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TREND ANALYSIS OF WATER QUALITY PARAMETERS IN THE MIDDLE PART OF THE DANUBE FLOW IN SERBIA

Abstract: The Danube River plays significant role not only for preserving natural ecosystems. The aim of this paper is to examine the Middle Danube water quality in the part flowing through Serbia in section Bezdan - Banatska Palanka. Water quality data were examined for seven control points for period 2004-2018, for seven parameters: suspended solids (SS), dissolved oxygen (DO), electrical conductivity (EC), nitrates (NO_3^- -N), total phosphorus (P_{tot}), biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD). Data analyses included the application of ANOVA, linear regression analysis and Mann-Kendall trend test. The Mann-Kendall tests in most (32/49) cases, i.e. in 65 %, confirmed the non-existence of a significant trend. Significant downward trends were confirmed in 17 cases. Water quality improvement was confirmed at following control points: Bezdan for NO_3^- -N, P_{tot} and BOD_5 ; Bogojevo for NO_3^- -N, P_{tot} , COD and BOD_5 ; Novi Sad for P_{tot} , BOD_5 and COD; Slankamen for BOD_5 and COD; Smederevo for NO_3^- -N and COD; Banatska Palanka for NO_3^- -N. Slight deterioration of water quality was confirmed only in two cases, at the Zemun and Smederevo where DO was decreasing. Water quality for the examined period was stable and can be characterised as excellent and/or very good (class I or class II). Results emphasise fact that water quality trends monitoring reveals river sectors where the process of water quality degradation is ongoing. Timely detected critical river sectors can draw the attention of decision-makers, who can improve the existing legislation that would lead to water quality improvement.

Keywords: Mann-Kendall test, self-purification, trend analysis, water quality

Introduction

Water demand has been growing at more than twice in the last century, therefore a number of countries around the world are reaching the limit at which water can be sustainably managed. Water resources management entails providing sufficient quantities of water of appropriate quality for the needs of different users (drinking, irrigation, industry, recreation, etc.). In such circumstances, the deterioration of water quality reduces its usability for down-stream users, which can negatively affect the development of the area and the life of the local population [1, 2]. Therefore, monitoring of basic water quality parameters of all types of water bodies should be among priorities in the water management system at global and local scale.

The quality of river water depends on a number of natural and anthropogenic influences. Geological and pedological, climatic and topographic characteristics of the area

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and current processes (runoff, erosion) have a great impact on water quality and usability. In addition, human activities, settlements, industry, agriculture, upstream activities, etc., directly affect water quality in the studied part of the flow [3].

The Danube is the second largest river in Europe, with a total length of 2826 km and a basin area of 817,000 km². The Danube basin encompasses parts of 19 countries and has 11 major tributaries, and hence it is the most international river basin in the world [4]. The Danube basin includes glacier-covered mountains in the Alps, the mid-mountains mostly covered with dense forests, karst regions with little vegetation, uplands, lowlands and plains [5].

The Danube River Basin is home to more than 80 million people and plays an important economic role in transportation, hydropower generation and water supply and bears unique ecological and cultural values [4]. However, due to the excessive human use and pollution, the water of the Danube even today is the recipient of raw sewage from cities, waste from factories (in non-EU countries), agricultural chemicals, oil stains and products of combustion of propulsion engines for ships [6]. Part of this pollution eventually deposits on the banks, where it deteriorates the natural balance of the ecosystem seriously threatening flora, fauna and habitats [7, 8]. By the degradation of water quality numerous natural reserves, national parks, and wetlands along the river banks of the Danube are directly endangered [9].

The problem of pollution of the Danube has been noticed relatively late, at the end of 1980s, after the chemicals in the water already caused the disappearance of part of the aquatic wildlife, especially fishes [10, 11]. Research, monitoring and analysis of the Action Plan for the Danube Region [12] have identified the major problems concerning the quality, chemical and ecological status of surface and groundwater within the Danube basin.

Therefore, this study includes a comparative analysis of chemical and physico-chemical water quality parameters and their trends along the Danube within the sector: Bezdan - Banatska Palanka (1427 - 1076.6) river-km. The examination of trends confined to the trends over time and finally, quantification of trends was performed to demonstrate their significance.

Material and methods

Study area

Within the Danube Basin three major subsections are distinguished (Fig. 1): Upper basin, Middle and Lower basin. The Middle Danube basin extends from Bratislava until the Iron Gates at the boundary between Serbia and Romania (until the Bazias station). The slope of the Danube River decreases substantially after Bratislava towards Pannonian plain [13].

