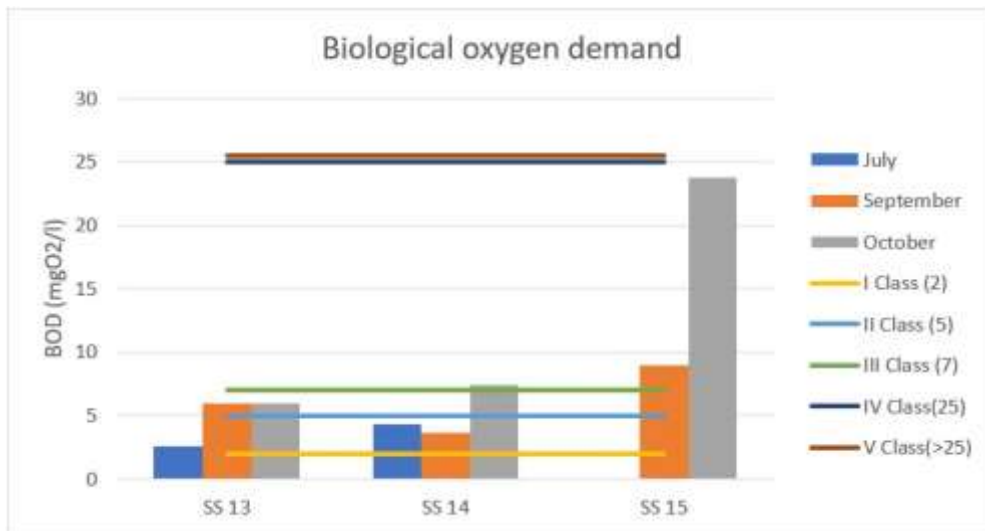


Fig. 7 – Biological Oxygen demand (mgO<sub>2</sub>/l)

All the samples were in the range of II and IV class of surface water. In July were recorded the minimal BOD values that classified both, SS13 and SS14, samples into the II class for surface water. In September, all the samples were classified into the different surface water classes. Sample SS13 were III class, sample SS15 were II class and SS15 were in III class. In October were, only SS13 remained in III class, while SS14 and SS15 were classified into the IV class of surface water quality.

Minimum BOD of 2.56 mgO<sub>2</sub>/l were measured in July at SS 13 and maximum of 23.80 mgO<sub>2</sub>/l at SS15 during the October. Average BOD was 7.83 mgO<sub>2</sub>/l.

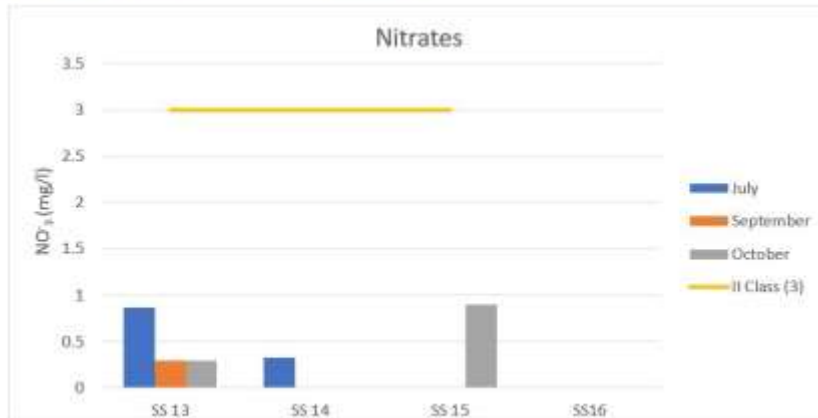


Fig. 8 – Nitrates concentration in Carska-Bara/Bega surface water (mg/l)

Concentration of nitrates ( $\text{NO}_3^-$ ) were extremely low, classifying all the samples into the 1<sup>st</sup> class for surface water quality. In some samples (SS14, SS15 and SS16 in September and S14 in October) concentrations were below the detection limit. Maximum nitrates concentration of 0.90 mg/l were measured in July at SS13. Average concentration for all three monitoring campaigns were 0.34 mg/l.

