

## CHEMICAL WATER QUALITY ASSESSMENT OF THE DANUBE RIVER IN THE LOWER COURSE USING WATER QUALITY INDICES

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*An attempt has been made to assess the chemical water quality of the Danube River using water quality indices (WQIs). Water quality data sets of 11 chemical parameters along with two important physical variables obtained during 1 year in four sampling sites (collected at monthly intervals) were used. The Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) and the Bascaron Water Quality Index (BWQI) were selected to express the chemical quality of water for drinking water abstraction and general uses respectively, in addition, to provide information on the spatial variations along the river. The results of CCME-WQI revealed that the water quality was found "fair" in all sampling stations except one station, which was "marginal". The outcomes of BWQI demonstrated that the water quality was "good" at all sampling stations. It was found that the CCME WQI has given more reasonable results and introduced representative outcomes of the raw data of the river.*

**Keywords:** Danube River, physico-chemical parameters, Water Quality Index

### 1. Introduction

Surface waters, such as rivers and streams, are important water sources for many human activities. The deterioration of surface water quality has increased due to the growth of population, urbanization, industrialization, and agriculture activities (e.g. fertilizer). The traditional process of water quality assessment is to compare the measured value of a parameter, in a water sample, with an existing allowable limit of that variable. Numerous water quality parameters are required to be measured to assess the quality of water. The most important water quality parameters that influence the aquatic environment are pH, nutrient, water temperature, dissolved oxygen and biochemical oxygen demand, total suspended and dissolved solids, total alkalinity and acidity and heavy metal contaminants. These chemical compounds can be toxic if they exceed the toxicological threshold values and thus, they should be monitored in order to preserve the quality of water for different uses. The tabulation processes of these variables can be very hard to

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the non-specialists in the water field [1]. Besides, it does not always give a comprehensive vision and integrated concept on the water quality status [2,3]. Consequently, various tools have been used to cope with this issue such as water quality indices (WQIs).

The Water Quality Index (WQI) can be defined as an aggregation of measured values of water quality parameters to obtain a single number that represents the overall description of the quality of water [4]. Usually, the WQI has a scale from 0 to 100, the highest value representing the best water quality and lowest value indicates poorest water quality [5]. Moreover, it can be used to express the quality of water for different uses such as drinking, irrigation and industrial uses.

Danube River was selected for a case study in which the river and its quality have been extensively studied in the literature [6, 7, 8]. However, its quality changes due to different pollution loads to which the river can be subjected. Therefore, it is highly required to assess the water quality of the river in order to provide useful information in a comprehensive way. This study covers 13 km of the Danube River starting at Gura Văii, 2 km downstream of Iron Gate I Hydroelectric Power Station, and extends to Drobeta-Turnu Severin city. This region is characterized by the presence of various industries located in the southwest (upstream of the city) and southeast (downstream of the city) of the Drobeta-Turnu Severin [9, 10]. These industries discharged their wastewater into the river after treatment [9]. However, the lack of proper sewage collection and treatment facilities in the Drobeta-Turnu Severin city may impair the river use for drinking and other uses.

In this paper, two different water quality index models were applied to explore the usefulness of these indices in assessing the water quality of Danube River and to provide information on the spatial variations along the river. The selected water quality index models are Canadian Council of Ministers of the Environment Water Quality Index (CCME-WQI) [11], and Bascaron Water Quality Index (BWQI) [12].

## **2. Materials and Methods**

### ***Water quality data***

In the present paper, data sets of 11 chemical parameters along with two important physical variables (total suspended solid and water temperature) obtained for one year, (Jan - Dec 2008), were subjected to two water quality index models (CCME-WQI, and BWQI). Water samples were collected at monthly intervals in four points namely, Gura Văii (SS1) which is about 2 km downstream of Iron Gate I, Dudașu Schelei (SS2), Schela Cladovei (SS3) and Drobeta-Turnu Severin (SS4) (Fig. 1). The analysis of samples was carried out in the water

quality laboratory of water directorate of JIU Craiova, S.G.A Mehedinti, following standard and recommended methods [13]. Table 1 shows the water quality parameters, abbreviations, units, analytical methods and descriptive statistical summary of water quality data in four sampling stations for 12 months along with the European Community (EC) standards for drinking water abstraction [14].

