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THE ASSESSMENT OF THE SURFACE WATER QUALITY USING THE WATER POLLUTION INDEX: A CASE STUDY OF THE TIMOK RIVER (THE DANUBE RIVER BASIN), SERBIA

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Keywords: Timok River, Borska Reka River, WPI (Water Pollution Index), mining, organic pollution.

Abstract: The Timok River (202 km long, 4547 km^2 basin area) is located in East Serbia. It is a right tributary of the Danube River and one of the most polluted watercourses in Serbia. On the basis of the data provided by the Republic Hydrometeorological Service of Serbia, the paper presents an analysis of water quality and pollution using the combined physico-chemical WPI index (Water Pollution Index) calculated for two periods – 1993–96 and 2006–2009 at four hydrological stations: Zaječar-Gamzigrad (Crni Timok River), Zaječar (Beli Timok River), Rgotina (Borska Reka River) and Čokonjar (Timok River). The following parameters were taken into consideration: dissolved O_2, O_2 saturation, pH, suspended sediments, Five Day Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD_{Mn}), nitrites, nitrates, orthophosphates, ammonium, metals (Cu, Fe, Mn, Hg, Ni, Zn, Cd), sulphates and coliform germs. 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 the I water quality class (according to the Regulation on the Hygienic Acceptability of Potable Water of the Republic of Serbia). The highest pollution degree was recorded in the Borska Reka River, where heavy metal levels (especially manganese and iron) were significantly increased. These metals are indicators of inorganic pollution (primarily caused by copper mining). Also, increased values of the organic pollution indicators (ammonium, coliform germs, Five-Day Biological Oxygen Demand – BOD_5) in the Borska Reka and the Timok rivers are the result of uncontrolled domestic wastewater discharge.

INTRODUCTION

When dealing with the ecological significance of surface waters, numerous hydrological studies address the quality and pollution of watercourses relying on the application of different mathematical and statistical methods. The methods proposed in relevant literature are based on defining different water quality indicators [6], determining the river's ecological state [17] or the use of mathematical indices. Authors most frequently refer to the WQI (Water Quality Index) as a simple indicator of watersheds pollution [14, 2] or to a modified index, such as the Oregon Water Quality Index, as a tool for evaluating water quality management effectiveness [4]. Along with the mentioned indices, in some recent studies, the WPI (Water Pollution Index) has also been applied. It was used as the indicator of the surface water quality in the rivers of Latvia [9], the water quality and pollution of the White Sea [5] and the potable water quality in the Evros Region in Greece [11], as well as for the assessment of the water quality and pollution in the Danube-Tisa-Danube canal system in Serbia [10]. Also, a modified version of the WPI was used to combine historical and geographical approaches to quantify environmental change in the Mersey River Basin in England [3].

The significance of the application of the WPI also rests in the fact that it enables to compare the water quality of various water bodies. As opposed to classification, which is limited to recording the values of particular parameters, this index enables to determine the pollution degree in greater detail. Namely, the WPI enables to establish to what extent the obtained values of a particular parameter are higher than the permitted values and to identify the elements which have the greatest effect on water pollution. The values used to calculate the WPI are not the measured values of particular parameters but the coefficients which enable us to easily identify the main pollutants. This paper presents an attempt to calculate the WPI for the Timok River Basin. This river basin has been chosen because one of the most important mining industry complexes in Serbia is located within it. Apart from the classification of the river water, further aims of the study have been to establish the parameters of organic and inorganic pollution.

The Timok River is the largest river in East Serbia (202 km) and the last tributary of the Danube River in Serbia. Its river basin is situated between 43°15' and 44°15' N and 21°30' and 22°45' E and covers an area of 4 547 km^2 (fig. 1). It is formed by the joining of the Beli Timok (49 km) and the Crni Timok (82.5 km) rivers, which meet at Zaječar. Its