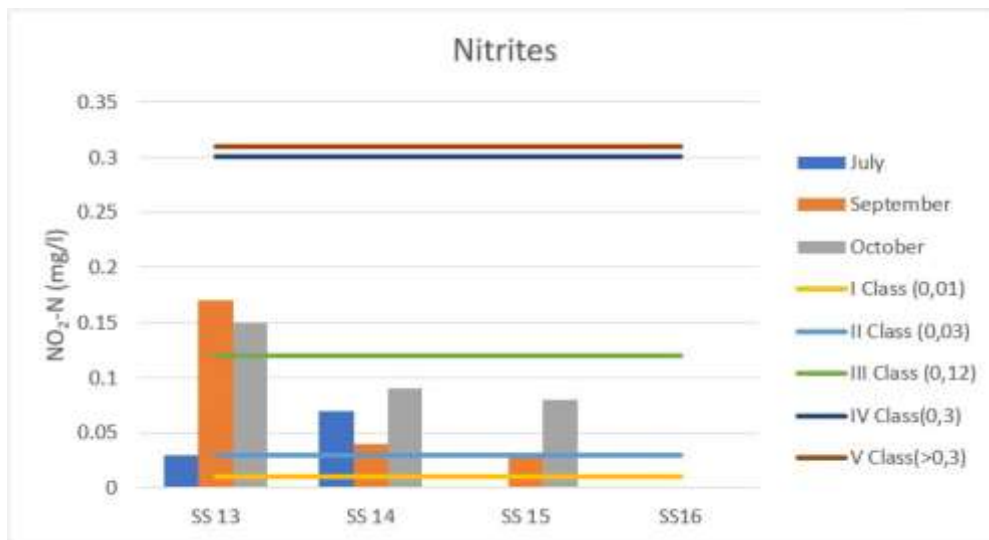


Fig. 9 – Nitrites concentration in Carska-Bara/Bega surface water (mg/l)

Concentration of nitrites ( $\text{NO}_2^-$ ) were high, especially at SS13. At SS13 samples taken in September and October were classified into the IV class of surface water quality. At SS14, nitrite concentrations were lower in comparison to the SS13, but still very high, classifying most of the samples into the III class for surface water quality. At SS16 nitrite concentration were very low. During all measurement campaign the highest nitrite

concentration were measured in October. Maximum nitrites concentration of 0.17 mg/l were measured in September at SS13.

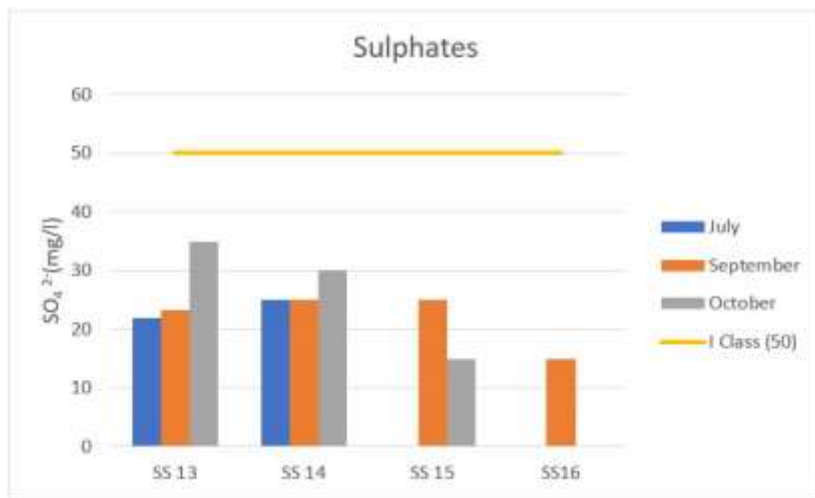


Fig. 10 – Sulphates concentration in Carska-Bara/Bega surface water (mg/l)

Concentration of nitrates ( $\text{SO}_4^{2-}$ ) were extremely low, classifying all the samples into the I<sup>st</sup> class for surface water quality. Minimum concentration of 15 mg/l were measured at SS15 during the October. Maximum concentration of 35 mg/l were measured at SS13 during the October. Average concentration of sulphates was 25.04 mg/l.

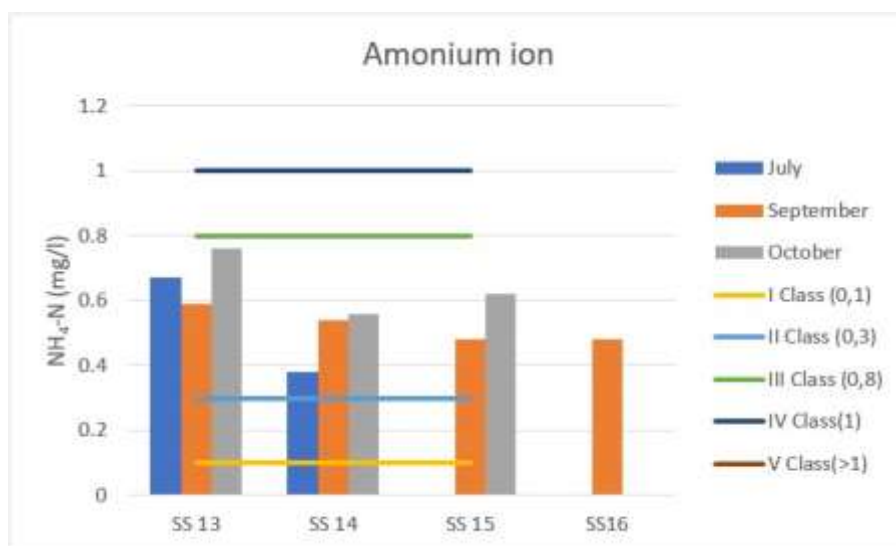


Fig. 11 – Ammonium ion concentration in Carska-Bara/Bega surface water (mg/l)

All the samples during all three monitoring campaign were classified in III class of surface water quality. Maximal concentration (0.76 mg/l) were measured at SS13 in October, and minimal concentration (0.38 mg/l) were



measured at SS14 in July. In general, there are increasing trend for all sampling sites.