Middle Danube which geographically belongs to Serbia, is divided into the Pannonian part and the Vlach part. In the Pannonian part (1427 - 1077) river-km, which is the subject of this study, there are rather significant inflows of tributaries. The major tributary in the north is the Tisa River, which is coming from the Carpathian Mountains. From the south, there are the Drava, Sava and Velika Morava. The Sava, as the largest tributary of the Danube (mean annual discharge (*MQ*) at Sremska Mitrovica ~1570 m³/s), contributes 25 % to the total runoff of the Danube, while the Tisa (*MQ* at Szeged ~840 m³/s), the largest subbasin (156.087 km²) of the Danube by area (~12 %), contributes only 12 % to the runoff [5].

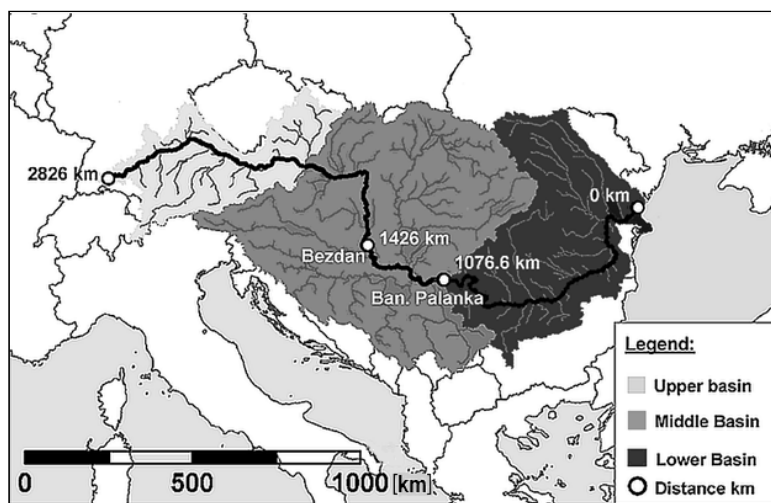


Fig. 1. The Danube catchment, its three sub basins and investigated section Bezdán-Banatska Palanka [9]

The Danube water quality, besides the influence of tributaries, is affected by urban agglomerations of cities Novi Sad and Belgrade, as well as smaller settlements with industry and agriculture [11]. Monitoring water quality included seven control points (CPs) on the Pannonian part (1427 - 1077) river-km (Fig. 2). Table 1 shows a detailed description of the CPs and the hydrological characteristics of the Danube.

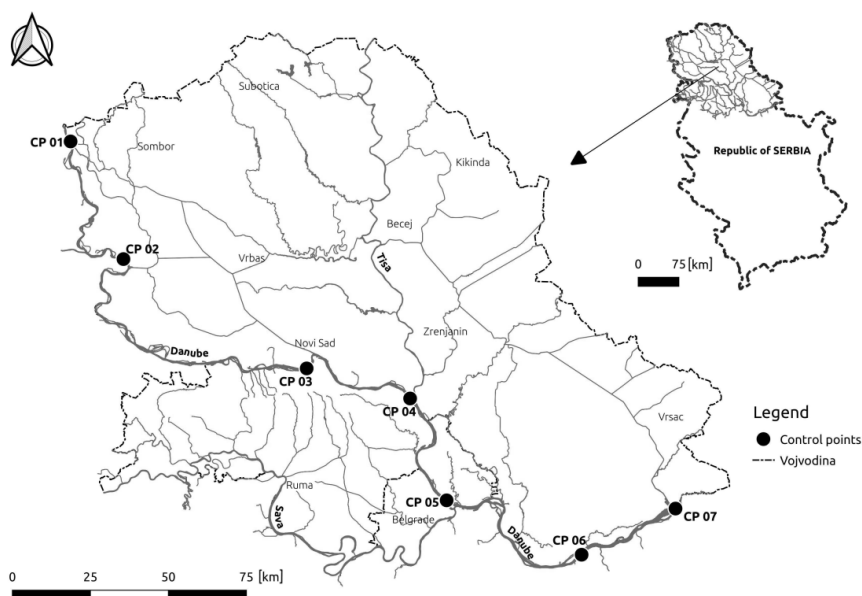


Fig. 2. Investigated section of the Middle Danube River with marked CPs

Table 1

List of monitoring control points

Location name/ Control points	Latitude [d.m.s.]	Longitude [d.m.s.]	Distance [km]	Catchment area [km ²]	Altitude [m.a.s.l.]	Profile location*	Mean annual discharge [m ³ /s]
Bezdan/CP1	45 51 15	18 51 51	1427.0	210,250	83.15	L	~ 2410
Bogojevo/CP2	45 31 49	19 05 02	1367.0	251,253	80.41	L	~ 3000
Novi Sad/CP3	45 13 28	19 51 40	1258.0	254,085	74.52	R	~ 3030
Slankamen/CP4	45 08 24	20 16 00	1215.5	254,961	72.58	R	~ 3070
Zemun/CP5	44 50 56	20 25 02	1174.0	412,762	70.76	R	~ 3800
Smederevo/CP6	44 41 37	20 57 53	1116.2	525,820	70.20	R	~ 5480
Banatska Palanka/CP7	44 49 06	21 20 42	1076.6	568,648	68.58	M	~ 5720