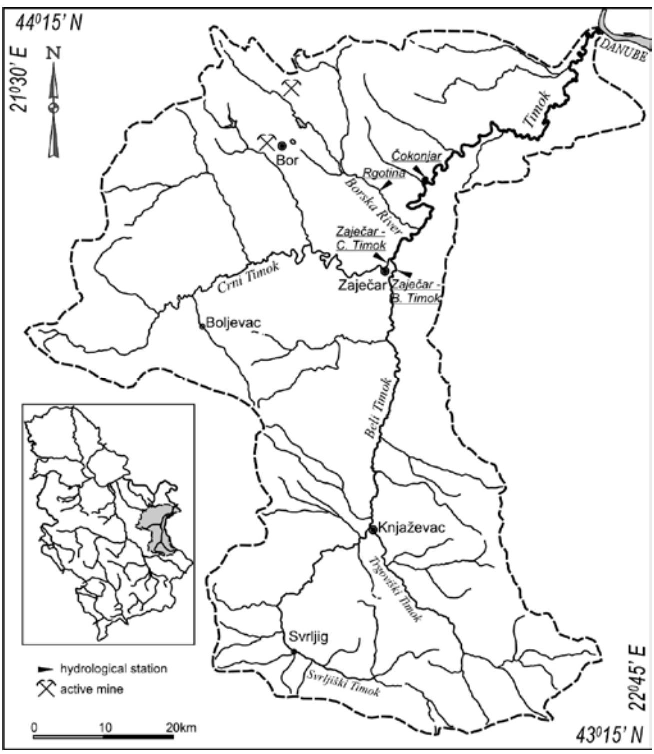

Fig. 1. Location of hydrological stations and active Cu mines in Timok River Basin

annual average discharge is 27 m^3/s, the lowest average monthly discharge is in August (6 m^3/s) and the highest in April (63 m^3/s). The Beli Timok River is formed by the joining of the Trgoviški Timok and the Svrljiški Timok rivers in Knjaževac. The river basin covers an area of 2190.5 km^2, which is 47% of the Timok River Basin. The Crni Timok River springs from the Kučaj Mountain. The river basin area is 1268 km^2 (27% of the Timok River Basin).

The greatest tributary of the Timok River is the Borska Reka River (47 km long), into which it flows to the north of Zaječar. Its river basin area is about 364 km^2. The Borska Reka River is one of the most polluted watercourses both in Serbia and in Europe; its water is unclassifiable in terms of quality classes and without any trace of life. The main source of pollution in the Borska River Basin is the Bor mining industrial complex with two active copper mines and ore processing plants in the Bor area.

Numerous researchers have studied the problem of the water quality and pollution of the Timok River and its tributaries within the scope of the analysis of environmental state or the watercourse quality [15] and the pollution caused by wastewater from human settlements [7]. Also, certain studies deal with the transboundary water pollution from metal mining activities in Serbia and Bulgaria in the Danube River Basin (the Timok and Maritsa rivers) [1]. Since the Borska Reka River, whose basin is affected by mining activity, is a major source of pollution in the Timok River Basin, special attention is paid to the analysis of the impact of mining on its water quality and contamination [8, 12].

MATERIALS AND METHODS

The data on the water quality of the Timok River for the two observed periods – 1993–96 and 2006–2009 – were provided by the Republic Hydrometeorological Service of Serbia. The defined time series enabled us to determine and compare the river water pollution degrees in a ten-year time span. The systematic analysis of the river water quality was carried out at four hydrological stations: Zaječar-Gamzigrad (Crni Timok River), Zaječar (Beli Timok River), Rgotina (Borska Reka River) and Čokonjar (Timok River).

Since the quality assessment implies the determination of physico-chemical parameters of the river water, different groups of standard international laboratory methods are used by the Republic Hydrometeorological Service of Serbia for such analyses: for dissolved oxygen – SRPS H.Z1.135; for suspended sediments – 13.060.30 SRPS H.Z1.160; for pH value – SRPS H.Z1.111; for ammonium ion (NH_4-N) – SRPS ISO 5664; for nitrites (NO_2-N) – SRPS ISO 6777; for nitrates (NO_3-N) – APHA AWWA WEF 4500 – NO_3; for orthophosphates (PO_4-P) – APHA AWWA WEF 4500 – P; for sulphates (SO_4^-) – APHA AWWA WEF 4500 – SO_4; for dissolved iron (Fe) and manganese (Mn) – APHA AWWA WEF 3111 B; for dissolved zinc (Zn), cadmium (Cd), copper (Cu) and lead (Pb) – APHA AWWA WEF 3113; for dissolved mercury (Hg) – EPA 245.1; for the Five-Day Biochemical Oxygen Demand (BOD_5) – EPA 360.2; for the Chemical Oxygen Demand (COD_{Mn}) – SRPS ISO 8467, ISO 8467.

