THE ANALYSIS OF THE QUALITY OF SURFACE WATER OF DANUBE IN THE REPUBLIC OF SERBIA FOR 2018.

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Abstract: Today, the quality of water in the world is changing significantly due to the increasing human impact on the environment. The paper presents an analysis of the surface water quality of the Danube river at five hydrological stations in Serbia for 2018. Using the relevant method - the water quality index, in this case, the Serbian water quality index (SWQI) ten physico-chemical and microbiological parameters (oxygen saturation, Five-Day Biochemical Oxygen Demand or BOD5, ammonium ion concentration, pH value, water) were analyzed Total Nitrogen or WTN, Total Suspended Solids or TSS, orthophosphate concentration, electrical conductivity, temperature and fecal coliform bacteria presence in water). The values obtained are classified in 5 classes depending on the water quality. The lowest (good) water quality was recorded on the Zemun – Smederevo river course, while in Bezdan, Novi Sad and Radujevac, the average annual water quality is very good.

Keywords: SWQI, Danube, Serbia, physico-chemical and microbiological parameters.

Introduction

Due to the increasing degradation of the environment by man, the quality of all media is called into question. Water is an essential element for all lifeforms, as well for the social and economical development of the mankind. It is anaturally regenerating medium, but its qualitative characteristics are vulnerableto polluters like waste, urban agglomeration, intensive agriculture and the lack of a good management in this field (Nistor et al., 2012).

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To properly control the quality of surface water, it is necessary to have appropriate devices at the hydrological stations that will identify the concentrations of physical, chemical and microbiological parameters in the river course. The study of the quality and pollution of watercourses in the world is usually based on the application of various mathematical and statistical methods (Urošev et al., 2009; Milanović et al., 2011; Brankov et al., 2012; Pantelic et al., 2012; Takić et al., 2017).

This paper aims to determine the surface water quality of Danube on the territory of the Republic of Serbia during 2018. and to analyze the physicochemical and ecological parameters that participate in the Serbian Water Quality Index method. By the Law on Waters, to prevent deterioration of the quality of water and the environment, physicochemical parameters and emission limit values for pollutants are determined. In addition to the physicochemical, the ecological status of surface waters is also analyzed.

Materials and Methods

Study area

Publication of the Environmental Protection Agency, that contains the data from 5 hydrological stations was used to analyze the water quality of the Danube. These five stations are Bezdan, Novi Sad, Zemun, Smederevo and Radujevac. In this way, by selecting hydrological stations, it is possible to determine the water quality of the Danube at the entry and exit in the Republic of Serbia for 2018. The Danube is the second-longest river in Europe, with a length of 588 km through Serbia.

Table 1: Coordinates of hydrological stations

Hydrological station	Coordinates	
Bezdan	45⁰ 51' 50.832'' N	18⁰ 51' 14.949'' E
Novi Sad	45⁰ 13' 28.219''	19⁰ 50' 31.310''
Zemun	44⁰ 50' 55.788''	20⁰ 25' 01.984''
Smederevo	44⁰ 41' 37''	20⁰ 57' 52.805''
Radujevac	44⁰ 15' 45.450''	22⁰ 41' 09.577''

The water quality of the Danube was analyzed at a total length of 576.2 km, or 6.2 km after the entry of the Danube into Serbia, to 5.6 km before leaving the country. The average annual flow during 2018. was 2036 m³/s in Bezdan and 2626 m³/s in Novi Sad. After the confluence of the Sava, Tisza and Tamis into the Danube, the river flow in Smederevo is much higher and amounts to 4839 m³/s.
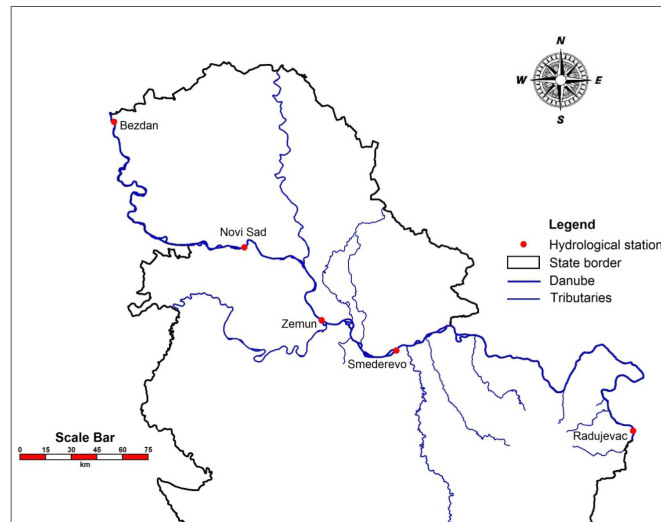
Figure 1. Danube course and its largest tributaries in Serbia

Metodology

In recent years, the analyses of watercourse quality based on mathematical indexes have become increasingly common. Authors from all over the world use the Water Quality Index as a reliable indicator of watercourse pollution (Bordalo et al., 2006; Lumb et al., 2006; Bharti & Katyal, 2011; Jakovljević, 2012; Singh et al., 2013; Tyagi et al., 2013; Ismail & Robescu, 2017).