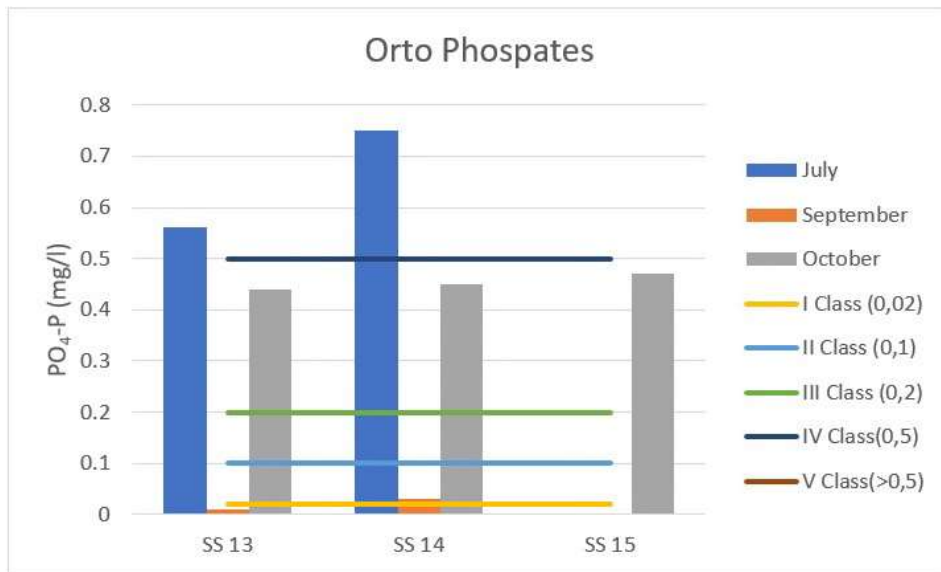


Fig. 12 – Orthophosphates concentration in Carska-Bara/Bega surface water (mg/l)

Arsenic was detected only in July. In sample S13 were detected 37.30 µg/l, and in S14 22.64 µg/l. In all samples taken during the monitoring campaigns in September in October concentration of As were below instrument detection limit (0.0041 mg/l).

In all samples concentrations of Cadmium, Cobalt, Mercury, Copper and Nickel were below instrument detection limit (DL: Cd-0.0019mg/l, Co-0.021mg/l, Hg-0.0378mg/l, Co-0.006 mg/l, Ni-0.0025 mg/l).

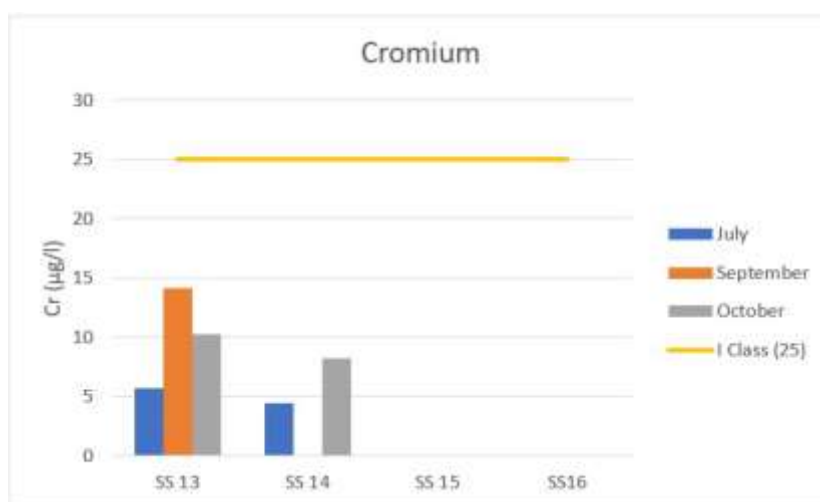


Fig. 13 – Chromium concentrations in Carska-Bara/Bega surface water (µg/l)

Concentration of chromium was extremely low in all samples during all three sampling campaigns. According to this metal, all samples were classified as 1<sup>st</sup> class of surface water quality.

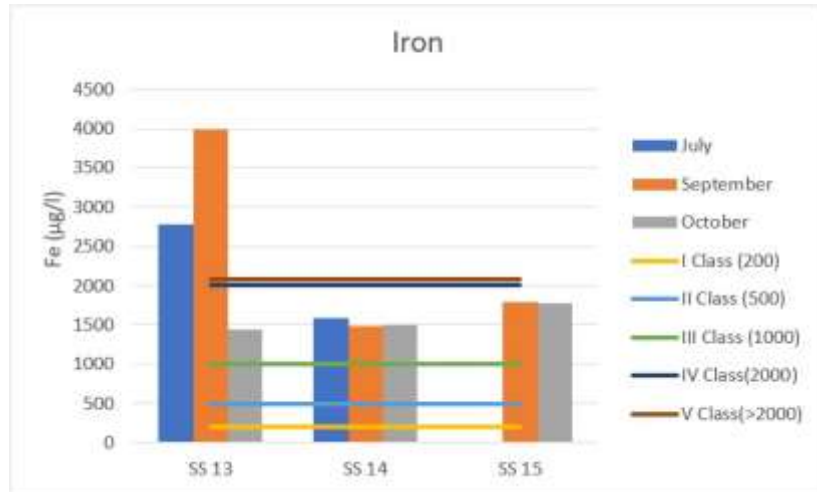


Fig. 13 – Iron concentrations in Carska-Bara/Bega surface water (µg/l)