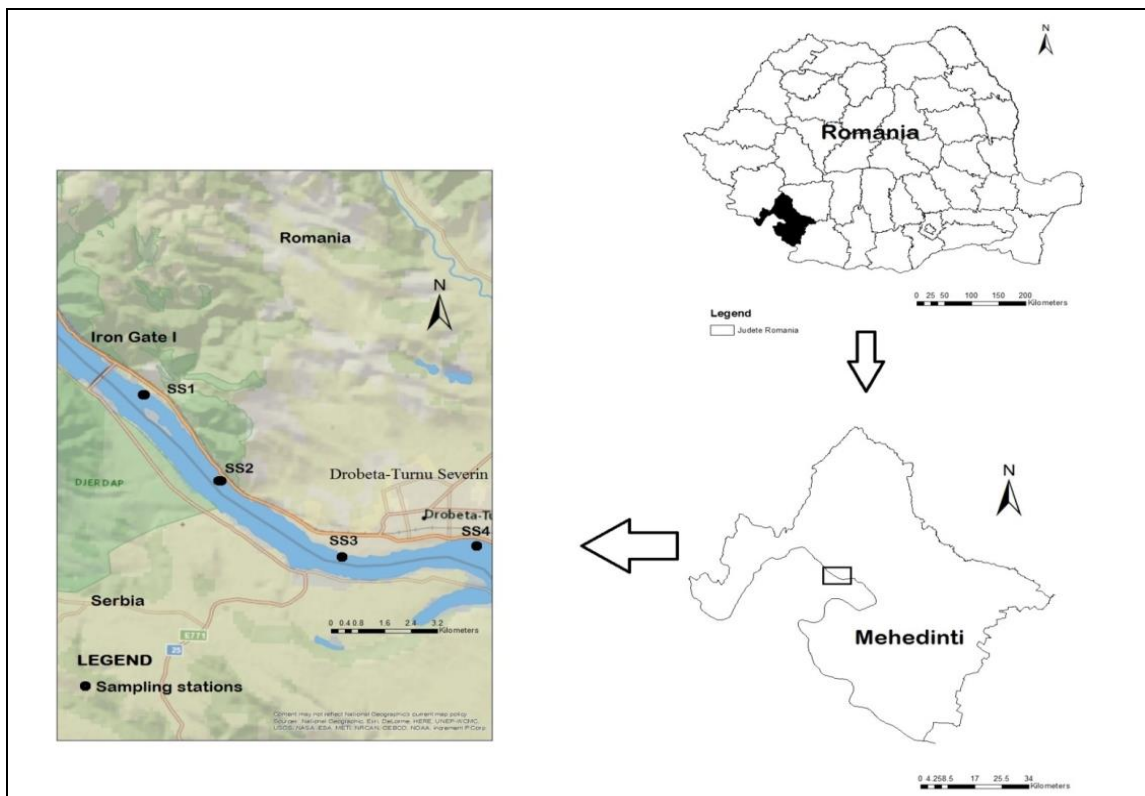


Fig. 1. Map of the study region

Table 1

Descriptive statistical summary of the water quality data in the Danube River.

Parameters	Abbrev.	Units	Instrument/techniques used [13]	Min.	Max.	Mean	Std. Dev. <sup>a</sup>	EC standards <sup>b</sup> (Guide Level) [14]
Dissolved Oxygen	BOD	mg/L	Winkler azide method	5.61	12.69	9.12	2.09	>70%
Biochemical oxygen demand	DO	mg/L	Winkler azide method	1.15	2.37	1.66	0.30	<3
Ammonium	NH <sub>4</sub>	mg/L	Spectrophotometric	0.087	0.522	0.19	0.07	0.05