*L - left bank, R - right bank and M - middle of the river

The subject of analysis in this study was water quality data of the Danube River for the period 2004-2018, within the sector Bezdan - Banatska Palanka (1427 - 1077) river - km. Monthly monitoring data of chemical parameters were obtained from the Republic Hydrometeorological Service of Serbia (2004-2011) [14] and the Agency for Environmental Protection of the Republic of Serbia (2011-2018) [15]. Chemical analyses were carried out by the following methods: concentration of suspended solids (SS) was measured according to the standard SRPS H.Z1. 160:1987 [16]; dissolved oxygen (DO) according to the SRPS ISO H.Z1.135:1970 [17]; conductivity (*EC*) after the method UP 1.95/PC 12 [18]; nitrates (NO₃⁻-N) by the APHA AWWA WEF 4500-NO3-B [19]; total phosphorus (P_{tot}) by the APHA AWWA WEF 4500-P (A,B,E) [20]; biological oxygen demand (BOD₅) according to the SRPS ISO 5815:1992 [21] and chemical oxygen demand (COD) as KMnO₄ according to the SRPS ISO 8467:1994 [22].

Based upon measured values samples are formed. Numeric characteristics of samples are representing mean annual values of the parameters, which are used for analyses and discussion of the results obtained. The methods used in this paper for statistical processing and data analysis were:

- Basic statistical analysis and ANOVA [23].
- Linear regression for trend analysis [24].
- Mann-Kendall nonparametric test for determination of trend significance [25].

The statistical processing of data and graphic representations in the paper were done using computer program R version 4.0.2. (2020-06-22) and Microsoft Excel (2007).

ANOVA

Analysis of variance (ANOVA) is a statistical model used for checking the existence of differences between more than two arithmetic means of the same or different basic sets. For statistical testing of the equality of means, ANOVA uses the *F*-test. The obtained values are compared to the critical values for the *F* distribution and defined degrees of freedom. The significance threshold values are $p = 0.05$ and $p = 0.01$. An obtained result is statistically significant if the obtained value is equal or greater than the critical value.

Linear regression

Linear regression is a statistical method used for the determination of the strength and character of the relationship between dependent (Y_i) and independent (X_i) variables. In our

case, X_i represents the time and Y_i represents the value of water quality parameters, considering that our case has temporal data. Linear regression is used to find a regression line with the right inclination for the data. Trends for the analysed parameters are obtained from the slope of the regression line.

Procedure for the Mann-Kendall test

Procedure for the Mann-Kendall test considers the time series of n data points and T_i and T_j as two subsets of data where $i = 1, 2, 3, \dots, n-1$ and $j = i+1, i+2, i+3, \dots, n$. The Mann-Kendall test involves computing a statistic S , which is the difference between the number of pairwise differences that are positive minus the number that are negative. If S is a large positive value, then there is evidence of an increasing trend in the data. If S is a large negative value, then there is evidence of a decreasing trend in the data.

The Mann-Kendall S Statistic is computed as follows:

$$S = \sum_{i=1}^{n-1} \sum_{j=i+1}^n \text{sign}(T_j - T_i) \quad (1)$$

$$\text{sign}(S) = \text{sign}(T_j - T_i) \begin{cases} 1 & \text{if } T_j - T_i > 0 \\ 0 & \text{if } T_j - T_i = 0 \\ -1 & \text{if } T_j - T_i < 0 \end{cases} \quad (2)$$

where T_j and T_i are the annual values in years j and i , $j > i$, respectively.

$$S = \text{Total}(\text{plusses}) - \text{Total}(\text{minuses}) \quad (3)$$

The variance of S , $\text{VAR}(S)$, by the following equation:

$$\text{VAR}(S) = \frac{1}{18} \left[n(n-1)(2n+5) - \sum_{p=1}^g t_p(t_p-1)(2t_p+5) \right] \quad (4)$$

where n is the number of data points, g is the number of tied groups (a tied group is a set of sample data having the same value), and t_p is the number of data points in the p^{th} group. The summation term in the numerator is used only if the data series contains tied values.