The obtained data were used to determine the water pollution degree in river water on the basis of the WPI (Water Pollution Index). The first step in the calculation of the WPI was the identification of suitable parameters which indicate organic, as well as inorganic water pollution. The WPI represents the sum of the ratio between the observed parameters and the regulated standard values:

$$WPI = \sum_{i=1}^{n} \frac{Ci}{SFQS} \times \frac{1}{n} \quad (1)$$

where C_i is the annual average concentration of the analyzed parameters obtained on the basis of the data concerning the river water quality, sampled approximately once a month. The following parameters are taken into consideration: dissolved O_2, O_2 saturation, pH, suspended sediments, BOD_5, Cod_{Mn}, nitrites, nitrates, orthophosphates, ammonium, metals (Fe, Mn, Hg, Cu, Pb, Zn, Cd), sulfates and coliform germs. QS stands for the standards for the I water quality class in Serbia (Table 1), while n indicates the number of parameters analyzed.

Table 1. Parameters standards for I water quality class in Serbia

Parameter	Measurment unit	Quality standards
O_2	mg/l O_2	8
O_2 saturation	%	90
pH	/	8.5
Suspended matter	mg/l	10
BOD (biological ox. demande)	mg/l O_2	2
COD (chemical ox. demande)	mg/l	10
Nitrites	mg /l	0.03
Nitrates	mg/l	50
Orthophosphates	mg/l	0.005
Ammonium	mg /l	0.1
Iron	mg/l Fe	0.3
Manganese	mg/l Mn	0.05
Mercury	µg/l Hg	1
Copper	µg/l Cu	2000
Lead	µg/l Pb	50
Zinc	µg/l Zn	3000
Cadmium	µg/l Cd	5
Sulphates	mg/l	250
Coliform germs	n/l	2000

On the basis of the obtained WPI values, water is classified into different classes of quality (Table 2). If the value of the WPI < 1, the watercourse is designated as “pure”, if the WPI > 2, the watercourse is considered polluted, and if WPI > 6, the watercourse belongs to the class of heavily polluted waters [9].

Table 2. Water quality classification according to WPI [9]

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

The statistical processing of data and graphic representations in the paper were done using Microsoft Excel, whereas the cartographic method and the Adobe Photoshop software were used to determine spatial relations.

RESULTS AND DISCUSSION

As it has already been mentioned, in order to assess water quality of the Timok River Basin over a longer period of time and trace the trends, two four-year sequences in a ten-year period were analyzed for the purpose of this study: the first sequence (1993–96) and the second sequence (2006–2009).

The annual WPI values indicate different pollution degrees in the basin, as well as the increasing downstream pollution. At the Zaječar-Gamzigrad station, which is near the mouth of the Crni Timok River, the river water mainly falls into classes III and IV (with the exception of 1994, when the watercourse quality was in VI Class due to a higher concentration of coliform germs). There are no big industrial complexes along the watercourse of the Crni Timok River; the area is surrounded by small villages and, therefore, the predominant type of pollution is organic pollution caused by wastewater from these rural settlements. Similar situation has been observed at the Zaječar hydrological station on the Beli Timok River, where owing to the pollution degree, water was classified as Class III and IV, whereas the WPI values are slightly higher (Table 3). In recent years, an increasing pollution trend has been observed: the river water belonged to Class IV in 2008 and 2009. An analysis of the pollution types shows generally high levels of ammonium and coliform germs, which indicates organic pollution caused mainly by wastewater from the city of Knjaževac and the surrounding rural settlements.

At the Rgotina hydrological station, the annual WPI values for all analyzed years indicate a high water pollution degree; accordingly, the water of the Borska Reka River falls into Class VI (heavily polluted) with WPI values > 6. According to Table 3, it can be concluded that the poorest water quality was recorded in 1996 (the average WPI value was 20.86), which is far above the limit value of 6. The WPI index values >10 were also registered in 2008. A comparison of the analyzed periods during the 1990s and after 2000 shows that, according to the WPI values, the general state has not improved, which means that the severe degradation of water resources, mainly caused by inorganic pollution, has still been present. The Borska Reka River and its tributary Kriveljska Reka are the final destination of wastewater originating from Jama and Veliki Krivelj copper mines and from the flotation process in the smelting processing complex Veliki Krivelj, as well from the untreated wastewater from human settlements.