Serbian Water Quality Index is environmental indicator, developed by Serbian Environmental Protection Agency (SEPA), based on method Water Quality Index (Development of a Water Quality Index, Scottish Development Department, Engineering Division, 1976; Jakovljević, 2012). This is an efficient method to indicate the current water quality and its trend in the observed area. The Water Quality Index was adopted by the European Union as a water quality assessment tool. In order to reduce the riskfor aquatic ecosystems, especially water quality, the experience of developed countries should be used (Zhukinskii, 2003). In Serbia, this method was used inan analysis of the water quality of the Danube River and the Danube-Tisza-Danube channel system (Veljković & Jovičić, 2007; Milanović et al., 2011). The index is a useful tool for communicating water quality information to the large public and to legislative decision makers; it is not a complex predictive model for technical and scientific application (Hallock, 2002; Yogendra, 2008).

The Water Quality Index (WQI) method combines standardized values (qi) of ten parameters, which describe the properties of surface waters to calculate a unique index value. This study reveals how these wide variations in different parameters can be reduced to a single number when reported with the help of WQI, thereby making it quite convenient to comment on the overall quality of the water sample from its pollution point of view (Kankal et al., 2012, S. P. Gorde et al., 2013).

The ten parameters have different relative significance for the overall water quality. Therefore, each parameter was assigned a weighting factor (w_i) and a number of points in accordance with the threat they pose to water quality. By summing up the products of the q_i and w_i values we arrive at an index value of 100 as an ideal sum of the values of particular parameters (Milijašević - Joksimović et al., 2018; Breabăn et al., 2012).

The Serbian Water Quality Index (SWQI) examines the following parameters:
- Oxygen saturation (%)
- Five-Day Biochemical Oxygen Demand – BOD_5 (mg/l)
- Ammonium ion concentracion (mg/l)
- pH value
- Water Total Nitrogen – WTN (mg/l)
- Orthophosphate concentration(mg/l)
- Total Suspended Solids – TSS (mg/l)
- Water temperature (ºC)
- Electrical conductivity (µS/cm)
- Fecal coliform bacteria (in 100 ml)

In case we miss the value of some parameter, the value of the arithmetically calculated WQI is corrected by multiplying the index with the 1/x value, where x represents the sum of the arithmetically calculated weighting factors of available parameters (Veljković et al., 2008).

The arithmetic formulation for the WQI is of the form:

$$WQI = \sum_{i=1}^{n} qi \cdot wi$$

where WQI is the water quality index, and is a number on the continuous scale from 0 to 100, *n* – number of parameters, qi – the water quality of the *i*-thparameter, wi – the weight attributed to the *i*-th parameter (Veljković et al., 2000).

At the end of the water quality calculation, a corresponding numerical value is obtained. The *Serbian Water Quality Index* method is used to classify the numeric indicator.

Table 2. Classification criteria standards according to the Serbian Water Quality Index

Serbian WQI	Descriptor category	Color
100-90	Excellent	
84-89	Very good	
72-83	Good	
39-71	Bad	
0-38	Very bad	

Source: www.sepa.gov.rs

The Water Quality Index classifies numerical values into one of five groups, depending on the quality of surface water. Water quality can be: excellent, very good, good, bad and very bad.

Results and discussion

During the 12 months of 2018., 5 hydrological stations calculated SWQI and the average annual value of each parameter of surface water quality.
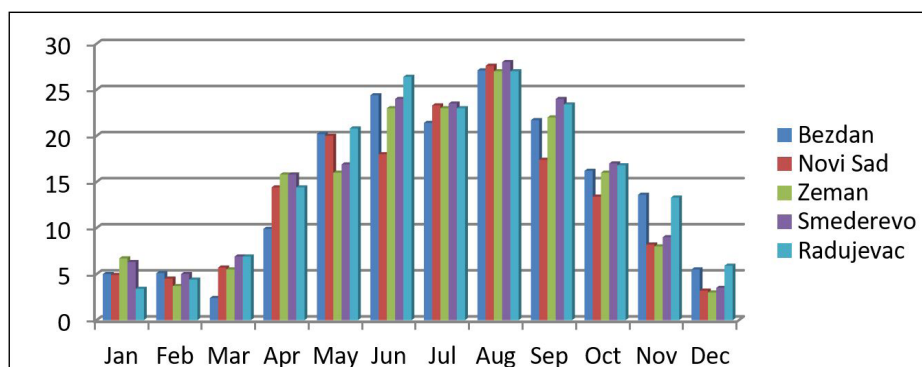
Figure 2. Water temperature (⁰C) during 2018.

The water temperature is the lowest in the winter months and ranges from 3-6 ⁰C in all parts of the Danube, while the highest temperature was recorded in August (above 26 ⁰C). When the water temperature is > 17 ⁰C, it causes a decrease in its quality. Water temperature is essential for the process of self-purification of water and has significant effects on water life. Toxicity of the metals, the speed of chemical processes, the solubility of the gases, and the deposition of the suspended particles depend on temperature.
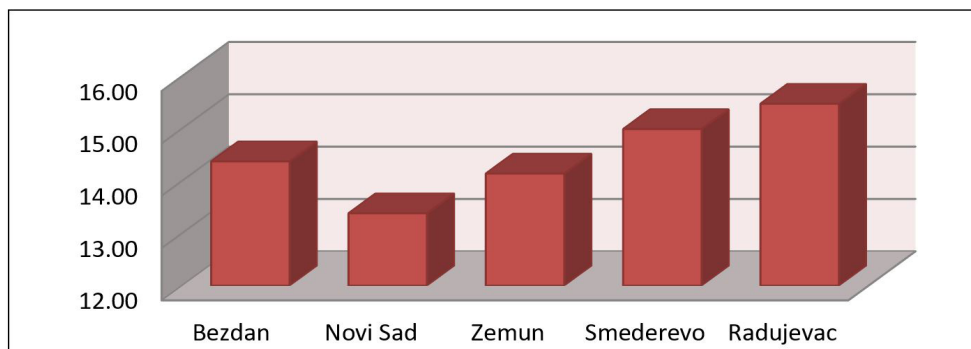
Figure 3. Average annual water temperature (⁰C)