The standard test statistic Z_0 is calculated as follows:

$$Z_0 = \frac{S - \text{sign}(S)}{\sqrt{\text{VAR}(S)}} \quad (5)$$

The test statistic Z_0 measures the significance of the trend. This test statistic is used to test the null hypothesis, H_0 . If $|Z_0|$ is greater than $z_{\alpha/2}$, where α represents the chosen significance level ($\alpha = 5\%$ with $z_{0.025} = \pm 1.96$) then the null hypothesis is invalid implying that the trend is significant.

Results and discussion

Monitoring results of CPs were analysed in two ways. Table 2 shows mean values calculated as average annual values of the seven parameters (SS, DO, EC, NO_3^- -N, P_{tot} , BOD_5 and COD) observed during 15 year period (2004-2018), for all seven CPs, their standard deviation and coefficients of the variation, as well as the results of ANOVA test. According to the obtained F values at the threshold level of significance set to $p = 0.05$ and

$p = 0.01$, null hypothesis about equality of mean values was rejected for the following parameters: SS, DO, EC, NO_3^- -N and COD. Based upon the ANOVA test and water quality values, of most of the parameters (5), it can be concluded that investigated section CP1-CP7 has been influenced mostly by tributaries and urban agglomerations.

Table 2
Mean values, standard deviation (SD), and coefficient of variation (CV) of physical-chemical parameters showing water quality for seven CPs at Danube and ANOVA results

Parameters	Desc. stat.	CP1	CP2	CP3	CP4	CP5	CP6	CP7	F	p
SS [mg/L]	Mean	27.6	30.4	24.6	26.6	20.7	17.9	29.4	7.337	0.000*
	SD	±7.1	±5.8	±3.8	±7.5	±3.9	±5.2	±10.1		
	CV	0.26	0.19	0.15	0.28	0.19	0.29	0.34		
DO [mg/L]	Mean	10.8	10.5	10.1	10.2	9.5	9.4	9.3	16.87	0.000*
	SD	±0.7	±0.4	±0.3	±0.5	±0.7	±0.6	±0.4		
	CV	0.07	0.04	0.03	0.05	0.07	0.07	0.04		
EC [µS/cm]	Mean	424.3	419.3	416.6	411.6	401.7	396.7	400.5	2.682	0.019*
	SD	±31.2	±22.4	±27.7	±30.1	±13.6	±17.1	±27.7		
	CV	0.07	0.05	0.07	0.07	0.03	0.04	0.07		
NO_3^- -N [mg/L]	Mean	1.839	1.690	1.688	1.565	1.130	0.927	1.309	18.87	0.000*
	SD	±0.307	±0.174	±0.176	±0.223	±0.562	±0.303	±0.114		
	CV	0.17	0.10	0.10	0.14	0.50	0.33	0.09		
P_{tot} [mg/L]	Mean	0.119	0.114	0.111	0.108	0.116	0.110	0.117	0.817	0.559
	SD	±0.023	±0.013	±0.016	±0.008	±0.023	±0.016	±0.017		
	CV	0.19	0.11	0.14	0.08	0.20	0.15	0.14		
BOD_5 [mg/L]	Mean	2.3	2.3	2.5	2.3	2.2	2.1	2.0	1.929	0.084
	SD	±0.4	±0.4	±0.3	±0.5	±0.4	±0.4	±0.6		
	CV	0.16	0.19	0.12	0.21	0.18	0.19	0.28		
COD [mg/L]	Mean	4.4	4.6	3.9	4.6	3.6	3.5	4.1	16.55	0.000*
	SD	±0.5	±0.4	±0.4	±0.5	±0.4	±0.4	±0.4		
	CV	0.12	0.08	0.10	0.11	0.11	0.11	0.09		

* $p < 0.01$ and $F > F_{0.01}$; $p < 0.05$ and $F > F_{0.05}$ ($F_{0.01} = 3.12$; $F_{0.05} = 2.25$)

The second analysis method tracks the trend of significance and results are shown in Table 3. For all parameters from seven CPs corresponding equations of linear regression are given along with Mann-Kendall statistic S . The sign of statistic S represents the direction of a possible (potential) trend. Next are calculated estimates of variance $\text{VAR}(S)$ of statistic S and Z_0 statistics. According to the normal distribution, on the threshold of significance $\alpha = 0.05$, for a two-sided test, the critical value of $z_{(\alpha/2)}$ is the normal distribution $z_{(0.05/2)} = z_{0.025} = \pm 1.96$.

