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The Assessment of the Danube River Water Pollution in Serbia

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Abstract Actual problems of water ecosystem pollution require the ecological classification and the identification of the most influential parameters on the variability of water quality, stressing the importance of both in the realization of the sustainable water management principles according to the Water Framework Directive European Union (WFD EU), and the preservation of the quality of the environment. The aim of this paper was the assessment of the ecological status of water quality and calculating water pollution index (WPI) of the Danube River in Serbia. For all surface waters, the WFD requires "good ecological status," i.e., low level changes of the natural state that occur as a result of human activities by 2015. The assessment was based on the data obtained from ten hydrological measuring stations on the Danube River in Serbia for 2014. It was ascertained that the ecological status of the Danube River water quality was class III, corresponding to "moderate ecological status" and deviating from the required "good ecological status." According to the calculated WPI = 1.352, the water pollution of the Danube River in Serbia was characterized as moderately polluted and corresponded to class III of surface water. The ecosystem approach clearly indicated that the concentration of physico-chemical parameters of the watercourse deviated from the target values. Therefore, there is an urgent need to take some measures to prevent pollution and improve the water quality of the Danube River as an integral part of the environment in Serbia.

Keywords The Danube River · Ecological status · Water pollution index · Physico-chemical parameters

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1 Introduction

The Danube River is the second longest, after the Volga, and the second water richest river in Europe. It flows through several major European capitals, Vienna, Bratislava, Budapest, and Belgrade, and flows into the Black Sea in Ukraine. With its length of 2850 km and basin area of 805,000 km^2, Danube is the longest river in the European Union. The Danube River flows through ten countries: Germany, Austria, Slovakia, Hungary, Croatia, Serbia, Romania, Bulgaria, Moldova, and Ukraine. This is probably one of the reasons why the European Commission considers it to be the "future central axis for the EU." Liska (2015) states that 19 countries share the

Danube catchment area, making it the world's most international river basin. Given the number of the countries and the diversity of social, political, and economic conditions, the transboundary river basin management is of supreme importance in the Danube River Basin. The Danube River Protection Convention signed in 1994 is a legal instrument for cooperation and transboundary water management, and it led into establishing the International Commission for the Protection of the Danube River (ICPDR).

The Danube River in Serbia has social, economic, and ecological dimensions, certainly is an important natural water resource, and therefore is significant for both quantitative and qualitative research (ICPDR 2006). Surface water quality is determined by natural processes (atmospheric conditions, the level of precipitation, and soil erosion), human activities (urbanization, industrial, and agricultural activities), and increased exploitation of water resources (Carpenter et al. 1998; Jarvie et al. 1998). Discharges of industrial and municipal wastewater as well as the agricultural effluents are considered persistent sources of pollution (Vega et al. 1998). According to the ranking of 18 major river flows in Serbia, the Danube River is in the second group of rivers and with the tendency of further deterioration of water quality (Ocokoljić et al. 2009). Milanović et al. (2010) analyzed the water quality of the Danube in Serbia and pollution and protection problems and presented the activities and projects in the EU, in which Serbia is also included, for the purpose of revitalization and protection of the Danube River flow. Ilijević et al. (2012) analyzed long-term changes in the eco-chemical status of the Danube River in the region of Serbia. A general interest to ensure the sustainable and equitable use of waters and water resources in the Danube River Basin led to the development of a system for monitoring the river, which would produce data sets of its eco-chemical status. The obtained results revealed a constant improvement and acceptable trends of the eco-chemical status of the Danube River, as well as substantial differences in the quality of the inflowing and outflowing water (Ilijević et al. 2012). Following the requirements of the WFD EU, a process of selecting pollutants relevant at the river basin scale started in 2001 (Slobodnik and von der Ohe 2015). A case study of the Danube River in Serbia included the actual and required water quality, water quality trends, long-term changes, and multicriteria analysis of ten selected water quality parameters (Takić et al. 2012). The surface water quality faithfully reflected the impact of human activities, particularly in terms of the impaired quality of watercourses and characteristics of aquatic ecosystems. A special attention must be given to the evaluation of the Danube River water quality, pollution problems, and protection, having in mind that it is one of the most valuable natural water resources in Serbia.

The EU gives great significance to the protection and preservation of water resources and environment, treating them as the base of sustainable development in the twenty-first century. Water resources are considered as the most important segment of the environment and protection of natural environment is unthinkable without adequate protection of water, which includes water monitoring, water classification, and regulation of water quality standards (ICPDR 2006).