Concentration of iron was very high in all samples reaching the IV and V class for surface water quality. Concentration at SS13 were highest in July and September and that classified that samples into V class for surface water quality. Maximum iron concentration of 3891.18 µg/l were measured at SS13 in September reaching the V class for surface water quality. Minimum iron concentration, but still very high, of 1439.45 µg/l was measured at the same sampling site in October.

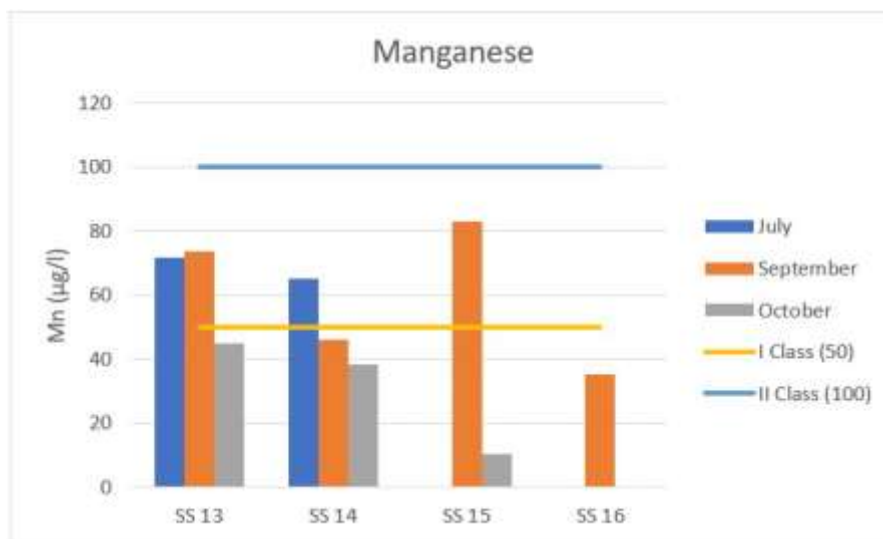


Fig. 14 – Manganese concentrations in Carska-Bara/Bega surface water (µg/l)

Concentration of manganese in samples taken in July at SS13 (71.82  $\mu\text{g/l}$ ) and SS14 (65.34  $\mu\text{g/l}$ ) were classified in II class for surface water quality. Samples taken at SS13 and SS15 in September were also classified in II class for surface water quality, while samples SS14 and SS16 were in I<sup>st</sup> class for surface water quality. All samples taken in October were classified as I<sup>st</sup> class for surface water quality. Maximal manganese concentration of 82.97  $\mu\text{g/l}$  were measured in September at SS15, minimal concentration of 10.46  $\mu\text{g/l}$  were at same sampling site in October. In general, manganese concentration has a decreasing trend for all sampling sites during the monitoring campaign.

Maximal allowed concentration (MAC) for lead is 14 mg/l. Concentration measured at all measurement sites were extremely low or below the instrument detection limit (0.0013 mg/l). Maximal lead concentration (31.88  $\mu\text{g/l}$ ) were measured at SS14 in October.



Fig. 15 – Zinc concentrations in Carska-Bara/Bega surface water ( $\mu\text{g/l}$ )

Limit values for Zinc for I<sup>st</sup> and II<sup>nd</sup> classes depend on  $\text{CaCO}_3$  concentration (mg/l) (Table 2). Since we sample different types of water bodies, Bega River that is navigable and its bayou “Carska bara” we could talk on different  $\text{CaCO}_3$  concentration [18]. However, zinc concentrations for all samples was very low, below the limit value defined for surface water with lowest  $\text{CaCO}_3$  content.



*Photo 11 – View of Carska-Bara ponds*

## 2. Nature reserve “Balta Nera”, the newest Delta in Europe

### 2.1. Introduction

The reservation is part of the European Biogeographical Region, according to European norms and is classified as nature reserve class IV-IUCN, with specific wetlands protected habitats. The Balta Nera reserve is relatively difficult to access, in her vicinity one can drive on DN57 from East or DJ57A from north, by the junction of Nera and Danube Rivers. The area covered by Ramsar protection is 10 hectares. The reservation is located on the administrative territory of Socol commune, Caras-Severin County, being an integral part of the Iron Gates Natural Park. It was declared Nature reserve in 1994 by Decision of Caras-Severin County Council, reconfirmed by law 5/2000 - regarding the approval of the National Territory Planning Plan - Section III - protected areas.