On the basis of the linear regression function (49 in total) and Mann-Kendall test for most cases (32), it was found that trend was not significant. Accordingly, the water quality in the last decade is stable. In seventeen cases significant downward trends were confirmed. Hence, an improvement of water quality was confirmed for CP1 for NO_3^- -N, P_{tot} and BOD_5 ; in CP2 for NO_3^- -N, P_{tot} , COD and BOD_5 ; in CP3 for P_{tot} , BOD_5 and COD; CP4 for BOD_5 and COD; at CP6 for NO_3^- -N and COD and at CP7 for NO_3^- -N. Mildly deterioration of water quality was confirmed at the CP5 and CP6 where DO was decreasing.

Table 3

Trend analysis of of water quality parameters at the CPs using the Mann-Kendall test

Parameters	Linear regression	Mann-Kendall statistic (S)	VAR(S)	Z ₀	Critical Z _{0.025} value, $\alpha = 0.05$	Increasing/Decreasing trend ($\nearrow/\searrow$)
Bezdan/CP1						
SS	$y = 0.262x + 25.53$	7	408.33	0.30	±1.96	No trend
DO	$y = -0.030x + 11.04$	-4	407.33	-0.15	±1.96	No trend
EC	$y = 2.200x + 406.7$	35	408.33	1.68	±1.96	No trend
NO ₃ ⁻ -N	$y = -0.044x + 2.194$	-47	408.33	-2.28	±1.96	Decreasing↘
P _{tot}	$y = -0.002x + 0.131$	-47	408.33	-2.28	±1.96	Decreasing↘
BOD ₅	$y = -0.063x + 2.766$	-60	407.33	-2.92	±1.96	Decreasing↘
COD	$y = -0.048x + 4.818$	-26	407.33	-1.24	±1.96	No trend
Bogojevo/CP2						
SS	$y = -0.157x + 31.63$	-11	408.33	-0.49	±1.96	No trend
DO	$y = -0.027x + 10.76$	-29	408.33	-1.39	±1.96	No trend
EC	$y = 1.417x + 407.9$	27	408.33	1.29	±1.96	No trend
NO ₃ ⁻ -N	$y = -0.030x + 1.927$	-61	408.33	-2.97	±1.96	Decreasing↘
P _{tot}	$y = -0.002x + 0.126$	-45	408.33	-2.18	±1.96	Decreasing↘
BOD ₅	$y = -0.070x + 2.758$	-62	407.33	-3.02	±1.96	Decreasing↘
COD	$y = -0.065x + 5.103$	-53	408.33	-2.57	±1.96	Decreasing↘
Novi Sad/CP3						
SS	$y = -0.151x + 25.76$	-9	408.33	-0.40	±1.96	No trend
DO	$y = -0.002x + 10.11$	-4	407.33	-0.15	±1.96	No trend
EC	$y = 1.627x + 403.6$	29	408.33	1.39	±1.96	No trend
NO ₃ ⁻ -N	$y = -0.021x + 1.854$	-39	408.33	-1.88	±1.96	No trend
P _{tot}	$y = -0.003x + 0.133$	-74	407.33	-3.62	±1.96	Decreasing↘
BOD ₅	$y = -0.044x + 2.854$	-53	408.33	-2.57	±1.96	Decreasing↘
COD	$y = -0.082x + 4.596$	-73	408.33	-3.56	±1.96	Decreasing↘
Slankamen/CP4						
SS	$y = -0.682x + 32.10$	-23	408.33	-1.09	±1.96	No trend
DO	$y = -0.021x + 10.39$	-3	408.33	-0.10	±1.96	No trend
EC	$y = 1.498x + 399.6$	21	408.33	0.99	±1.96	No trend
NO ₃ ⁻ -N	$y = -0.023x + 1.750$	-34	407.33	-1.64	±1.96	No trend
P _{tot}	$y = -0.001x + 0.115$	-33	408.33	-1.58	±1.96	No trend
BOD ₅	$y = -0.071x + 2.917$	-43	408.33	-2.08	±1.96	Decreasing↘
COD	$y = -0.075x + 5.200$	-47	408.33	-2.28	±1.96	Decreasing↘
Zemun/CP5						
SS	$y = 0.258x + 18.67$	25	408.33	1.19	±1.96	No trend
DO	$y = -0.113x + 10.43$	-51	408.33	-2.47	±1.96	Decreasing↘
EC	$y = -0.483x + 405.6$	-15	408.33	-0.69	±1.96	No trend
NO ₃ ⁻ -N	$y = -0.071x + 1.698$	-26	407.33	-1.24	±1.96	No trend
P _{tot}	$y = 0.001x + 0.105$	17	408.33	0.79	±1.96	No trend
BOD ₅	$y = -0.036x + 2.528$	-35	408.33	-1.68	±1.96	No trend
COD	$y = 0.014x + 3.481$	1	408.33	0.00	±1.96	No trend
Smederevo/CP6						
SS	$y = -0.442x + 21.47$	-28	407.33	-1.34	±1.96	No trend
DO	$y = -0.107x + 10.21$	-59	408.33	-2.87	±1.96	Decreasing↘
EC	$y = -0.356x + 404.4$	-23	408.33	-1.09	±1.96	No trend
NO ₃ ⁻ -N	$y = -0.041x + 1.255$	-41	408.33	-1.98	±1.96	Decreasing↘
P _{tot}	$y = -0.001x + 0.118$	-21	408.33	-0.99	±1.96	No trend
BOD ₅	$y = -0.062x + 2.614$	-38	407.33	-1.83	±1.96	No trend
COD	$y = -0.047x + 3.867$	-48	407.33	-2.33	±1.96	Decreasing↘