In reaction to the requirements of the WFD, for the first time, this study applied new objective criteria in the classification of water quality by determining the ecological status and pollution of the Danube River in Serbia. The results of the research should indicate whether the actual water quality corresponds to the required water quality and the planned regime of use, in accordance with the requirements of the WFD. The aim of this paper is to assess the ecological status and water pollution of the Danube River in the year 2014, applying the method of WPI.

2 Study Area

The Danube River is a major international river, which runs for 588 km through Serbia. The main tributaries of the Danube River in Serbia are the rivers Tisa, Sava, and Velika Morava. The investigation of the Danube River water quality in Serbia includes teen hydrological measuring stations at given distances from the river mouth: Bezdan—entry point—1425.59 km, Bogojevo—1367.4 km, Novi Sad—1254.98 km, Slankamen—1215.5 km, Zemun—1, 174 km, Smederevo—1116.9 km, Banatska Palanka—1076.6 km, Tekija—956.2 km, Brza Palanka—883.8 km, Radujevac—exit point—852 km. Figure 1 shows the map of profiles where the Danube River water analysis was performed.

3 Materials and Methods

The most recent available data from the Republic Hydrometeorological Service of Serbia (RHSS) water

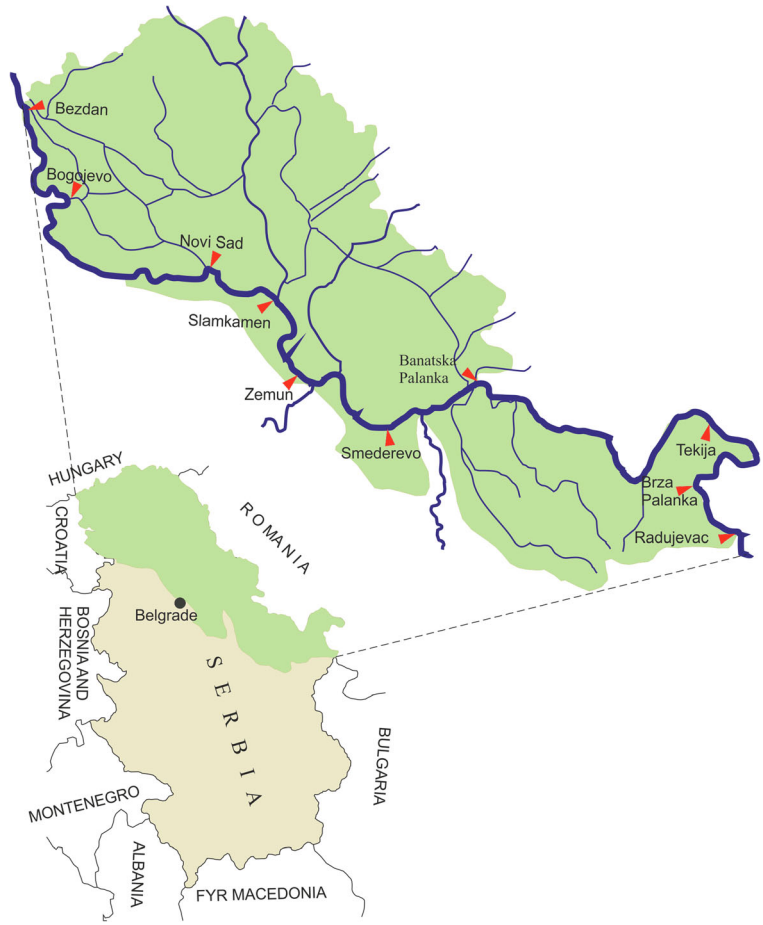

Fig. 1 Map of the hydrological measuring stations on the Danube River in Serbia

quality were used, for the year 2014, obtained from ten hydrological measuring stations on the Danube River (Ministry of Agriculture and Environmental Protection Republic of Serbia 2015). The enactment of the regulation on determining the water bodies of surface water and groundwater (Official Gazette of the RS, No. 67/ 2011) and the regulation on the parameters of ecological and chemical status of surface water and parameters of the chemical and quantitative status of groundwater (Official Gazette of the RS, No. 74/ 2011) enabled the conditions for RHSS monitoring in accordance with the requirements of the Water Framework Directive EU (WFD2000/60EC) from 2012 (Regulation on determining the water bodies of surface water and groundwater, "Official Gazette of the RS," No. 67/ 2011; Regulation on the parameters of ecological and chemical status of surface water and parameters of the chemical and quantitative status of groundwater, "Official Gazette of the RS," No. 74/ 2011; WFD 2000). The WFD requires EU classification of surface waters through the assessment of the ecological status of surface waters. The ecological status indicates the quality of the structure and functioning of an aquatic ecosystem joined to surface waters and classification in line with the special regulation.