The highest average water temperature is in Radujevac, while the lowest is in Novi Sad. Increased water temperature may indicate a higher presence of pollutants generated by various anthropogenic activities.
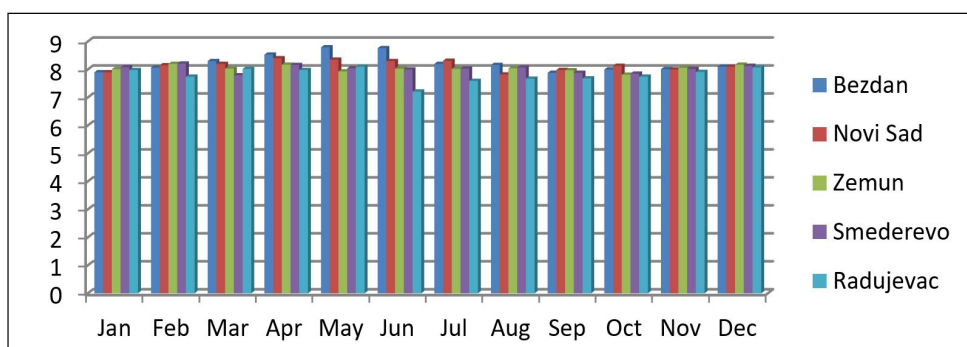

Figure 4. Water pH value during 2018.

The pH scale ranges from 0 (very acidic) to 14 (very basic). The pH value of water in all tested hydrological stations ranges from 7-9, which means that for most of the year, water has a neutral or slightly basic value. Chemically pure water at 25^oC has a pH value of 7 (neutral). Natural waters generally have a pH of 4.5 to 8.3, which depends on the balance between the carbon dioxide and the bicarbonate ion. Acidic water contains hydrolysis of salts, and base value water contains waste base substances. Acid and base water are harmful because they corrode the pipeline or cause sludge formation (Драгићевић и други., 2008).
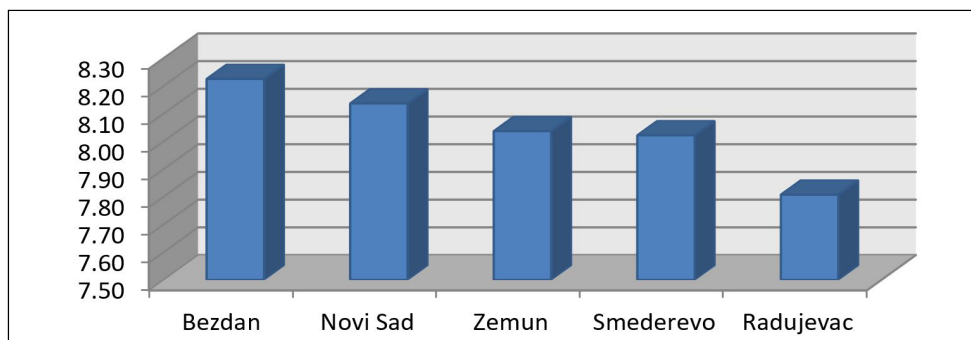
Figure 5. Average annual pH value of water during 2018.

The highest average pH value was recorded at the Danube entry into Serbia at the Bezdan hydrological station, while the lowest pH value at the Danube exit at Radujevac. When it comes to this parameter, it is noticeable that the slightly basic value does not significantly impair the water quality.
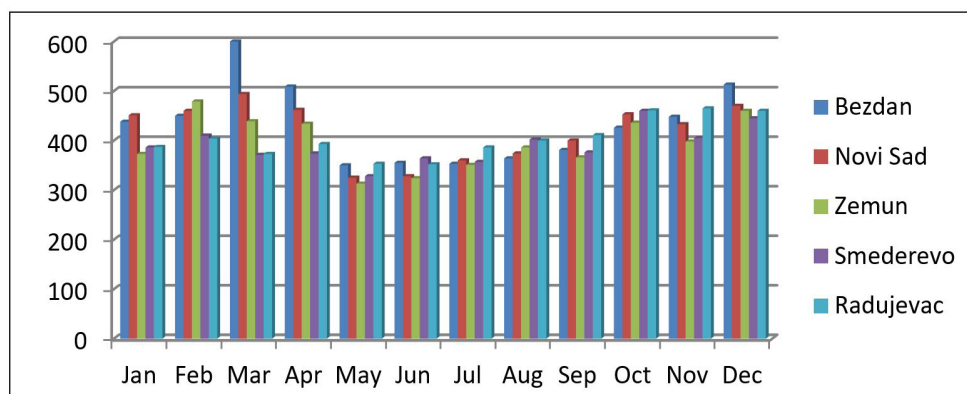

Figure 6. Electrical Conductivity of the Danube water (µS/cm)

The conductivity k, is the electrical property of water. Water and aqueous solutions, depending on the ion concentration, can conduct electricity. The conductivity depends on the ions present in the water, their concentration, mobility and electric charge. It also depends on the temperature at which the conductivity is determined. At all tested hydrological stations, the conductivity valuesof water are in the range 313-600 µS/cm. Excellent water quality requires an electrical conductivity of less than 200 µS/cm.