Banatska Palanka/CP7						
SS	$y = 0.657x + 24.10$	23	408.33	1.09	± 1.96	No trend
DO	$y = 0.028x + 9.088$	35	408.33	1.68	± 1.96	No trend
EC	$y = 1.991x + 384.6$	39	408.33	1.88	± 1.96	No trend
NO ₃ ⁻ -N	$y = -0.017x + 1.441$	-45	408.33	-2.18	± 1.96	Decreasing
P _{tot}	$y = -0.001x + 0.126$	-31	408.33	-1.48	± 1.96	No trend
BOD ₅	$y = 0.016x + 1.904$	-1	408.33	0.00	± 1.96	No trend
COD	$y = -0.005x + 4.189$	-5	408.33	-0.20	± 1.96	No trend

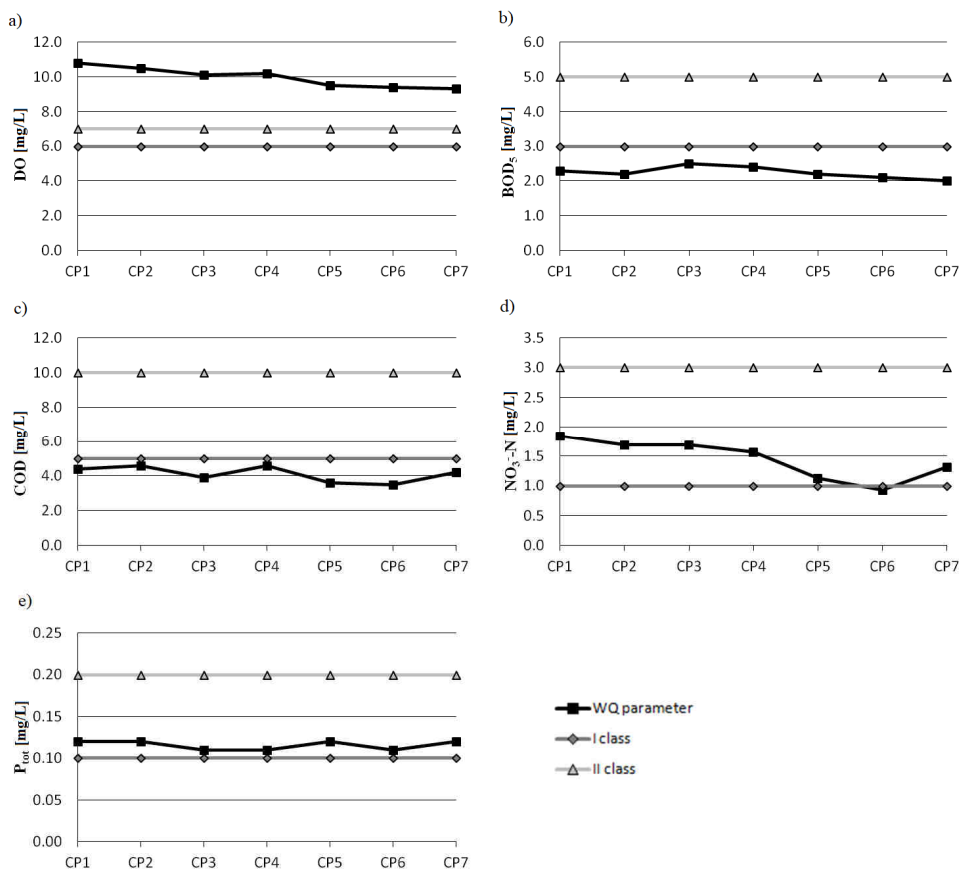


Fig. 3. Mean values of Danube River water quality (WQ) parameters for period 2004-2018 with boundaries of classes I and II, along investigated section for: a) DO, b) BOD₅, c) COD, d) NO₃⁻-N and e) P_{tot}