Table 3. Annual average WPI values and water classes in Timok River Basin

Hydrological St.	River	1993	1994	1995	1996	2006	2007	2008	2009
Zaječar-Gamzigrad	Crni Timok	1.13	7.51	1.47	2.56	4.03	1.30	2.50	1.26
		III	VI	III	IV	V	III	IV	III
Zaječar	Beli Timok	1.57	7.91	1.70	3.54	1.42	2.29	3.19	3.01
		III	VI	III	IV	III	III	IV	IV
Rgotina	Borska	9.69	6.10	7.58	20.39	7.29	6.51	10.75	5.97
		VI	VI	VI	VI	VI	VI	VI	VI
Čokonjar	Timok	2.75	2.73	2.07	2.21	2.14	2.94	4.19	5.61
		IV	IV	IV	IV	IV	IV	V	V

The WPI values for the Čokonjar hydrological station on the Timok River, after receiving the Borska Reka River, varied from 2.07–2.75 in the 1993–96 period, which means that the water of this watercourse belonged to Class IV. In the 2006–2009 period, an increasing trend of pollution was observed (the WPI values ranged from 2.14 to 5.61) and the river water was classified as Class V. These high pollution values are greatly due to the Borska Reka River, as well as to the wastewater from the city of Zaječar.

Along with the annual average WPI values which determine the water quality class of the Timok River Basin, the analysis of the influence of some parameters on the pollution degree is also important. As it can be seen from the data presented in Table 4, in both periods – 1993–96 and 2002–2006, certain parameters (pH, nitrites, sulphates, lead, cadmium etc) are within the permitted limits of the regulated standard values for the Class I water quality in Serbia, and, accordingly, they do not have any influence on the pollution in the Timok River Basin.

On the other hand, the values of the elements which are organic pollution indicators (ammonium, coliform germs, BOD_5) increased considerably, just like the levels of some heavy metals (especially iron and manganese) in the Borska Reka River.

The increased levels of coliform germs (fig. 2) and ammonium (fig. 3) indicate considerable pollution that comes from untreated communal wastewater from households of Knjaževac, Bor, Zaječar and the surrounding settlements which are directly discharged into the Timok River. Also, the increased concentrations of orthophosphates (table 4) are observed at all hydrological stations, as a result of the significant amounts of these compounds in the wastewater from households (compounds are used in detergents).

Higher levels of ammonium were recorded throughout the observed period at the hydrological stations Rgotina and Čokonjar, while the increased ammonium values were registered in the 1993–96 period at the hydrological stations Zaječar-Gamzigrad and Zaječar; since 2006, the recorded values were within the permitted limits. Although ammonium values in all analyzed years in the Borska Reka and the Timok rivers were above the permitted limit for the Class I water quality, significantly lower values were observed in

Table 4. Ratio of average concentration and standards of the I surface water quality class for analized parameters

Year	Diss. O_2 mg/l	O_2 saturat.	pH	Susp. Sedim.	Nitrates mg/l	Nitrites mg/l	Ortho phosph.	Ammon. mg/l	Sulphat. mg/l	Fe mg/ll	Mn mg//l	Hg µg/l	Zn µg/l	Cu µg/l	Pb µg/l	Cd µg/l	BOD_5 mg/l	COD_{Mn} mg/l	Coli. g. n/l
Hydrological station Zaječar- Gamzigrad (Crni Timok River)																			
1993	1.50	1.24	0.93	0.55	0.03	0.48	6.80	1.16	0.17	0.70	0.78	0.19	0.013	0.010	0.09	0	3.72	0.40	2.75
1994	1.39	1.06	0.94	1.40	0.03	0.03	4.80	10.40	0.12	0.69	0.34	0	0	0	0.10	0	1.12	0.27	120.00
1995	1.41	1.14	0.94	0.67	0.03	0.03	10.00	2.20	0.12	0.42	1.02	0.20	0.004	0.006	0.09	0	0.76	0.23	8.63
1996	1.50	1.20	0.95	0.98	0.07	0.03	2.40	1.70	0.07	0.33	0.03	0.20	0.031	0.016	0	0	0.85	0.28	38.00
2006	1.35	1.12	0.95	0.83	0.02	0.01	6.00	0.50	0.15	0.29	0.09	0.40	0.0003	0.009	0.02	0.06	0.69	0.30	63.75
2007	1.25	1.03	0.95	0.64	0.03	0.01	11.60	0.10	0.22	0.51	0.07	0.29	0.003	0.020	0.03	0.09	1.13	0.35	6.31
2008	1.45	1.23	0.95	0.80	0.001	0.07	8.80	0.20	0.13	0.28	0.26	0.10	0.003	0.006	0.01	0.01	0.96	0.24	32.00
2009	1.30	1.11	0.95	0.19	0.03	0.33	16.00	0.40	0.12	0.48	0.24	0.10	0.003	0.028	0.03	0.01	0.93	0.25	1.45
Hydrological station Zaječar (BeliTimok River)																			
1993	1.74	1.45	0.94	3.99	0.02	0.05	4.40	0.80	0.10	0.88	0.98	0	0.001	0.008	0.30	0.17	1.62	0.33	12.00
1994	1.34	1.05	0.94	6.30	0.02	0.07	10.0	7.10	0.11	1.03	0.52	0	0.0003	0.001	0.51	0	0.97	0.27	120.00
1995	1.50	1.22	0.94	1.41	0.02	0.07	10.0	1.30	0.11	0.60	1.86	0	0.002	0.004	0.15	0	0.80	0.30	12.00
1996	1.49	1.23	0.95	0.86	0.05	0.03	5.40	2.90	0.06	1.02	0.54	0	1.290	0.019	0.25	0.06	0.97	0.28	49.83
2006	1.38	1.16	0.89	2.02	0.03	0.02	17.40	0.40	0.13	0.40	1.70	0.40	0.0003	0.091	0.02	0.06	0.61	0.27	0.06
2007	1.60	1.09	0.93	1.16	0.03	0.01	18.40	0.20	0.16	0.37	0.82	0.22	0.002	0.038	0.02	0.03	0.92	0.32	17.30
2008	1.32	1.23	0.94	0.62	0.03	0.01	16.00	0.60	0.12	0.27	0.40	0.13	0.003	0.017	0.01	0.01	1.17	0.32	37.40
2009	1.29	1.10	0.95	1.17	0.03	0.06	38.00	0.30	0.10	0.46	0.34	0.13	0.003	0.005	0.04	0.19	1.01	2.75	9.22