*Photo 12 – Aerial view of Balta Nera [19]*

The territory is located in the land of the Western Carpathians, the land of the Banat Mountains, the geomorphological unit of the Locva Mountains which are part of the group of mountains and limestone plateaus. However, the adjacent mountainous area is characterized by very low altitudes and granitic rocks. From a geological point of view, the territory is part of the Danube domain. Balta Nera is a European biogeographical region, at the confluence of the Nera and the Danube, being characterized by hydrophilic and hygrophilous vegetation, specific to wetlands.

The flora is represented by hydrophilic and hygrophilous species, such as *Salix* spp. (Willow species), *Phragmites* spp. (Reed), *Carex* spp. (sedge), *Salvinia natans*, *Marsilea quadrifolia* (rock clover), *Typha* spp.



*Photo 13 – View of Balta Nera*

The fauna is very rich, from insects to mammals. The most well-known faunal elements in the area are waterfowl, the reserve meeting the bioecological conditions necessary for them for food, reproduction and nesting. The invertebrate fauna is poorly known in the area, but you can find many species of butterflies, dragonflies, moths, many species with protection status. As expected, ichthyofauna is very well represented, one of the very important elements being *Umbra krameri*. In addition to this, there are also the *Aspius aspius*, *Barbus meridionalis*, *Gobio kessleri*, broad strip - *Cobitis elongata*, *Cobitis taenia*, *Misgurnus fossilis*, *Cottus gobio*. Among amphibians and reptiles, species such as *Bombina bombina* (red-bellied marsh owl), *Bombina variegata* (yellow-bellied marsh owl), *Bufo viridis* (green toad), *Bufo bufo* (toad), *Ribundunda* frog (lake frog), *Ranadalmatina* (forest frog), *Hyla arborea* (frog), *Testudo hermanni beottgeri* (Herman's tortoise), *Emys orbicularis* (water turtle), *Natrix tessellata* (water snake), *Elaphe longissima* (snake of Aesculapius).



*Photo 14 – View of Balta Nera*

The avifauna is represented by species that benefit from the protection status offered by the community legislation - Birds Directive, ratified by GEO 57/2007 by the Government of Romania. Among these species we mention: Phalacrocorax pygmaeus (small cormorant), Botaurus stellaris (marsh owl), Ixobrychus minutus (dwarf heron), Egretta garzetta (small egret), Egretta alba (large egret), Alcedo atthis but also species of predators, such as Tyto alba and Circus aeruginosus. [19]

## 2.2. Limit values of pollutants in surface waters, Romania

The surface water quality and sediments is governed in Romania by the Ministry of Environment and Water Management Ordinance no. 161 from 16.02.2006, published in the Romanian Official Gazette 511` in 13.06.2006. The Ordinance establishes 5 ecological states are established for natural rivers and lakes: very good (I), good (II), moderate (III), poor (IV) and bad (V), based on biological, hydro morphological, chemical and physicochemical quality elements.

Table 8. Physicochemical quality elements and standards in surface waters. [20]

Parameter	Unit	Limit values				
		I class	II class	III class	IV class	V class
pH	-	6.5 – 8.5				
Conductivity	µS/cm	-				
Dissolved oxygen (DO)	mgO <sub>2</sub> /l	9	7	5	4	< 4
Biochemical oxygen demand (BOD – CBO5)	mgO <sub>2</sub> /l	3	5	7	20	> 20
Chemical oxygen demand (COD – CCO-Cr)	mgO <sub>2</sub> /l	10	25	50	125	> 125
Ammonia (NH <sub>4</sub> <sup>-</sup> )	mg/l	0.4	0.8	1.2	3.2	> 3.2
Nitrates (NO <sub>3</sub> <sup>-</sup> )	mg/l	1	3	5.6	11.2	> 11.2
Nitrites (NO <sub>2</sub> <sup>-</sup> )	mg/l	0.01	0.03	0.12	0.3	>0.3
Total Nitrogen (TN)	mg/l	1.5	7	12	16	> 16
Orto phosphate (P-PO <sub>4</sub> <sup>3-</sup> )	mg/l	0.1	0.2	0.4	0.9	> 0.9
Sulphates (SO <sub>4</sub> <sup>2-</sup> )	mg/l	60	120	250	300	>300
Chloride (Cl <sup>-</sup> )	mg/l	25	50	250	300	> 300
Sodium (Na <sup>+</sup> )	mg/l	25	50	100	200	> 200
Calcium (Ca <sup>2+</sup> )	mg/l	50	100	200	300	> 300
Mercury (Hg)	µg/l	0.1	0.3	0.5	1	> 1
Arsenic (As <sub>3</sub> <sup>+</sup> )	µg/l	10	20	50	100	> 100
Lead (Pb)	µg/l	5	10	25	50	> 50
Zinc (Zn <sup>2+</sup> )	µg/l	100	200	500	1000	> 1000
Cadmium (Cd)	µg/l	0.5	1	2	5	> 5
Manganese (Mn - total)	mg/l	0.05	0.1	0.3	1	> 1
Iron (Fe – total)	mg/l	0.3	0.5	1.0	2	> 2