Nitrate nitrogen	NO <sub>3</sub>	mg/L	Spectrophotometric	0.195	3.614	1.98	0.88	25
Total phosphorous	TP	mg/L	Spectrophotometric	0.132	1.44	0.43	0.27	0.1 <sup>c</sup>
Water Temperature	T	°C	Mercury thermometer	4	27	15.72	7.27	22
pH	pH	-	pH-meter	7.1	7.7	7.43	0.15	6.5-8.5
Total suspended solids	TSS	mg/L	Gravimetric	21	34	26.44	2.93	25
Cadmium	Cd	µg/L	Flame atomic absorption spectrophotometer	0.11	0.44	0.28	0.07	1
Cooper	Cu	µg/L	Flame atomic absorption spectrophotometer	1.5	4	2.16	0.71	20
Chromium	Cr	µg/L	Flame atomic absorption spectrophotometer	1.4	3.5	1.97	0.53	50 <sup>c</sup>
Nickel	Ni	µg/L	Flame atomic absorption spectrophotometer	1.1	1.8	1.43	0.19	50 <sup>c</sup>
Lead	Pb	µg/L	Flame atomic absorption spectrophotometer	0.7	1.9	1.37	0.34	50 <sup>d</sup>

<sup>a</sup> Std. Dev. – Standard Deviation, <sup>b</sup> Directive 75/440/EEC, <sup>c</sup> Romanian Standard (STAS 4706/1988), <sup>d</sup> Maximum allowable concentration

### ***The Canadian Council of Ministers of the Environment Water Quality Index (CCME-WQI)***

The CCME-WQI index has been used by researches from various countries all over the world to assess water quality [3, 15, 16, 17]. The main advantage of this index is that a large number of variables can be included in the calculation steps of CCME-WQI. Therefore, in this study, all the 13 water quality parameters were considered. It has a totally different approach and uses three factors for calculating the final index as [18]:

$$CCMEWQI = 100 - \left[ \frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732} \right] \quad (1)$$

where  $F_1$  (Factor 1) is known as *scope* and,  $F_2$  (Factor 2) is known as *frequency* and  $F_3$  (Factor 3) is known as *amplitude*.  $F_1$  (scope) is calculated as follows:

$$F_1 = \left( \frac{\text{Number of failed variables}}{\text{Total number of variables}} \right) \times 100 \quad (2)$$

The number of failed variables represents the percentage of variables which exceed the allowable limit value at least once during the monitoring period, relative to the total number of measured variables.  $F_2$  (frequency) is calculated as:

$$F_2 = \left( \frac{\text{Number of failed tests}}{\text{Total number of variables}} \right) \times 100 \quad (3)$$

The number of failed tests represents the percentage of individual tests that exceed the allowable limit value, relative to the total number of tests conducted during the monitoring period.  $F_3$  (amplitude) can be calculated in 3 steps:

1. The calculation of the excursion

$$\text{excursion}_i = \left( \frac{\text{Failed test value}_i}{\text{Objective}_i} \right) - 1 \quad (4)$$

$$\text{excursion}_i = \left( \frac{\text{Objective}_i}{\text{Failed test value}_i} \right) - 1 \quad (5)$$

Excursion represents the number of times that the value of the variable exceeds the allowable limit value (objective). Eq. 4 is used if the value of a variable must not be greater than the allowable limit value such as BOD. Whereas, Eq. 5 is used if the value of a variable must not be less than the allowable limit value such as DO.

2. Evaluation of normalized sum of excursions (nse)

$$\text{nse} = \left( \frac{\sum_{i=1}^n \text{excursion}_i}{\text{Total number of tests}} \right) \quad (6)$$

*nse* is the ratio of the sum of excursions obtained for individual tests dividing by the total number of tests (both meeting and not meeting the objective values).

3. The last step is the calculation of  $F_3$

$$F_3 = \left( \frac{\text{nse}}{0.01 \text{ nse} + 0.01} \right) - 1 \quad (7)$$

The calculation of CCME WQI value in each station has been determined by Eq. 1 in order to produce a value between 0 and 100. Then, water quality is ranked in the following categories [11]:

- Excellent: (CCME WQI values 95–100)
- Good: (CCME WQI values 80–94)
- Fair: (CCME WQI values 60–79)
- Marginal: (CCME WQI values 45–59)
- Poor: (CCME WQI values 0–44).