For surface waters, the overall objective of the WFD EU for Member States is to achieve "good ecological status" and "good chemical status" in all water bodies of surface water by 2015. For water bodies that have been identified as "significantly modified water bodies" and "artificial water bodies" instead of "good ecological status," the main objective of the WFD is that these water bodies achieve "good ecological potential" and "good chemical status." The regulation on the parameters of ecological and chemical status of surface waters and parameters of the chemical and quantitative status of groundwater lays down the parameters of the ecological and chemical status of rivers and lakes and the parameters of the ecological potential of artificial water bodies and significantly changed water body and parameters of the chemical and quantitative status of groundwater,

based on which the status assessment of water bodies of surface water and groundwater is performed. The ecological status is determined according to the parameters sorted into the following quality elements: biological, physical-chemical, and hydromorphologic. Overall, the ecological status of the river is classified as excellent (class I), very good (class II), good (class III), poor (class IV), and very poor (class V). The standard threshold values for all parameters correspond to class I ecological status and determine the target quality that a body of water needs to achieve (WFD 2000).

The assessment criteria of the ecological status in function of physico-chemical quality elements realistically reflect current pollution of the surface water. If some parameters exceed the limit values of the required good status, the ecosystem approach clearly indicates the need to take continuous monitoring in order to prevent pollution. Comprehensive evaluation of contamination definitely needs to analyze a larger number of pollutants in water, sediment, and microbiological pollutants. The sediment monitoring has become an integral part of the existing water management and protection programs, in particular to assess the ecological status of a body of water (Reuther 2009).

The paper analyzes data for nine physical-chemical parameters, those being pH, dissolved oxygen (DO), biochemical oxygen demand (BOD5), total organic carbon (TOC), ammonium ion (NH_4-N), nitrate (NO_3-N), orthophosphate (PO_4-P), total phosphorus (TP), and chloride (Cl). Since the quality assessment implies the determination of physical-chemical parameters of the Danube River water, the relevant standard methods were used for such an analysis: pH—SRPS H.Z1.111; DO—SRPS ISO H.Z1.135:1970; BOD5—SRPS ISO 5813:1994; TOC—SRPS ISO 8245:2007; NH_4-N—SRPS ISO 5664; NO_3-N—JUS ISO 7890; PO_4-P—SRPS EN ISO 6878:2008; TP—SRPS EN ISO 6878:2008; and Cl—SRPS ISO 9297:1997. According to the Regulation on determining the water bodies of surface water and groundwater, the Danube River is classified as the aquatic water body of type 1. The Danube is a type of large river with a dominance of fine sediment, type 1, for which the applicable regulations defined the target concentration of physico-chemical parameters for the appropriate class of the ecological status of water (Table 1) (Regulation on the parameters of ecological and chemical status of surface water and parameters of the chemical and quantitative status of groundwater, "Official Gazette of the RS," No. 74/ 2011).

Table 1 Physico-chemical limits of ecological status for water bodies type 1

Parameter	Limits between the classes of ecological status			
	I–II	II–III	III–IV	IV–V
pH	6.5–8.5	6.5–8.5	6.5–8.5	< 6.5; > 8.5
DO (mg L^{-1})	8.5	7.0	5.0	4.0
BOD5 (mg L^{-1})	2.0	5.0	8.0	20.0
TOC (mg L^{-1})	2.0	5.0	9.0	23.0
NH_4-N (mg L^{-1})	0.1	0.3	0.8	1.0
NO_3-N (mg L^{-1})	1.00	3.00	6.00	15.00
PO_4-P (mg L^{-1})	0.02	0.1	0.2	0.5
TP (mg L^{-1})	0.05	0.2	0.4	1.0
Cl (mg L^{-1})	50	100	/	/

It is important to point out that the assessment of the ecological status of the Danube River water quality highlights the actuality of a new approach in assessing the quality of surface water and adjustment of the national legislation in the field of water to WFD EU. The assessment of the ecological status of the Danube River water quality involves a method of comparative analysis of average annual concentration values of the observed physical and chemical parameters with the limit values of concentrations determined in ecological classification (Regulation on the parameters of ecological and chemical status of surface water and parameters of the chemical and quantitative status of groundwater, "Official Gazette of the RS," No. 74/ 2011).