For the evaluation of the quality of the Danube River water, the Water Quality Classification was used, developed by Trans National Monitoring Network in the Danube River Basin (TNMN), [26]. In this classification scheme, five classes are used for the assessment and target value is the limit value of class II. The class I should represent reference conditions or background concentrations. The results are shown in Table 4 and graphically in Figure 3. Reference conditions for excellent water quality are achieved for

most of the parameters, and water quality of the Danube in the sector is considered excellent and/or very good (class I or class II), Figure 3a-e. The applied classification does not give limit values for SS and EC. The Fish directive [27] sets a guide value for SS of ≤ 25 mg/L and Drinking water directive [28] requires EC to be ≤ 1000 μ S/cm.

Table 4

Estimate of the Danube River water quality on sector Bezdan - Banatska Palanka

Parameters	CP1	CP2	CP3	CP4	CP5	CP6	CP7
DO [mg/L]	Excellent 10.8	Excellent 10.5	Excellent 10.1	Excellent 10.2	Excellent 9.5	Excellent 9.4	Excellent 9.3
NO ₃ ⁻ -N [mg/L]	Very good 1.84	Very good 1.69	Very good 1.69	Very good 1.57	Very good 1.13	Excellent 0.93	Very good 1.31
P _{tot} [mg/L]	Very good 0.12	Very good 0.12	Very good 0.11	Very good 0.11	Very good 0.12	Very good 0.11	Very good 0.12
BOD ₅ [mg/L]	Excellent 2.3	Excellent 2.2	Excellent 2.5	Excellent 2.4	Excellent 2.2	Excellent 2.1	Excellent 2.0
COD [mg/L]	Excellent 4.4	Excellent 4.6	Excellent 3.9	Excellent 4.6	Excellent 3.6	Excellent 3.5	Excellent 4.2
SS [mg/L]	27.6	30.4	Excellent 24.6	26.7	Excellent 20.7	Excellent 17.9	29.4
EC [μ S/cm]	Excellent 424.3	Excellent 419.3	Excellent 416.6	Excellent 411.6	Excellent 401.7	Excellent 396.7	Excellent 400.5

Table 4 and Figure 3 show that there is a slight variability in some parameter values between CPs. Bezdan/CP1 represents the inflow of the Danube River into the sector Bezdan - Banatska Palanka. Bogojewo/CP 2 - reflects the influence of the Drava River after it joins to the Danube inducing higher values of SS and simultaneously NO₃⁻-N and DO reduction. Better water quality is recorded at Novi Sad/CP3, before discharging of the city's sewage, indicated reduction of SS, COD and DO. Slankamen/CP4 reflects the impact of urban agglomeration Novi Sad and the canal HS DTD Novi Sad-Savino Selo, which joins the Danube. This CP is characterised by reduction of NO₃⁻-N and higher values of SS and COD. Zemun/CP5 represents the water quality after the confluence of the Tisa River, which improves values of almost all parameters, except for DO. Smederevo/CP6 reflects the Danube water quality after joining the waters of the Sava and the Tamis River, as well as urban agglomerations Belgrade and Pancevo. Despite pollution originating from city's sewages and other effluents, it seems that the Sava River has significant influence since after its confluence there is a reduction of SS and NO₃⁻-N. Final CP of the section Banatska Palanka/CP7 represents the quality the Danube water after it joins the Velika Morava River and the canal HS DTD Banatska Palanka-Novı Becej, which causes an increase in SS, COD and NO₃⁻-N.

The investigated Danube sector (1427 - 1077) river-km, 350.4 km in length, is under the influence of the major tributaries - the Drava, Tisa and Sava, as well as smaller rivers (the Tamis, Begej and the canals of the HS DTD). Within the section, the flow rate from 2410 m³/s reaches up to 5720 m³/s (Table 1). Besides, the amounts of water, tributaries have a significant impact on water quality. Urban agglomerations Novi Sad (~350,000 inhabitants), Belgrade (~1,660,000 inhabitants) and Pancevo (~90,000 inhabitants), and settlements along the watercourse also have an impact on the quality of the Danube and may contribute to its deterioration. Most of the settlements, including cities Novi Sad and Belgrade, do not have facilities for wastewater treatment and are significant polluters of the

Danube. Concerning the average values of water quality parameters in the sector, presently, mentioned sources of pollution do not have a greater impact on water quality deterioration, due to height self-purification ability of the Danube. Besides, based on the values of water quality parameters improvement is evident for most of the analysed parameters (Fig. 3).