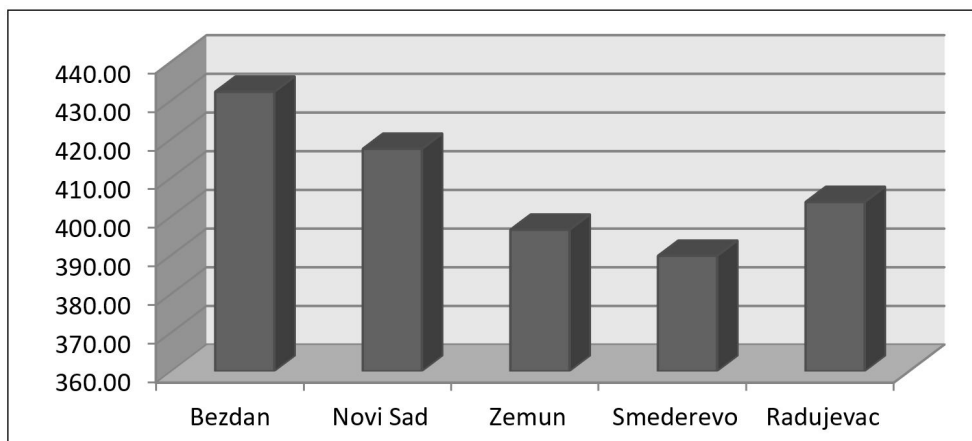*Figure 7. Average annual electrical conductivity (µS/cm) for 2018.*

The lowest average electrical conductivity of water was recorded at the hydrological station in Smederevo (389.83 µS/cm), while the highest average value was recorded in Bezdan (432.25 µS/cm). Such values of electrical conductivity of water do not significantly affect the quality of surface water.
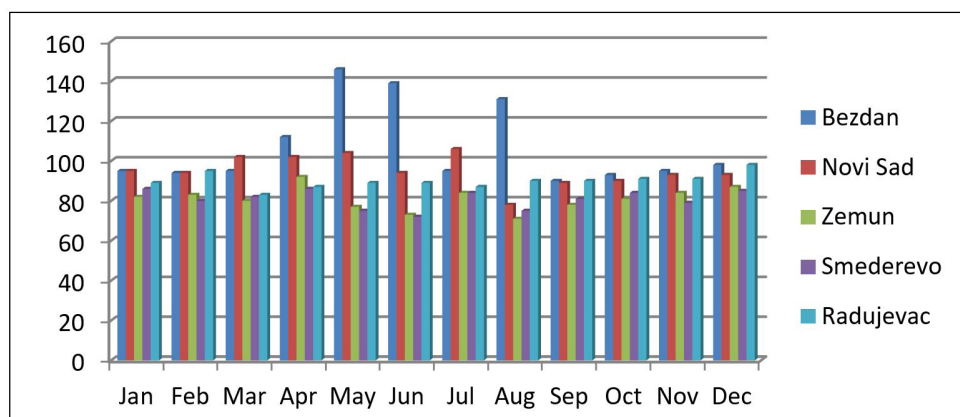

Figure 8. Oxygen saturation in water (%)

The degree of oxygen saturation depends directly on the temperature and intensity of the photosynthesis process in the water. In conditions of low dissolved oxygen concentration, aquatic ecosystems become imbalanced, which can lead to fish death and an unpleasant smell (Mladenović-Ranisavljević, 2012). By far the highest oxygen saturation was recorded at a hydrological station in the Bezdan. Oxygen water saturation, together with BOD_5, has the highest score in calculating SWQI.
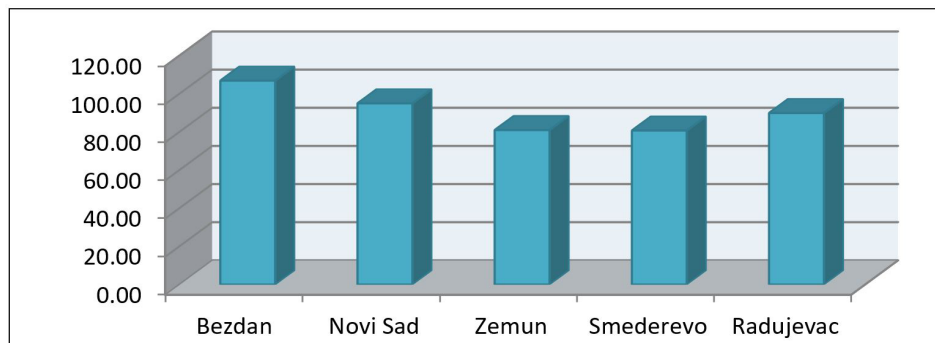
Figure 9. Average annual oxygen saturation (%)