### Bascaron WQI (BWQI)

The Bascaron WQI (BWQI) came from Europe (Spain) [12] and has been widely used over the world [1, 2, 5, 19]. The overall index is being estimated as subjective water quality index

$$BWQI_{sub} = k \frac{\sum_{i=1}^n C_i P_i}{\sum_{i=1}^n P_i} \quad (8)$$

where  $n$  = the total number of variables,  $C_i$  = value assigned to the variable  $i$  after normalization,  $P_i$  = relative weight assigned to each variable which ranged from 1 to 4 according to its influence on the water quality (4 for highest impact and 1 for less impact),  $k$  = subjective constant identified by the visual impression of river contamination. The values of  $k$  may be 0.25, 0.5, 0.75, or 1. The basic criteria to select one of these values have been given in Pesce and Wunderlin (2000) [1]. However, in this study, the value of  $k$  was adopted as 1 to account only for the variations due to measured variables [2].

$$BWQI = \frac{\sum_{i=1}^n C_i P_i}{\sum_{i=1}^n P_i} \quad (9)$$

The major advantage of BWQI is that a large number of water quality variables can be included in calculating the final index after assigning the normalization factors as well as their weights. However, only 22 water quality variables were found that already have been normalized and weighted in previous studies [1, 2, 5]. In this study, eight water quality parameters were included in the evaluation process, namely T, pH, DO, BOD, NH<sub>4</sub>, NO<sub>3</sub>, TP, and TSS as these parameters are already normalized and weighted. The normalization factors along with their weights given in Table 2 were used for the selected parameters to produce the final BWQI.

Table 2

Water quality variables that have been normalized and weighted in the present study, adopted from [1, 2, 5]

Variables	Rel. weight (P <sub>i</sub> )	Normalization Factor (C <sub>i</sub> )										
		100	90	80	70	60	50	40	30	20	10	0
T	1	21/1 6	22/1 5	24/14	26/12	28/10	30/5	32/0	36/-2	40/-4	45/-6	>45/<-6
pH	1	7	7-8	7-8.5	7-9	6.5-7	6-9.5	5-10	4-11	2-12	2-13	1-14
DO	4	>=7. 5	>7	>6.5	>6	>5	>4	>3.5	>3	>2	>=1	<1
TSS	4	<20	<40	<60	<80	<100	<120	<160	<240	<320	<400	>400
TP	1	<0.2	<1.6	<3.2	<6.4	<9.6	<16	<32	<64	<96	<160	>160
NH <sub>4</sub>	3	<0.0 1	<0.0 5	<0.1	<0.2	<0.3	<0.4	<0.5	<0.75	<1	<=1.25	>1.25
NO <sub>3</sub>	2	<0.5	<2	<4	<6	<8	<10	<15	<20	<50	<=100	>100
BOD	3	<0.5	<2	<3	<4	<5	<6	<8	<10	<12	<=15	>15

The following classification scheme was adopted to classify the water quality [19]:

- Excellent: 90-100
- Good: 71-90
- Medium: 51-70
- Bad: 26-50
- Very bad: 0-25

### 3. Results and discussion

The spatial variations of the physico-chemical parameters and the heavy metals in the Danube River water are shown in Fig.2 and Fig. 3, respectively. All the physico-chemical parameters were within the standards limits EC or Romanian Standard (Table 1), except for NH<sub>4</sub>, T and TSS.

Generally, the heavy metal concentrations in water samples obtained between Jan to Dec, 2008 were within the standards limit set by EC or Romanian Standard (Table 1). Moreover, the heavy metal concentrations in all sampling points was found to be in sequence of Cu>Cr>Ni>Pb>Cd (Fig. 3).

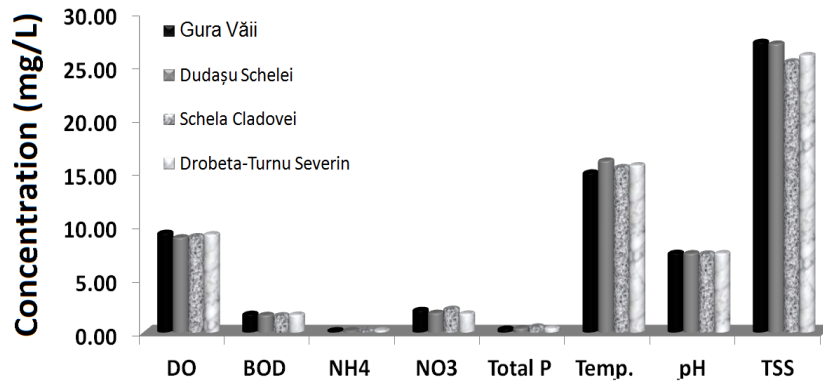


Fig. 2. Physico-chemical parameters of the Danube River in four sampling points, all values in mg/L except Temp. (°C) and pH. (b) Heavy metals content