Table 4. Ratio of average concentration and standards of the I surface water quality class for analized parameters (Continuation)

Year	Diss. O_2 mg/l	O_2 saturat.	pH	Susp. Sedim.	Nitrates mg/l	Nitrites mg/l	Ortho phosph.	Ammon. mg/l	Sulphat. mg/l	Fe mg/ll	Mn mg//l	Hg µg/l	Zn µg/l	Cu µg/l	Pb µg/l	Cd µg/l	BOD_5 mg/l	COD_{Mn} mg/l	Coli. g. n/l
Hydrological station Rgotina (Borska River)																			
1993	1.12	0.81	0.86	9.56	0.06	0.50	1.00	89.60	0.12	16.73	49.60	0	0	2.290	1.06	0.65	5.73	0.88	4.65
1994	1.50	1.05	0.81	25.67	0.06	0.07	2.00	47.90	1.26	9.97	16.60	0	0	0.050	0.35	0	1.86	1.20	7.58
1995	1.02	0.84	0.77	19.72	0.05	0.17	1.60	64.20	0.23	8.90	38.80	2.43	0.050	0.310	0.17	0	1.28	0.54	4.48
1996	0.84	0.68	0.64	12.57	0.37	0.23	11.20	112.00	0.72	132.33	93.60	0	0.001	26.720	1.91	0.35	1.12	1.11	1.88.
2006	1.35	1.15	0.65	28.50	0.04	0.10	2.00	10.90	2.01	1.26	74.60	1.00	0.014	7.310	0.23	1.74	0.98	0.40	6.33
2007	1.14	1.05	0.61	27.00	0.05	0.10	4.00	12.30	2.33	1.46	68.60	0.38	0.200	3.780	0.40	1.24	1.36	0.54	1.05
2008	0.97	0.87	0.56	44.50	0.03	0.19	2.00	14.50	1.65	2.06	64.20	0.10	0.430	3.520	0.92	1.12	2.42	1.25	65.00
2009	0.89	0.75	0.65	29.40	0.04	2.13	12.00	1.50	1.35	1.13	67.20	0.15	0.140	0.510	0.04	0.86	1.59	2.01	2.76
Hydrological station Čokonjar (Timok River)																			
1993	1.51	1.31	0.89	2.17	0.05	4.67	9.80	14.10	0.48	3.32	10.20	0	0.0005	0.030	0.37	0	2.77	0.39	0.25
1994	1.29	1.05	0.92	3.77	0.05	0.33	2.40	10.90	0.27	0.34	10.40	0	0.004	0.142	0.51	0.35	2.85	0.35	16.00
1995	1.31	1.12	0.87	9.52	0.06	0.10	6.40	2.50	0.21	1.90	6.40	0.73	0.150	0.032	0.22	0	0.85	0.32	6.72
1996	1.33	1.05	0.80	4.19	0.04	0.33	0.60	12.40	0.36	1.06	13.40	0	0.002	0.238	0.04	0	0.73	0.40	5.02
2006	1.28	1.02	0.86	2.61	0.04	0.73	3.10	3.40	1.08	0.24	23.20	0.23	0.030	0.154	0.03	0.27	0.93	0.38	1.10
2007	0.98	0.84	0.89	2.78	0.03	2.03	10.80	2.00	0.49	0.48	14.00	0.15	0.030	0.077	0.03	0.16	0.83	0.37	19.00
2008	1.17	0.95	0.88	3.05	0.03	6.17	10.80	3.20	0.70	0.47	10.40	0.10	0.048	0.035	0.02	0.09	1.54	0.55	39.50
2009	1.17	0.98	0.89	8.84	0.02	0.90	18.40	3.43	0.44	0.73	8.40	0.11	0.010	0.044	0.05	0.11	1.16	0.44	60.50