The average water saturation of the Danube was in Bezdan - 106.92%, while the lowest recorded saturation was in Zemun (81%) and Smederevo station (80.75%). At all hydrological stations except Bezdan, oxygen saturation is not sufficient for excellent quality. For excellent water quality, oxygen saturation should be 93-110%. The five-day biochemical oxygen demand (BOD_5) is the amount of oxygen dissolved in the water needed for the oxidation and decomposition of organic material. If the biochemical oxygen demand is high, it may indicate water pollution caused by the excessive decay of the material. With increasing temperature, the rate of oxygen consumption increases (Mladenović-Ranisavljević, 2012).
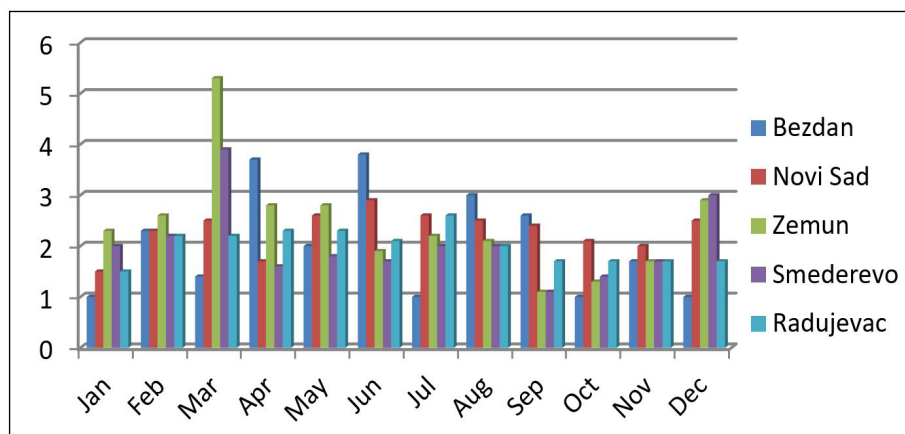

Figure 10. BOD5 value during 2018. (mg/l)

The value of biochemical oxygen consumption in all hydrological stations varies in the range of 1-4 mg/l. The most significant deviation was observed in Zemun in March when BOD_5 was as high as 5.3 mg/l.
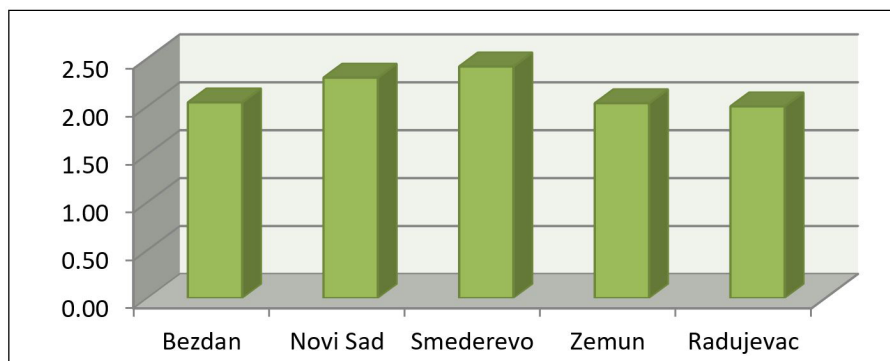
Figure 11. Average annual BOD5 (mg/l)

The lowest average BOD_5 value was measured in Radujevac (2 mg/l), while the highest value was recorded in Smederevo (2.42 mg/l). All measured values significantly affect the quality of surface water. It is necessary to carry out the testing, control and implementation of appropriate actions for the suppression of the excessive amount of organic matter in this part of the Danube. Excellent water quality requires a BOD_5 concentration of less than 1 mg/l.
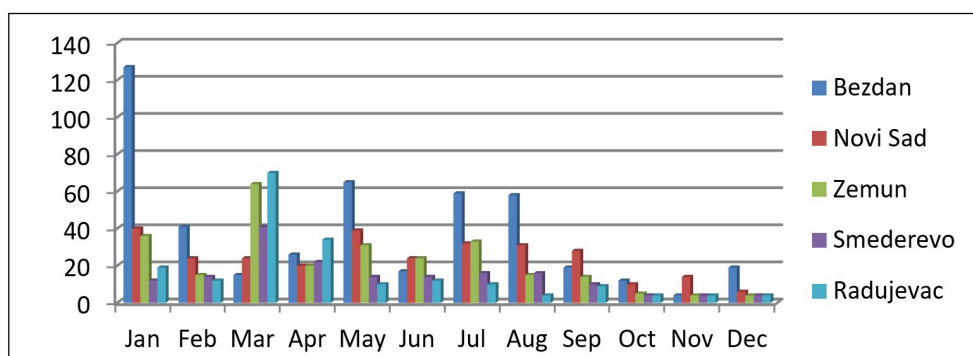

Figure 12. Total Suspended Solids (mg/l)

The concentration of suspended solids varies from one hydrological station to another. In the territory of Serbia and the stations from the study, the suspended solids have a significant impact on the reduction of water quality. The value of suspended particles was high, especially in the Bezdan, where a maximum of 127 mg/l was recorded during January.
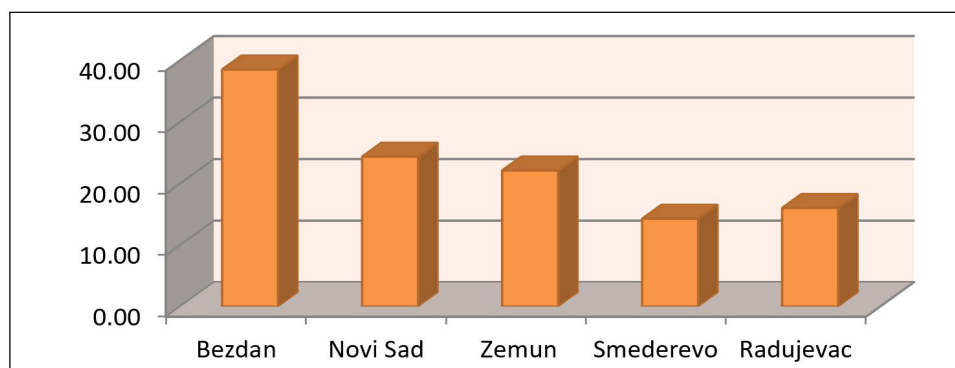
Figure 13. Average annual suspended solids concentration (mg/l)