### 2.3. In-situ and laboratory analysis, Balta Nera

The surface water samples were taken in 5 spots from Balta Nera nature reserve, in 5<sup>th</sup> august 2020 and 23<sup>rd</sup> September 2020. The in-situ analysis (for pH, temp, chlorides, total hardness, chromate and dissolved oxygen) were performed on site. All samples were preserved in-situ for laboratory analysis with acids: HNO<sub>3</sub> (nitric acid) for metal concentration analysis on ZEE nit 700P, H<sub>3</sub>PO<sub>4</sub> (phosphoric acid) for total organic and inorganic analysis on Analytik Jena Multi N/C 3100 and H<sub>2</sub>SO<sub>4</sub> (sulfuric acid) for Chemical Oxygen Demand analysis on Velp Eco6 and ammonia, phosphor, nitrite, nitrate, phosphate, a.o. on Analytik Jena Specord 250plus.



Photo 14 – View of in situ analysis, Nera / Balta Nera



Photo 15 – View of sampling spots, Nera / Balta Nera [22]



Balta Nera is classified as IV IUNC category. Category IV protected areas aim to protect certain species or habitats, and their management reflects this priority. Many Category IV protected areas require regular active interventions to meet the requirements of certain species or maintain habitats, but this is not a requirement of the category. [21]

A detailed GPS coordinates for sampling spots is given in table 9 and the visualisation of the sampling spots in photo 15.

Table 9. Samplings spots on Balta Nera site.

Sample No	Sampling site	Protection zone	Coordinates
BN1	Balta Nera	IV IUCN <sup>1</sup> "Nature conservation reservation"	N44°50'11.42" / E21°21' 21.50"
BN2			N44°50'11.93" / E21°21' 31.11"
BN3			N44°50'08.20" / E21°21' 28.78"
BN4			N44°49'58.50" / E21°21' 20.10"
BN5			N44°50'02.55" / E21°21' 32.98"

1 - Category IV protected areas protect fragments of ecosystems or habitats, which often require ongoing management interventions to maintain. Category I<sup>st</sup> areas, on the other hand, must be largely self-sustaining and their objectives prevent such management activities or a regular visitation rate for category IV from the outset. Category IV protected areas are often established to protect certain species or habitats, rather than specific ecological objectives as in category I.

#### 2.4. Physical-chemical parameters of Balta Nera surface water

In table 10 the methods applied for analysis of Balta Nera surface waters parameters are given.

Table 10. Methods for parameter analysis in samples of Balta Nera.

Parameters	Measurement methods
pH	Electrode - electric potential difference
Conductivity	Electrolytic probe
Dissolved oxygen (DO)	Galvanic probe
Biochemical oxygen demand (BOD – CBO5)	Specord 250Plus – photometric method
Chemical oxygen demand (COD – CCO-Cr)	
Ammonia (NH <sub>4</sub> <sup>+</sup> )	
Nitrates (NO <sub>3</sub> <sup>-</sup> )	
Nitrites (NO <sub>2</sub> <sup>-</sup> )	
Total Nitrogen (TN)	Multi N/C 3100. Corrosion-free Focus-Radiation NDIR detection and furnace technology of combustion.
Orto phosphate (P-PO <sub>4</sub> <sup>3-</sup> )	Specord 250Plus – photometric method
Sulphates (SO <sub>4</sub> <sup>2-</sup> )	
Chloride (Cl <sup>-</sup> )	
Sodium (Na <sup>+</sup> )	
Calcium (Ca <sup>2+</sup> )	

Mercury (Hg) Arsenic (As <sub>3</sub> <sup>+</sup> ) Lead (Pb) Zinc (Zn <sub>2</sub> <sup>+</sup> ) Cadmium (Cd) Manganese (Mn - total) Iron (Fe - total)	ZEEnit 700 P Compact Tandem Spectrometer. Atomic Absorption Spectrometry – equipped with flame, hydride and graphite furnace, with Zeeman magnetic field control and Deuterium and Zeeman background correction.
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The results obtained from 2 sampling campaigns, in August and September 2020 are given in Tables 11 and 12.

Table 11. Results obtained for parameter analysis in samples of Balta Nera, on 5<sup>th</sup> august 2020