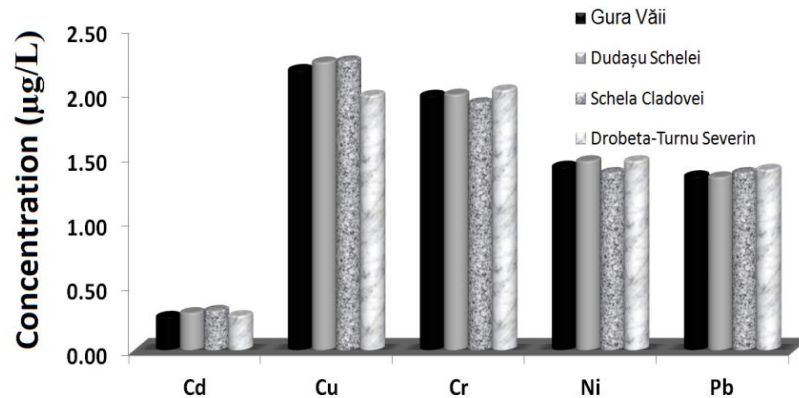


Fig. 3. Heavy metals in the *Danube* River water in four sampling points

The results of CCME-WQI are shown in Table 3. The European Community (EC) standards for drinking water abstraction were used for CCME-WQI calculation and are presented in Table 1 [14]. The EC standards proposed guidelines for surface water used as raw water for drinking based on three types: simple physical treatment and disinfection (A1), normal full physical and chemical treatment with disinfection (A2) and intensive physical and chemical treatment with disinfection (A3). Moreover, EC has presented the water quality standards as Guide Level (GL) and Maximum Allowable Concentration (MAC) values for various parameters. GL is expressing the maximum desirable concentration [14]. In this study, GL values in the A1 were considered for all variables except for Cr and Pb. The TP and Ni were not included in EC standards and therefore, Romanian Standard (STAS 4706/1988) was used. In CCME-WQI, all the variables were taken into account for the evaluation process. The water quality classification scheme for sampling stations was found “fair” in SS1, SS2 and SS4, whereas “marginal” in SS2 (Table 3). The most important variables that affect the water quality were  $\text{NH}_4$ , TP, T and TSS.

Table 3

The calculated *F* factors along with WQI and categorization values of CCME-WQI index

Stations	F1	F2	F3	CCME-WQI	Categorization
SS1	30.7	26.0	39.4	67.5	Fair
SS2	38.5	26.9	40.1	64.3	Marginal
SS3	30.7	23.7	44.7	65.8	Fair
SS4	30.7	24.3	41.3	67.1	Fair

The second index used in this study is the BWQI. The calculated sub-index along with the final values and categorization of the water quality are given in Table 4. The categorization of water quality was found as “good” in all stations.



The most important parameters that affect adversely the water quality were  $\text{NH}_4$  and T.

Table 4

The sub-index values along with relative weight, WQI and categorization values of BWQI index

Sta-tions	Sub-index values									
	DO	BOD	$\text{NH}_4$	$\text{NO}_3$	TP	T	pH	TSS	BWQI	Cate-gory
SS1	98.33	87.50	66.67	85.00	90.83	73.33	90.00	90.00	86.32	Good
SS2	95.83	88.33	68.33	87.50	90.83	72.50	90.00	90.00	86.40	Good
SS3	95.83	89.17	65.00	85.00	90.83	72.50	90.00	90.00	85.75	Good
SS4	95.83	89.17	65.83	88.33	90.83	72.50	90.00	90.00	86.23	Good
Relative weight ( $P_i$ )	4	3	3	2	1	1	1	4	$\sum P_i = 19$	

The selected water quality index models have different approaches in the implementation process. It was observed that the CCME-WQI has a totally different approach and distinct characteristics in comparison to BWQI. CCME-WQI has the ability to take into account all the water quality variables, in addition to its flexibility of the selection of the water quality standards and comparatively tolerant in case of missing data [20]. Moreover, it can be applied to assess the water quality for different uses and it does not utilize sub-index to transform the measurement of water quality into a dimensionless number. It comprised three factors for the evaluation process (scope, frequency, and amplitude). However, this index is not free of flaws such as considering that all the water quality parameters have the same relative weight as well as it can be applied only when there are available water quality standards.