the period between 2006 and 2009. One of the reasons for the reduced ammonium values in this river basin is the construction of communal sewage systems in several towns in East Serbia, including Bor, between 2005 and 2007. In 2007, due to a high degree of organic pollution in the Svrljiški Timok and Beli Timok and increased ammonium amounts in water, fish mortality was recorded in these rivers. The food industry plants of Knjaževac (Džervin Kop Komerc, Džersi, Stokoimpeks and Venus) have had the greatest impact on excessive river water pollution and, therefore, they were forced to stop operating after the mentioned occurrence of fish deaths. This action has also resulted in decreasing ammonium values during the past years.

The increased values of BOD_5 indicate the biological activity of wastewater and represent the main indicator of organic pollution. During the observed periods, the increased BOD_5 values were recorded in the Borska Reka River, and, in some of the years, in the

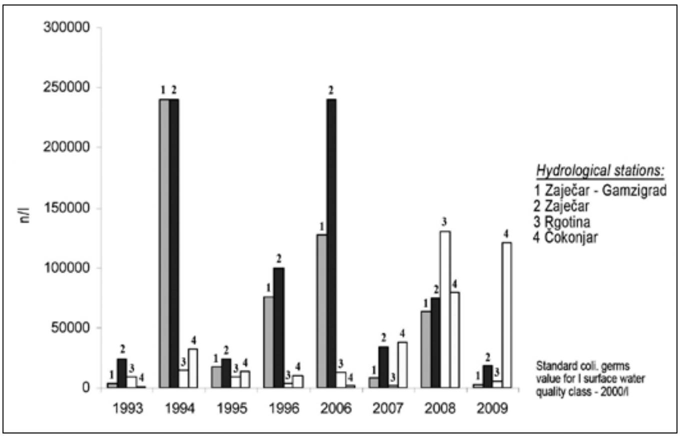

Fig. 2. Annual average coliform germs values in 1993–1996 and 2006–2009 period

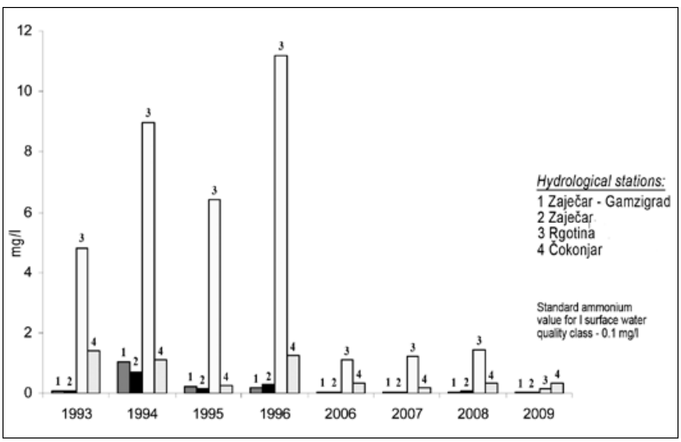

Fig. 3. Annual average ammonium values in 1993–1996 and 2006–2009 period

Crni Timok and Timok rivers. The causes of the increased values of the aforementioned parameters should certainly be sought for in the presence of communal landfills near Zaječar and Bor. In Bor, it is located in the abandoned part of a mine pit, where waste is disposed without any previous treatment or covering with earth after disposal. Besides, in the surroundings of the cities and rural settlements, there are numerous uncontrolled waste dumps (unorganized landfills). Due to mining pollution and significant depopulation of the area, there are no favourable conditions for significant agricultural production and, consequently, it cannot have influence on the Timok River pollution rate. For example, the total area of degraded agricultural land in the Bor Municipality is estimated at over 25 500 ha, which is 60.6% of the Municipality's total land area. Land is degraded by mining and metallurgical processes, as well as by copper ore smelting involving sulphur dioxide emissions, which leads to soil acidification, vegetation devastation and erosion [19].