On average, in 2018, the highest amount of suspended solids was recorded in Bezdan (38.5 mg/l) and the lowest in Smederevo (14.25 mg/l). The concentration of suspended solids depends on several factors: hydrological, geological, climatic, geomorphological, etc. Loose geological substrates in the territory of Vojvodina, can increase the concentration of suspended solids, while tributaries of the Danube flowing through the same or similar substrate can only further increase the concentration of suspended material. Also, great importance has the amount of precipitation in the study area. The water of excellent quality should have a concentration of suspended solids of < 10 mg/l.
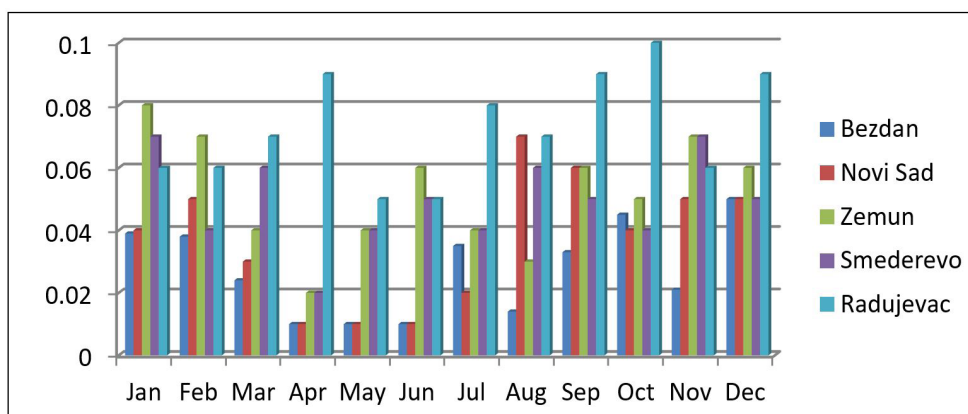

Figure 14. Orthophosphate concentration (mg/l)

Significant variations during the year occur in the content of orthophosphates in water. Phosphorus is a limiting factor in controlling algal overgrowth and accelerated eutrophication (Mladenović-Ranisavljević, 2012). For excellent

water quality, the orthophosphate content should be less than 0.05 mg/l. The lowest values occur in the summer months at all hydrological stations except in Radujevac, where maximums (0.09-1 mg/l) have been recorded.
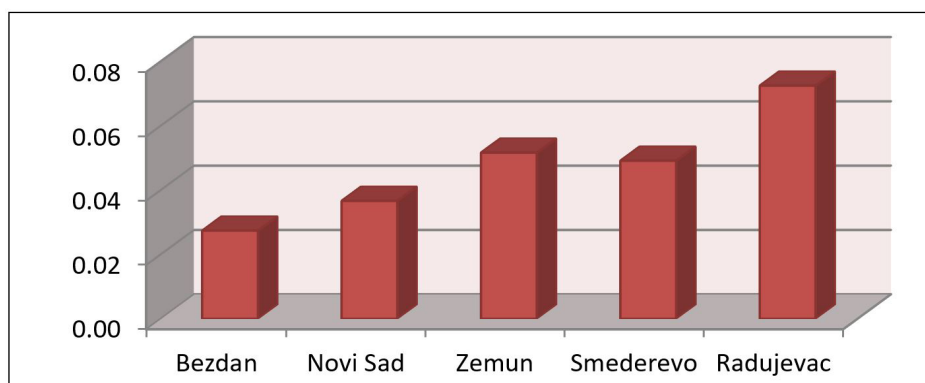

Figure 15. Average annual orthophosphate concentration (mg/l)

Excessive concentration of orthophosphates can indicate pollution caused by inadequate wastewater management, which is discharged from households and industrial plants. The lowest level of orthophosphates is at the entry of the Danube into Serbia (0.03 mg/l), and the highest at the exit of the Danube from the country (0.07 mg/l).
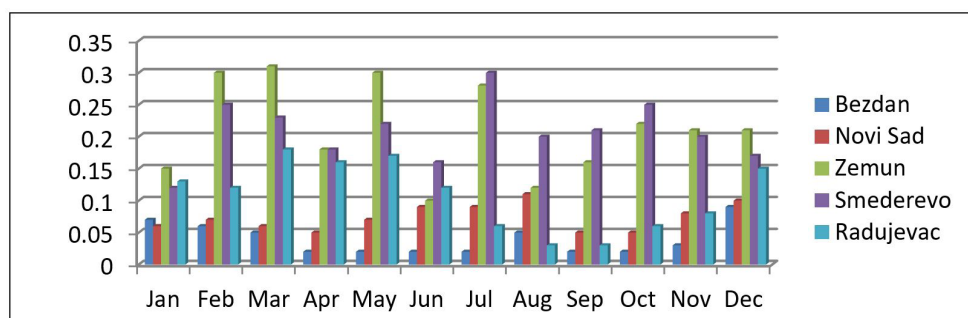
Figure 16. Ammonium ion concentration (mg/l)