In water quality conditions assessment, a water quality index (*WQI*) is frequently used in expert and scientific research [29-31]. It is easily understood by managers and provides a mechanism for numeric expression for a level of water quality [32]. Takic et al. [31] applied aforementioned index for the period 2005-2009. For the examined annual average values *WQI* is 85 and corresponds to class I. The lowest *WQI* = 81 is determined near Pancevo. Furthermore, by using the method of clusters Mladenovic-Ranisavljevic et al. [6] identified locations Pancevo and Bezdan as the most polluted spots on the Danube in Serbia.

However, the risk of contamination exists. Pannonian part of the Middle Danube in Serbia, the investigated sector, runs through lowland region with a dense network of canals on the left side of the river (in Vojvodina), where agriculture and industry are dominant economy branches. The main canal network of Hydro system Danube-Tisa-Danube (Hs DTD), 960 km in length of which 600 km are navigable, together with a network of secondary canals of the drainage system about 20.000 km are draining 19,300 km² of arable land [33]. Water quality in the main canals of the Hs DTD and natural watercourses in Vojvodina is not satisfying and is ranging from moderate to poor [34]. Pantelic et al. [35] pointed out that a reach of Hs DTD Veliki Backi canal is one of the most polluted in Europe. Measured results showed bad water quality at CP Vrbas for a period 2002-2011 [36]. The Tisa River is connected to the Hs DTD and is also one of the biggest tributaries in the investigated section of the Danube. Along its flow through Serbia its quality decreases slightly downstream, but overall water quality could be characterised as good [32].

Right side tributaries also have to be taken into consideration. According to Gvozdic et al. [37], the lower Drava River showed slight organic pollution downstream of the city Osijek. Persic et al. [38] are reporting only moderate signs of distortion, as a result of anthropogenic activities in watercourses draining the forested catchment of the Spacva River basin. Upon determining Water Pollution Index of the Sava River, near Belgrade, Popovic et al. [39] concluded, that generally, its quality has improved from polluted in 2007, to moderately polluted for the period 2008-2010 and slightly polluted in 2011. Assessment of organic load of Velika Morava [40] confirmed moderately polluted water.

The research of Kolarevic et al. [41] of the Danube water, on section Slankamen-Kostolac, showed moderate organic load (by the method of index of phosphatase activity). Studies of sediments in canals and rivers tributaries [42, 43] found that there is a risk of heavy metals pollution. Isvoran et al. [44] point to the problem of heavy metal pollution, originating from the mining industry, which reaches the Danube through its tributaries. Finally, although the anthropogenic impact on the quality of watercourses is far more intensive, natural factors, i.e. air temperature, can also affect up to a certain extent the increase, or reduction of water pollutant concentrations [45].

Conclusion

The results of this study are indicating that the Danube water quality on the investigated section (1427 - 1077) river-km, for most of the parameters, is affected by the inflow of tributaries and urban agglomerations. Reference conditions for achieving

excellent quality are reached for most of the parameters and water quality of the Danube in the sector is considered excellent and/or very good (class I or class II). Based on the equations of the linear regression of examined parameters and Mann-Kendall test, in most cases, i.e. in 65 %, it was found that there is no significant trend of changes. Significant downward trends were confirmed in seventeen cases. An improvement of the Danube water quality can be expected at Bezdan/CP1 for NO_3^- -N, P_{tot} and BOD_5 ; near Bogojevo/CP2 for NO_3^- -N, P_{tot} , COD and BOD_5 ; near Novi Sad/CP3 on the basis of P_{tot} , BOD_5 and COD; near Smederevo/CP6 for NO_3^- -N and COD; in Banatska Palanka/CP7 concerning NO_3^- -N. Slight decreasing of DO was confirmed at Zemun/CP5 and Smederevo/CP6.

The decreasing trends indicate the locations where it is necessary to pay more attention during further monitoring, ie they indicate the need for detailed research of activities and changes in certain part of the basin and monitoring of the quality parameters of the main tributaries. Also, the results can serve as a basis for comparison for researchers from the region dealing with the water quality of this important European river. Future research of this type should focus on assessing water quality from the aspect of the needs of different users (e.g. drinking, irrigation), which includes the analysis of a wider range of water quality parameters.

During past decades Serbia's economy has undergone a serious recession, which has been reflected positively on natural resources by reducing pressures on them. However, in recent years there is a slight increase of economic growth and if this continues in future it might represent a potential threat to the environment and deterioration of water resources, as final recipients of pollution. Therefore, future development of economy in Serbia in accordance with the Action plan of the EU Strategy for Danube Region [12] has to be followed, by simultaneous implementation of measures focused on environmental protection.

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