The values of metals in water were within the allowed limits for the Class I water quality in all of the observed rivers except for the Borska Reka, which presents the main source of inorganic pollution in the Timok River Basin. Manganese, iron, and, to lesser extent, copper have the greatest pollution impact. Although there is a copper mine in the Borska Reka River Basin, the measured copper values in water fluctuated in the observed periods. After the increase in 1993, during the years to follow, the copper values were within the permitted limits. Increased values of copper were recorded from 2006 until 2009, when they were within the permitted limits. Higher copper levels in water were not reported at the other hydrological stations in the basin.

Iron values at hydrological stations on the Beli Timok and Crni Timok rivers were mostly within the permitted limits. At Čokonjar, on the Timok River, higher iron values were recorded during the 1995–96 period and the situation was similar at Rgotina on the Borska Reka River throughout the period observed. Contrary to the values of copper, the amounts of iron and manganese in the Borska Reka during the 1990s and 2000s were considerably higher than the permitted values. The amounts of dissolved iron in water were over 10 times higher than the permitted values in the 1993–96 period. Certain changes can be noticed in between 2006 and 2009, when the percentage of iron in water was considerably lower and slightly above the allowed limit (Fig. 4). The increased iron values are the consequence of the copper production from sulphide ores (chalcopyrite $CuFeS_2$) in the pyrometallurgical process, in which different elements appear as dross by-products (among which, iron is present in significant concentrations).

Manganese (Mn) is also one of the most represented elements in the mining and flotation wastewater. According to Fig. 5, it can be noticed that the manganese amounts were above the allowed limits in all of the observed rivers in the basin and especially in the Borska Reka River, where they were constantly increasing. For example, during 1993, the manganese values in the Borska Reka were almost 50 times higher than the regulated values for the Class I water quality in Serbia. The analysis carried out for the 2006–2009 period has shown the increasing trend of the manganese concentration in water, as opposed to the iron concentration, which decreased. The values increased by as much as 70 times above the permitted ones. Technically pure manganese metal is used in the copper and bronze deoxidation as an alloy component. Copper alloys with manganese (up to 15% Mn) are used as resistor metals, as well as for temperature-resistant structural parts.

In the metallurgical processes in the Bor mining industrial complex, 700–1000 t of tailings are produced daily. Smelting tailings dumps with around 16.5 million tons of