By far the highest ammonium ion content was recorded at hydrological stations in Zemun and Smederevo. Maximum values range from 0.25-0.31 mg/l, while the ideal value is below 0.1 mg/l. In the water, ammonium exists in the form of ions (NH_4^+) or the form of ammonia gas (NH_3). Increase of ammonia in water is related to an increase in temperature and a decrease in the concentration of oxygen in water (Mladenović-Ranisavljević, 2012).
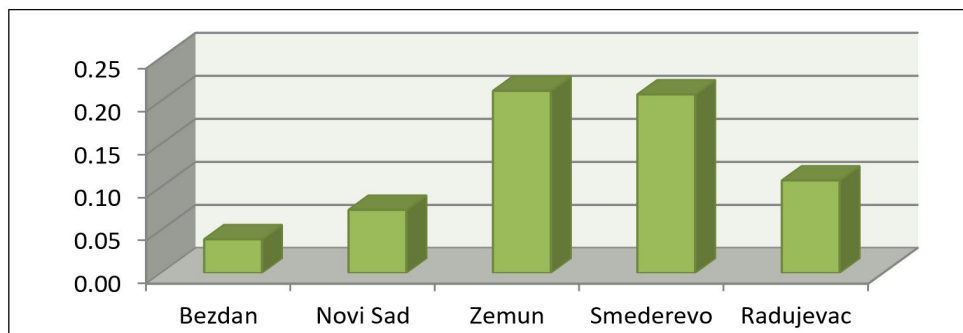
Figure 17. Average annual ammonium ion concentration (mg/l)

Ammonium ion content does reduce the quality of surface water in the Bezdan and Novi Sad. The lowest NH_4^+ values were recorded in Bezdan (0.04 mg/l), while the highest values were identified in Zemun and Smederevo (0.21 mg/l) and represent a risk to water quality.
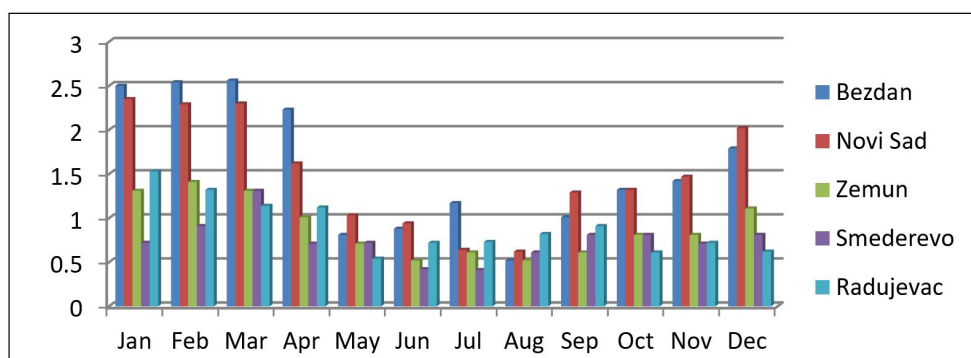
Figure 18. Total nitrogen oxides (mg/l)

Total nitrogen oxides represent the sum of nitrates and nitrites in the water. Nitrites, together with nitrates at higher concentrations, can cause significant health problems (Mladenović-Ranisavljević, 2012). The highest levels of nitric oxide are recorded in Bezdan and Novi Sad, where values in some months exceed 2 and 2.5 mg/l. For the excellent quality of water, the amount of nitric oxide must be less than 0.5 mg/l.

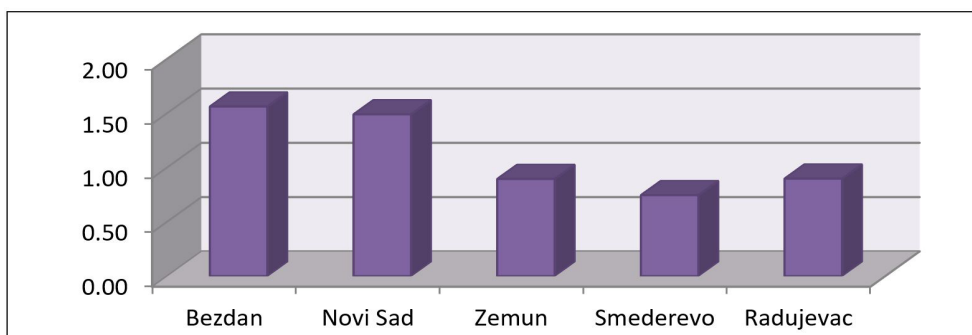*Figure 19. Average annual concentration of nitrogen oxide (mg/l)*

The highest concentration of nitrite and nitrate occurs in Bezdan (1.56 mg/l), while the lowest is recorded in Smederevo (0.75 mg/l). At all stations, total nitrogen oxides affect the decrease in water quality. The last but also a very significant parameter in the overall calculation of the water quality index is the presence of fecal coliform bacteria.
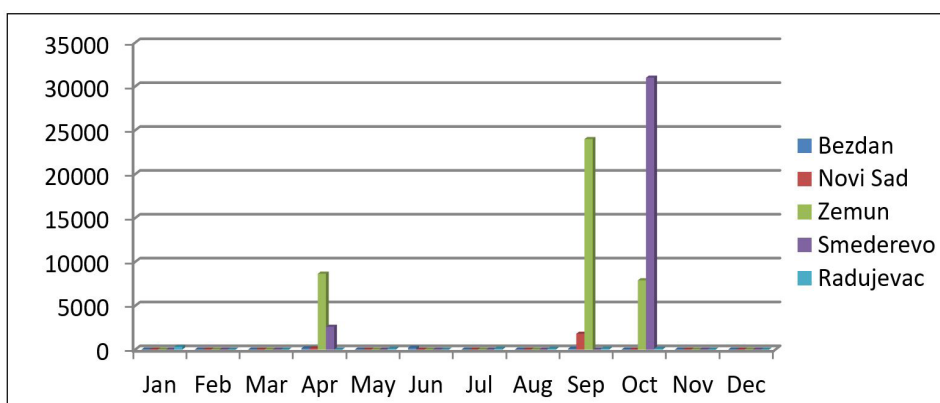
Figure 20. Fecal coliform bacteria in water (in 100 ml)