The water pollution index (WPI) method proposed is based on the relevant literature (Filatov et al. 2005). WPI is calculated as the sum of the ratio of the measured annual average value (Ai) and the standard threshold values (T) for each parameter, divided by the number of used parameters (n):

$$\mathrm{WPI} = \frac{1}{n} \sum_{n=1}^{n} \frac{\mathrm{Ai}}{T}$$

The current regulation defines the target allowable concentrations of certain parameters for the given classes of the ecological status. The standard threshold values for all parameters are specific for each country and in Serbia are given as a national legislative (Official Gazette of the RS, No. 74/ 2011).

The standard threshold values for Class I are given in Table 2.

Table 2 The standard threshold values (*T*) for class I

Parameter	Measurement unit	The standard threshold values (*T*)
pH	/	8.5
DO	mg/L	8.5
BOD5	mg/L	2
TOC	mg/L	2
NH_4-N	mg/L	0.1
NO_3-N	mg/L	1
PO_4-P	mg/L	0.02
TP	mg/L	0.05
Cl^-	mg/L	50

Based on the obtained WPI values, watercourses are classified into different classes of quality (Table 3). If the value of the WPI < 1, the watercourse is marked as pure, if the WPI > 2, the watercourse is polluted, and if WPI > 6, the watercourse belongs to a group of heavily polluted waters (Lyulko et al. 2001).

Authors most frequently use the WPI methods as simple indicators of watershed pollution, as a tool for evaluating water quality management effectiveness. Independent of the presence of pollutants, WPI is a combined physical-chemical index which makes it possible to compare the water quality of various water bodies. Therefore, it has wide application and it is used as an indicator of sea and river water quality (Filatov et al. 2005). Estimating water pollution and determining changes in the values of the selected indicators of water quality for the river along its course were conveyed using the WPI (Jabłońska 2008). A case study of the Hydro-system Danube-Tisa-Danube, Serbia, presents an assessment of the surface water quality using the water pollution index (Milanović et al. 2011). The application of the WPI in the assessment of surface water quality and the ecological status of rivers—a case study of the Sava River and a case study of the Timok River (The Danube River Basin) in Serbia—demonstrates that the WPI could be effectively used as a metric for ecological assessment according to the requirements of the WFD EU (Brankov et al. 2012; Popović et al. 2016).

Table 3 Water quality classification based on the WPI

Class	Characteristics	WPI
I	Very pure	≤ 0.3
II	Pure	0.3–1.0
III	Moderately polluted	1.0–2.0
IV	Polluted	2.0–4.0
V	Impure	4.0–6.0
VI	Heavily impure	> 6

4 Results and Discussion

The WFD EU is the most important legal instrument in the field of water and a prerequisite for successful integrated water resource management. The preparation of our country for the EU integration process entails the harmonization of a national legislation in the water sector with the EU directives. For all surface waters, WFD EU requires "good status," i.e., a low level of natural changes that occur as a result of human activities until 2015 (WFD EU 2000). Therefore, it is the right moment to analyze the ecological status of the Danube River water quality, based on the analysis of the physico-chemical parameters at the measuring stations along the river and the application perspectives of integrated water resource management in Serbia after EU recommendations. The annual average values of physical-chemical parameters at hydrological stations of the Danube River in 2014 are given in Table 4.

The water of the Danube River in Serbia has alkali character at all measuring stations with pH values that aim toward limits of the permitted range of the required quality status. The oxygen regime is relatively balanced observing indicators of river water loads with organic matter DO and BOD5, while the highest values of TOC are recorded at Bogojevo. The measured concentrations of TOC at Bogojevo measuring station in 2014 were significantly higher than the measured concentrations at the outlet of the Danube River in Serbia, i.e., Brza Palanka and Radujevac measuring stations. The increased presence of nutrient PO_4-P is also noticed at Tekija and Radujevac, where the measured concentrations exceed the value of the good ecological status of water quality. Significant fluctuations in the concentration of chloride at Bezdan and Radujevac measuring stations are recorded for the observed period.