Parameter	Unit	Measured values - 5th august 2020					ecological state
		BN1	BN2	BN3	BN4	BN5	
pH	-	7.94	7.88	8.05	7.92	7.98	-
Conductivity	μS/cm	293	302	296	299	308	-
Dissolved oxygen (DO)	mgO <sub>2</sub> /l	10.4	9.9	10.1	9.7	10.9	I <sup>st</sup>
Biochemical oxygen demand (BOD – CBO5)	mgO <sub>2</sub> /l	2.9	2.8	3.1	3.1	2.9	I <sup>st</sup> -II <sup>nd</sup>
Chemical oxygen demand (COD – CCO-Cr)	mgO <sub>2</sub> /l	9.7	10.2	10.1	9.7	10.2	I <sup>st</sup> -II <sup>nd</sup>
Ammonia (NH <sub>4</sub> <sup>-</sup> )	mg/l	0.38	0.41	0.35	0.39	0.40	I <sup>st</sup> -II <sup>nd</sup>
Nitrates (NO <sub>3</sub> <sup>-</sup> )	mg/l	0.53	0.61	0.56	0.55	0.54	I <sup>st</sup>
Nitrites (NO <sub>2</sub> <sup>-</sup> )	mg/l	0.041	0.053	0.048	0.045	0.044	II <sup>nd</sup>
Total Nitrogen (TN)	mg/l	1.12	1.14	1.12	1.16	1.14	I <sup>st</sup>
Orto phosphate (P-PO <sub>4</sub> <sup>3-</sup> )	mg/l	0.16	0.17	0.16	0.15	0.16	II <sup>nd</sup>
Sulphates (SO <sub>4</sub> <sup>2-</sup> )	mg/l	15.6	14.3	15.1	14.7	14.9	I <sup>st</sup>
Chloride (Cl)	mg/l	0.4	0.4	0.4	0.4	0.4	I <sup>st</sup>
Sodium (Na <sup>+</sup> )	mg/l	3.6	3.2	3.2	3.5	3.4	I <sup>st</sup>
Calcium (Ca <sup>2+</sup> )	mg/l	33.7	34.5	29.7	30.4	33.1	I <sup>st</sup>
Mercury (Hg)	μg/l	0.021	0.017	0.018	0.011	0.015	I <sup>st</sup>
Arsenic (As <sub>3</sub> <sup>+</sup> )	μg/l	0.33	0.14	0.21	0.17	0.11	I <sup>st</sup>
Lead (Pb)	μg/l	0.088	0.094	0.091	0.081	0.085	I <sup>st</sup>
Zinc (Zn <sub>2</sub> <sup>+</sup> )	μg/l	12.7	14.1	13.7	12.9	13.5	I <sup>st</sup>
Cadmium (Cd)	μg/l	0.007	0.007	0.010	0.008	0.007	I <sup>st</sup>
Manganese (Mn - total)	mg/l	0.022	0.021	0.025	0.024	0.025	I <sup>st</sup>
Iron (Fe - total)	mg/l	0.893	0.955	1.021	0.912	0.897	III <sup>rd</sup>

Note: ambient air conditions: t = 30.5 °C, RH = 55.6%, p<sub>b</sub> = 1002.1 mbar  
Water temperature: 20.1 °C

Table 12. Results obtained for parameter analysis in samples of Balta Nera, on 23<sup>rd</sup> September 2020

Parameter	Unit	Measured values – 23 <sup>rd</sup> September 2020					ecological state
		BN1	BN2	BN3	BN4	BN5	
pH	-	7.45	7.44	7.51	7.52	7.49	-
Conductivity	µS/cm	441	455	447	453	450	-
Dissolved oxygen (DO)	mgO <sub>2</sub> /l	8.5	8.4	8.4	8.3	8.3	II <sup>nd</sup>
Biochemical oxygen demand (BOD – CBO5)	mgO <sub>2</sub> /l	4.2	4.4	4.3	4.2	4.2	II <sup>nd</sup>
Chemical oxygen demand (COD – CCO-Cr)	mgO <sub>2</sub> /l	14.4	14.8	14.5	14.7	14.5	II <sup>nd</sup>
Ammonia (NH <sub>4</sub> <sup>-</sup> )	mg/l	0.45	0.48	0.43	0.46	0.48	II <sup>nd</sup>
Nitrates (NO <sub>3</sub> <sup>-</sup> )	mg/l	0.68	0.66	0.65	0.66	0.67	I <sup>st</sup>
Nitrites (NO <sub>2</sub> <sup>-</sup> )	mg/l	0.055	0.052	0.056	0.058	0.055	III <sup>rd</sup>
Total Nitrogen (TN)	mg/l	1.33	1.28	1.30	1.29	1.28	I <sup>st</sup>
Orto phosphate (P-PO <sub>4</sub> <sup>3-</sup> )	mg/l	0.22	0.24	0.24	0.23	0.22	III <sup>rd</sup>
Sulphates (SO <sub>4</sub> <sup>2-</sup> )	mg/l	20.1	21.1	20.5	20.6	20.3	I <sup>st</sup>
Chloride (Cl <sup>-</sup> )	mg/l	0.3	0.4	0.5	0.3	0.4	I <sup>st</sup>
Sodium (Na <sup>+</sup> )	mg/l	3.3	3.4	3.5	3.4	3.4	I <sup>st</sup>
Calcium (Ca <sup>2+</sup> )	mg/l	30.7	29.8	29.4	30.1	28.9	I <sup>st</sup>
Mercury (Hg)	µg/l	0.013	0.011	0.010	0.011	0.009	I <sup>st</sup>
Arsenic (As <sub>3</sub> <sup>+</sup> )	µg/l	0.15	0.16	0.17	0.17	0.18	I <sup>st</sup>
Lead (Pb)	µg/l	0.071	0.077	0.079	0.080	0.076	I <sup>st</sup>
Zinc (Zn <sup>2+</sup> )	µg/l	14.9	14.7	15.1	14.7	14.9	I <sup>st</sup>
Cadmium (Cd)	µg/l	0.006	0.006	0.008	0.008	0.007	I <sup>st</sup>
Manganese (Mn - total)	mg/l	0.031	0.033	0.031	0.032	0.033	I <sup>st</sup>
Iron (Fe – total)	mg/l	1.118	1.083	1.103	1.094	1.107	IV <sup>th</sup>