For most of the year, coliforms do not appear at all in most hydrological stations. During April, September and October, a vast number of coliform bacteria appeared in Zemun. For excellent water quality, there has to be a complete absence of bacteria or content of < 300 coliforms in water. For most of the year, the presence of bacteria was not recorded at the hydrological stations, but a large number of coliform bacteria appeared in some months. By far, the most significant amount of coliform bacteria was recorded in Zemun (40.550), in Smederevo 33.600, and Radujevac 810. In Bezdan, coliform bacteria do not affect water quality while in Novi Sad, bacteria decrease water quality during September.

Figure 21. Water quality index by months for 2018.

Surface water quality was determined based on the analysis and calculation of the values of all parameters during the 12 months in 2018.

Table 3. Surface water quality in 2018.

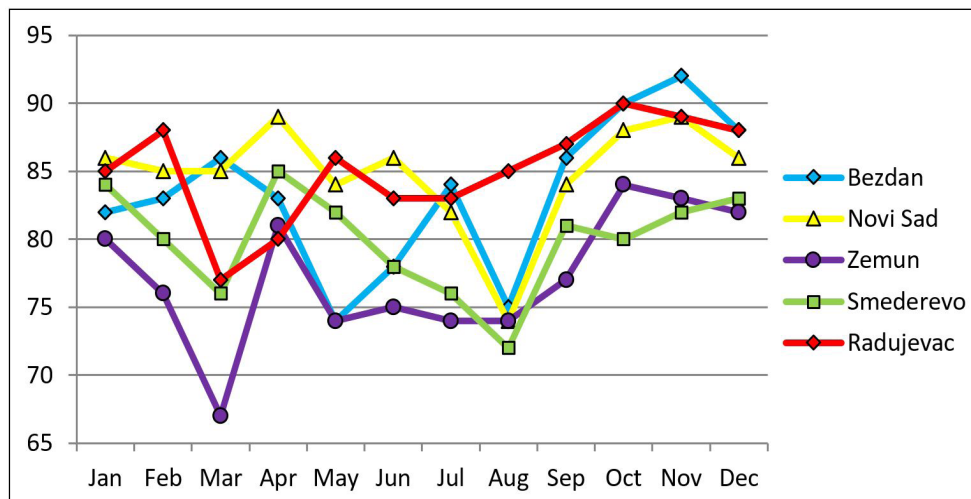|	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	A	AWQ
B	82	83	86	83	74	78	84	75	86	90	92	88	**87**	Very good
NS	86	85	85	89	84	86	82	74	84	88	89	86	**88**	Very good
Z	80	76	67	81	74	75	74	74	77	84	83	82	**80**	Good
S	84	80	76	85	82	78	76	72	81	80	82	83	**81**	Good
R	85	88	77	80	86	83	83	85	87	90	89	88	**87**	Very good

Note: B-Bezdan, NS-Novi Sad, Z-Zemun, S-Smederevo, R-Radujevac; A-Average, AWQ-Average water quality

On the yearly bases hydrological stations in Bezdan, Novi Sad and Radujevac record very good water quality of the Danube. During October and November, stations in Bezdan and Radujevac registers excellent water quality while in Zemun and Smederevo, the water quality is good on an annual basis. The lowest water quality was recorded in Zemun. In March, this station records bad water quality due to the increased BOD_5 concentration.

Conclusion

The water quality of the Danube when entering and leaving Serbia, is very good. During the autumn and winter of 2018, water quality in this area is slightly higher than in other periods of the year. What disrupts the water quality in Bezdan and Novi Sad is the higher electrical conductivity of the water, the high concentration of suspended solids, the increased concentration of nitrogen oxide, as well as the high value of BOD_5. The Danube water quality is greatly influenced by all the countries through which the Danube flows before it reaches Serbia.

What seems to be the problem is the Zemun-Radujevac river course. During 2018., the water quality in Zemun was good, while in March was registered bad quality. In the hydrological station Zemun, parameters that were well above permitted values were fecal coliforms, ammonium ion concentration, insufficient oxygen saturation, and the highest recorded BOD_5 value. Water quality is also good in Smederevo, but slightly better than in Zemun. Rivers Sava, Tisza and Tamis flow into the Danube on his course from Zemun to Smederevo. Here, the flow of the Danube is much larger than that of Zemun, and this is probably the reason for the slightly better water quality in Smederevo. This vast stream has much more pollutants than in Zemun, but on average, per litre, this value is smaller.

Accumulation - Djerdap Lake in Radujevac has a significant impact on better water quality. This reservoir is a vast "precipitator" or "filter", which with two dams holds a certain amount of pollutants. The same SWQI value in Bezdan and Radujevac indicates that pollutants are similarly represented in mg/l. Still, due to the large tributaries which enter into the Danube after the Bezdan, the water flow is much higher when leaving the country, and therefore the total pollutant concentration in water is higher.

The significant problems with the reduced quality of the Danube water in Serbia are the lack of wastewater treatment plants and insufficient financial resources for their construction, as well as the lack of filters for the treatment of water from sewage systems in larger cities and rural places.

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