The ecological status of the Danube River water quality was determinated in terms of nine physico-chemical parameters. Table 5 shows the class of the ecological status according to individual physical and chemical indicators of quality for all measuring stations of the Danube in Serbia in 2014.

Table 4 Annual average values of physical-chemical parameters at the Danube River study sites in 2014

Station	pH	DO mg/L	BOD5 mg/L	TOC mg/L	NH_4-N mg/L	NO_3-N mg/L	PO_4-P mg/L	TP mg/L	Cl^- mg/L
Bezdan	8.1	10.6	1.9	4.0	0.06	1.95	0.042	0.188	21
Bogojevo	8.2	10.6	1.9	5.2	0.06	1.83	0.049	0.129	19
Novi Sad	8.2	9.9	2.4	4.6	0.06	1.74	0.046	0.108	20
Slankamen	8.2	10.5	2.0	4.1	0.06	1.80	0.044	0.1	19
Zemun	8.1	9. 3	2.0	4.6	0.13	0.80	0.042	0.09	21
Smederevo	7.9	8.9	1.9	3.6	0.15	0.73	0.041	0.08	19
Banat. Palanka	8.0	9.5	1.8	4.3	0.12	1.45	0.04	0.097	20
Tekija	8.0	8.6	1.8	3.9	0.15	0.73	0.052	0.088	17
Brza Palanka	8.1	9.0	1.6	3.3	0.12	0.70	0.038	0.074	16
Radujevac	7.9	8.9	1.6	3.2	0.10	0.77	0.074	0.107	17

The ecological classification of a watercourse is determined in accordance with the methodology prescribed by the regulation on parameters of the ecological and chemical status of surface water and the parameters of the chemical and quantitative status of groundwater that paragraph 5 of Article 5 strictly defines as follows: "If one or more parameters of ecological status exceed the limits of good status, ecological status of surface waters can be mostly classified as moderate" (WFD EU 2000).

Ecological classification analyzed as a function of the physical and chemical parameters, in accordance with the regulation, at Bezdan measuring station corresponds to classes I and II, compared to values of pH, DO, BOD5, NH_4-N, and Cl^-, or TOC, NO_3-N, PO_4-P, and TP, respectively. At the Bogojevo measuring station, the content of the observed parameters corresponds to classes I and II, while the concentration of TOC is within the limits of class III. At profiles of Novi Sad, Slankamen, Zemun, Smederevo, and Banatska Palanka, water quality corresponds to class II ecological status observing the concentration of the measured parameters. Water quality at the Bela Palanka measuring station is in the scope of classes I and II regarding all the parameters. The measured concentration PO_4-P impair water quality to class III at the Tekija measuring station and at the outlet of the Danube River in Serbia.

It can be concluded that from the group of observed physical and chemical parameters, the concentrations of TOC and PO_4-P significantly exceed the value of good status, so that the summarized quality of the Danube River corresponds to class III and moderate ecological status. Moderate ecological status provides conditions

Table 5 Ecological classification of water quality of the Danube River at the measuring stations

Station	pH	DO	BOD5	TOC	NH_4-N	NO_3-N	PO_4-P	TP	Cl^-	Ecol. status
Bezdan	I	I	I	II	I	II	II	II	I	II
Bogojevo	I	I	I	III	I	II	II	II	I	III
Novi Sad	I	I	II	II	I	II	II	II	I	II
Slankamen	I	I	I	II	I	II	II	II	I	II
Zemun	I	I	I	II	II	I	II	II	I	II
Smederevo	I	I	I	II	II	I	II	II	I	II
Ban. Palanka	I	I	I	II	II	II	II	II	I	II
Tekija	I	I	I	II	II	I	III	II	I	III
B. Palanka	I	I	I	II	II	I	II	II	I	II
Radujevac	I	I	I	II	I	I	III	II	I	III

that correspond to the values of biological parameters which are typical for the given status, but the ecological changes of the watercourse are not irreversible for the environment.

The results of the analysis showed that the Danube River water quality corresponds to moderate ecological status or class III surface water. Ecological classification identifies a moderate deviation from the values of the parameters in the natural state and indicates a need for a program of measures and operational monitoring to assess the results in the coming years, with the aim of achieving the required ecological status of the Danube River water quality in Serbia.

The WPI represents an arithmetical way of integrating parameters for assessing the chemical and ecological status of surface waters. Based on physical and chemical parameters, WPI simplifies the evaluation of water pollution. The advantage of the WPI is that it allows a combination of different parameters; in addition, there is no limitation to the number or types of used parameters.