Note: ambient air conditions: t = 28.4 °C, RH = 66.1 %, p<sub>b</sub> = 1001.2 mbar  
Water temperature: 18.2 °C

Results presented in Table 11 and Table 12 allows us to assess the water quality during the study period according to national norms. In Romania water quality assessment is regulated by the Ministry of Environment and Water Management Ordinance no. 161 from 16.02.2006. The Ordinance establishes 5 ecological states are established for natural rivers and lakes: very good (I), good (II), moderate (III), poor (IV) and bad (V).

According to the limits set in this Order, values of measured nutrients (nitrites, phosphorus) range between class II (good) and class IV (poor). The oxygen status in Balta Nera for BOD, OD and COD ranges between I<sup>st</sup> and II<sup>nd</sup> quality class (very good to good).

The (heavy) metals concentrations in surface water on Balta Nera were all found at very low concentrations, well inside I<sup>st</sup> class for surface water quality, with the exception of iron (Fe) that was in class IV.

### 3. Study conclusions - **Special Nature Reserve “Carska bara”** and Delta (Balta) Nera

The area of Banat region, in both Romanian and Serbian side, has a numerous unique natural site that are rich in biodiversity and natural beauty. Still, it seems they are insufficient popularized to the citizens.

Hence, this study was provided with the intention to popularize two special, water based, areas: Balta Nera (Nera delta to Danube) and special natural reservation “Carska Bara” (Bega delta to Tisa, near Zrenjanin). They are both unique wetlands environments. Carska Bara is a UNESCO RAMSAR protected wetland and Delta Nera is classified IV IUCN protected area of national interest and the newest delta in Europe.

In this study an evaluation of surface water quality in these two regional significant and unique sites were provided. According to the identified environmental pressures the relevant parameters were analysed. Hence, extensive measurement of water quality COD, CBO5, ammonia, nitrates, nitrites, phosphates, and conductivity were analysed. Also, for the first time in this area, some metals (Mercury, Lead, Nickel, Zinc, Copper and Arsenic) were provided.

Analysis of Carska Bara samples identified that concentration of ammonia and phosphates were extremely high in all samples during all campaigns. Ammonia concentration classified samples in III class of water quality. Also, extremely high concentrations of phosphates were recorded in July and October. Concentration of phosphates in some samples were so high that V water quality class were assigned.

Concentration of nitrites recorded in samples from July and October were higher than 0.3 mg/l which is a limit value for V water quality class. Maximum nitrites concentration (0.75 mg/l) were recorded in July.

Consequently, at all sampling sites, an exceptionally low concentration of dissolved oxygen (lower than 4 mgO<sub>2</sub>/l) were recorded. According to dissolved oxygen concentrations, surface water was in V class of water quality. Additionally and quite expected, very high values of biological oxygen demand (BOD) were recorded. In majority of the samples, BOD concentration higher than 5 mgO<sub>2</sub>/l (III water quality class) were recorded.

Analysis of Balta Nera samples identified that concentration of ammonia were in I<sup>st</sup> class in all samples during August and fall under II<sup>nd</sup> class in September campaigns. Also, relatively high concentrations of phosphates and nitrites were recorded, entering the II<sup>nd</sup> and III<sup>rd</sup> surface water quality class.

Due to relatively high nutrients concentration (ammonia, nitrites, phosphates) the biological oxygen demand (BOD) in Balta Nera were relatively high, around 3 mgO<sub>2</sub>/l in August and around 4 mgO<sub>2</sub>/l in September, classified as II<sup>nd</sup> quality class.

*Finally we can conclude that surface water analysis provided in the protected natural area of „Carska bara“, identified typical pollution by nutrients (nitrous and phosphorous compounds) and consequently low oxygen concentration. Agricultural activities, intensive fish farming and presence of weekend resorts in the vicinity, have led to the continuous degradation, primarily to the eutrophication of this valuable nature area.*

*In the case of „Balta Nera“ nature reserve we can conclude that the surface water quality is under threat by so called nutrients pollutants - ammonia, nitrites and phosphorus. As Balta Nera is the delta formed by Nera river, its surface water quality is directly depended on Nera surface water status and marginally by Danube, in the rare cases of high Danube waters. The pollution with ammonia, nitrites and phosphates is relatively normal and expected, as Nera flows at its 124 km directly thru numerous villages, with its inhabitants traditionally **raising cattle's, pigs and chickens, and the manure by-products** are traditionally spread on land for micro(family)-farming.*

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**Cooperation beyond borders.**

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Environmental protection  
and risk management

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