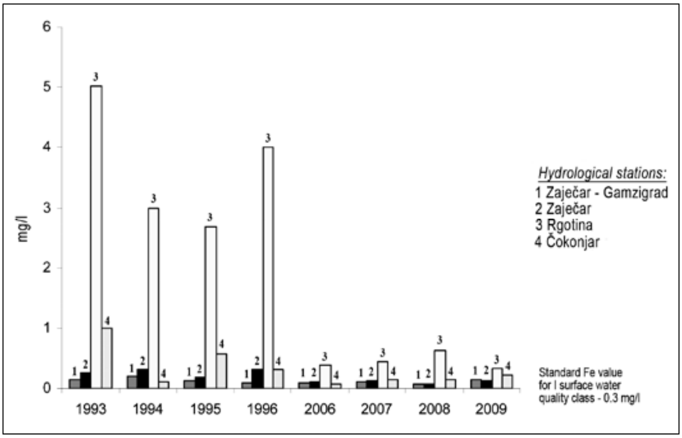

Fig. 4. Annual average Fe values in 1993–1996 and 2006–2009 period

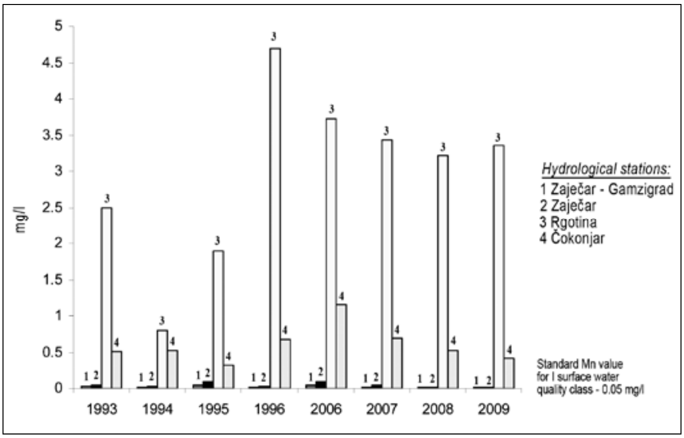

Fig. 5. Annual average Mn values in 1993–1996 and 2006–2009 period

waste, with the copper content of 0.7–0.8%, gold content of about 0.4 g/t and the silver content of 7.5 g/t as the main useful components, have an economic potential and present a technological challenge, but they are also a major environmental threat [16]. By leakage from the old flotation tailing ponds, large amounts of flotation materials were discharged into the Borska Reka and the Timok rivers. Rivers located downstream from mining and metallurgical complexes and the places of wastewater discharge act as open wastewater collectors. Since they cannot be used for any purpose, such rivers are limiting factors for economic development and the subsistence of local population in the villages on their banks. The leakage from flotation tailing ponds located on their banks results in the spreading of pollution into the groundwater of this region. The groundwater contaminated with various pollutants (Cu, Zn, Pb and SO_4^{2-}, Cl^- and organic compounds) is unfit to drink and may be harmful for vegetation as well [13]. There is no unified system for wastewater management and monitoring the quality of surface waters. Soils are damaged by mining and sulphur dioxide action and owing to that the coastal area of the Borska Reka River is covered with a layer of flotation tailings.

CONCLUSION

Based on the use of the WPI (Water Pollution Index), this study presents a geographical approach to the assessment of the water quality within the Timok River Basin and a general evaluation of the rivers' health. During the observed period, the annual WPI values have shown that the pollution levels in the Timok River Basin were different and that the pollution rate increased downstream. According to the WPI values, the water of the Crni Timok River belongs mainly to classes III and IV, and a similar trend was also observed in the Beli Timok River, where the WPI values are slightly higher. The WPI index values for the Timok River, after receiving the Borska Reka, indicated Class IV in the 1993–96 period, whereas after 2006, the increased pollution rate was observed and the river water has been classified as Class V in recent years. The Borska Reka River and wastewater of the Municipality of Zaječar have the greatest impact on the high WPI values. According to the calculated WPI values, the Borska Reka is classified into Class VI (heavily polluted). The worst water quality was registered in 1996 (the average WPI value was 20.86), which is far above the limit value – 6.

The general conclusion is that the values of some parameters which indicate organic pollution (BOD_5, ammonium, coliform germs, etc.) and the presence of metals (Fe, Mn, Cu) are far above the permitted limits, indicating severe organic and inorganic pollution in this area. This is a consequence of the activities of various subjects. The main sources of Timok River Basin pollution are untreated communal wastewater (from Knjaževac, Zaječar, Bor) and the wastewater from the Bor mining industrial complex. Communal wastewater contains high levels of ammonium, coliform germs and orthophosphates, which cause organic pollution in the Timok River Basin. The lack of an adequate sewage infrastructure, collection and wastewater treatment in the observed area should also be pointed out. Technological processes related to copper ore exploitation and processing in the Bor mining industrial complex are accompanied by the separation of wastewater. Two kinds of such water (wastewater from the mining process and wastewater from metallurgical and chemical processes in industrial plants) are discharged into the Borska Reka. Water leakage from old tailings ponds, which causes soil and water degradation in a wider area, is also an important source of pollution.

Although there is appropriate legislation in place, little has been done for the protection of the Timok River Basin. The lack of appropriate devices for wastewater treatment in factories and an unplanned urbanization failing to address the issue of wastewater evacuation are major problems. The solution to the problem of water quality and environment protection lies in the construction of appropriate wastewater treatment plants. Some progress in developing technologies and implementing projects aimed at improving environment protection has recently been made: in the Bor mining industrial complex the construction of wastewater purification plant was undertaken in 2005; it will enable to separate copper and iron for further processing and to reduce the discharge of untreated water into the Borska Reka River. Also, the sewerage systems of bigger cities in the Timok River Basin have been enlarged, owing to which the amount of communal wastewater has been reduced.

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