The average WPI values were calculated for the observed periods based on the comparison of the annual average values of the listed parameters and defined standard values for class I of water quality (Official Gazette of the RS, No. 74/ 2011). Based on the data from Table 3, the results obtained using the WPI method are presented in Table 6.

The calculated WPI value for each measuring point shows that the water pollution of the Danube River along its course through Serbia was within the range from 1.12 to 1.54, which corresponds to the descriptive indicators of "moderately polluted" water. Observing the hydrological measuring stations, the lowest WPI values were registered at Brza Palanka and Smederevo, approaching the characteristics of pure surface water, while the highest WPI values were registered at Bezdan and Bogojevo. The WPI assessment as a function of nine physico-chemical parameters of the ecological status of water quality shows that the water is more polluted at the Bezdan input profile compared to the Radujevac output profile—the WPI values were 1.54 and 1.38, respectively. According to objective criteria, the WPI values show that the Danube water quality at the exit of Serbia is slightly better than at the entry.

Table 6 WPI values, water classes, and characteristics at Danuve River study sites

Station	WPI	Class	Characteristics
Bezdan	1.539	III	Moderately polluted
Bogojevo	1.520	III	Moderately polluted
Novi Sad	1.423	III	Moderately polluted
Slankamen	1.364	III	Moderately polluted
Zemun	1.305	III	Moderately polluted
Smederevo	1.224	III	Moderately polluted
Banatska Palanka	1.337	III	Moderately polluted
Tekija	1.303	III	Moderately polluted
Brza Palanka	1.125	III	Moderately polluted
Radujevac	1.381	III	Moderately polluted

The overall water pollution of the Danube River on Serbian territory, determined by the median of index values, amounted to WPI = 1.352 for 1-year period, which corresponds to class III, i.e., the typical "moderately polluted" surface water. It is important to present the parameters which influence pollution the most. The standard threshold values (*T*) for class I ecological status are a target function of surface water quality. The most important parameters with values higher than the permitted limits are as follows: total organic carbon (TOC), orthophosphate (PO_4-P), and total phosphorus (TP). TOC is a measure of water contamination and it shows an increased organic load, while PO_4-P and TP are the major nutrient that influences the primary production in aquatic ecosystems of the Danube River.

5 Conclusion

The quality of watercourses accurately reflects the level of human activity by observing the variability of aquatic ecosystems, as well as the level of pollution at the hydrological profiles of the Danube through Serbia. The results of this study show differences in the observed ecological classification of ten measuring stations of the Danube and can clearly be explained by differences in methodological approaches. The assessment of the ecological status involves the method of comparative analysis of the measured values of the individual parameters with the limit values for a given class type of a body of water. According to WFD, a crucial principle is "one out-all out" so that the measured parameter value which exceeds the upward threshold determines the summary ecological status of the Danube. The calculation of the WPI values as a function of the same physical-chemical parameters of the ecological status involves the use of an equation that summarizes the proportion by weight of all

the parameters and calculates the total water pollution at the measuring stations.

The assessment of the ecological status of the Danube River water quality in Serbia highlights the actuality of a new approach in assessing the quality of surface water and adjustment of the national legislation in the field of water to WFD. The ecological status of the Danube River water quality ascertained in 2014 was class III, corresponding to "moderate ecological status" and deviating from the required "good ecological status."

This study presents an assessment of the water quality, and the WPI values indicate that the pollution levels are different at the measuring stations. The assessment WPI as a function of nine physico-chemical parameters of the ecological status of water quality shows that the water pollution of the Danube River in Serbia, according to the calculated WPI = 1.352, was characterized as "moderately polluted" and corresponds to class III of surface water. The water quality classification based on the WPI confirms the results of the ecological status of the Danube River.

The results of this investigation are important from the aspect of environmental protection and as a basis for further monitoring of changes in this aquatic ecosystem. TOC, PO_4-P, and TP are the important parameters which influence pollution the most. The results demonstrate that the WPI could be effectively used in the assessment of water quality. The ecological classification identifies a moderate deviation from the values of the parameters in the natural state and points to the need to introduce a program of measures to protect the water of the Danube and to introduce operational monitoring to assess the results in the coming years. The success of the implementation and realization of the key objectives of WFD EU directives will be assessed by achieving the required ecological status of the Danube River water quality in Serbia.

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