The BWQI water quality index model relies on sub-indices values in the calculation process with different aggregation method than CCME0-WQI. It uses weighted sum function for aggregation process and segmented linear sub-index (step type). This model assigns a relative weight for each water quality variable. The results of BWQI demonstrate that the river water quality is good at all sampling stations. BWQI has eclipsed the effect of  $\text{NH}_4$  during the aggregation process. The major issue in this index is that the given relative weight for each variable may be varied due to multiple perspectives of the experts.

Based on the above discussion and the outcomes depicted in Fig. 4, it can be concluded that the CCME-WQI has provided realistic results in comparison to the raw data of the Danube River. The results of CCME-WQI were fair in three stations (SS1, SS3 and SS4) and marginal in one station (SS2). According to CCME (2001) [11], fair category indicates that “the water quality is frequently threatened or impaired; conditions often depart from natural or desirable levels”, whereas marginal category indicates that “the water quality is almost always threatened or impaired; conditions usually depart from natural or desirable levels”. The results of the BWQI did not explain the raw data of the river properly due to the eclipsing problem which appeared in the aggregation process.

The effect of industrial pollution in this region was also reported by Andrița [21]. This study has investigated the effect of the CELROM industry on the water quality of Danube River. Moreover, Ismail and Robescu [22] have simulated different water quality parameters such as DO, BOD, and pH using a one-dimensional model to examine the impact of tributaries (Jidostita and Topolnita) in the Drobeta-Turnu Severin region on the Danube River. They stated that the discharges of these tributaries have a significant effect on the water quality of the river and the Topolnița tributary was the major sources influencing the water quality of the river in the study region. It should be noticed that the Topolnita is receiving the discharge of wastewater from the most industries located in the study area [21]. Generally, the results of these studies were compatible with the results of the present study.

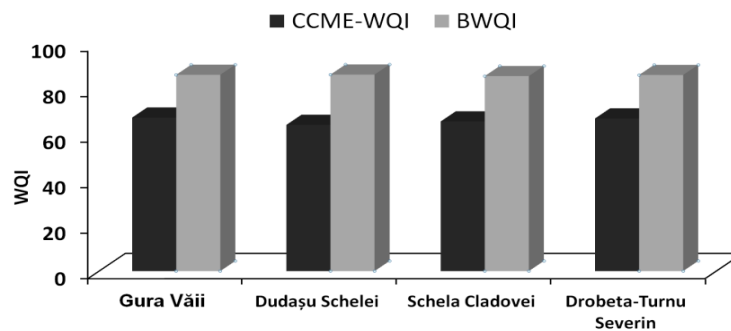


Fig. 4. WQI values of different water quality indices in four sampling stations

#### 4. Conclusions

This study comprises the applications of two water quality index models (CCME-WQI and BWQI) to assess the physico-chemical water quality in the Danube River at Drobeta-Turnu Severin. The quality of water in the study area in four sampling stations was ranged from marginal to fair for CCME-WQI and good for BWQI. The most important variables that affect adversely the water quality were  $\text{NH}_4$ , TP, T and TSS for CCME-WQI and  $\text{NH}_4$  and T for BWQI. The

reason is that the variables of CCME-WQI (NH<sub>4</sub>, TP, T and TSS) were above the standard limits in certain months, whereas the variables of BWQI (NH<sub>4</sub> and T) had a low value in the sub-index in comparison with other parameters.

CCME-WQI uses a formula and does not include sub-indices for the implementation process. It comprised three factors for the evaluation process (scope, frequency, and amplitude). Moreover, all the water quality variables have been used in the calculation of CCME-WQI. BWQI have eclipsed the effect of NH<sub>4</sub> during the aggregation process. It can be concluded that the CCME-WQI gave more reasonable results in comparison to BWQI. The results revealed that the CCME-WQI can be applied to assess the water quality in Danube River as it can express the results more closely. However, the comparison process would be unfair due to the different number of parameters that have been applied to the two indices. Furthermore, this study did not include the biological parameters to evaluate the overall water quality status in the river.

Generally, the results of the BWQI (k=1) did not explain the raw data of the river properly due to the eclipsing problem which appeared in the aggregation process.

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