Lower Danube Water Quality Assessment Using Heavy Metals Indexes

PETRA IONESCU[1,2*], VIOLETA-MONICA RADU[1], DEÁK GYÖRGY[1], ALEXANDRU ANTON IVANOV[1], ELENA DIACU[2]
[1]National Institute for Research & Development in Environmental Protection, No. 294 Spl. Independentei, 060031Bucharest, Romania
[2]Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Polizu Str., 011061, Bucharest, Romania

The presence of heavy metals in aquatic systems represents a threat on environment biodiversity and on human health, becoming a significant concern worldwide. This paper proposes the Lower Danube water quality assessment by using two metal indices, heavy metal pollution index and metal index. To evaluate these indexes, ten locations were selected in Lower Danube River between km 375 to km 175, and the following six metals: Zn, Ni, Cd, Cu, Pb and Cr were analyzed in water samples, for a period of 24 months. All obtained values for heavy metal pollution index were below the limit of 100, established on the basis of the pollution index. The metal index values indicate that the water quality in the monitored areas falls within class I and class II according to the classification of water quality using the metal indexes. The introduction of these two heavy metal indexes can contribute significantly to water quality assessment, becoming a useful tool for water pollution level monitoring, and being also able to predict its tendency for the future.

Keywords: heavy metal pollution index, metal index, Danube River

Among the most frequent inorganic pollutants in the environment, the heavy metals originating both from natural and anthropogenic sources play a special role [1]. Ubiquitous presence of heavy metals in the aquatic environment has raised many issues worldwide [2, 3] because of lack of biodegradability [4-6] and because of the tendency to bio-accumulate persistence and also because of potential transmission to the food chain [7-9].

Some of these metals (Hg, Cd and Pb) are highly toxic to living organisms even at very low concentrations [9]. This can cause disorders of the nervous system and of internal organs [4] as well as skin problems, cardiovascular problems and even cancer. However, some metals (Cu, Fe, Mn, Ni and Zn) are essential for proper functioning of vital processes [10-12] becoming alarming only at high concentrations.

In Romania, the Danube is the general collector of the wastewater discharged by the 10 countries it crosses [13]. All waste water loaded with organic and inorganic pollutants originating from lack of urban sewage treatment plants, combined with the leaks that occur on agricultural land reach the Lower Danube and are further discharged into the Black Sea. Lower Danube also known as the Carpathian-Balkan section has a length of about 1075 km [3] and is divided into five sectors.

This paper aims to assess the water quality related to heavy metal content of the sector situated between Calarasi (km 375) and Braila (km 175), considering the possible accumulation of high levels of heavy metals in this part of the river, related to recent construction works taking place in this area for the improvement of navigation conditions.

Assessment of heavy metal pollution in this area was done by calculating the heavy metal pollution index and the metal index. Evaluation of these two indices can be a useful tool for monitoring the water pollution level, being also able to predict its tendency for the future.

Experimental part

Study area

The study area is represented by the Lower Danube between km 375 - km 175. For this purpose, ten sampling locations were established, marked from L1 to L10 (table 1 and fig. 1) from which water samples were collected monthly [14, 15] between September 2011 - August 2013.

Sample collection

To assess the heavy metal contamination during the 24 months, water samples were collected from both the left bank and the right bank from a depth of 0.5 m as well as

Table 1
WATER SAMPLING LOCATIONS [14, 15]

Location No	*Length Km*	*Geographical coordinates*	
		longitude	*latitude*
L1	347	27°34'9.55"	44°11'24.35"
L2	345		
L3	344		
L4	343		
L5	340	27°37'2.35"	44°11'59.10"
L6	341		
L7	334		
L8	197	27°54'3.93"	45°4'0.32"
L9	196		
L10	195		

* email: petraionescu2012@yahoo.ro

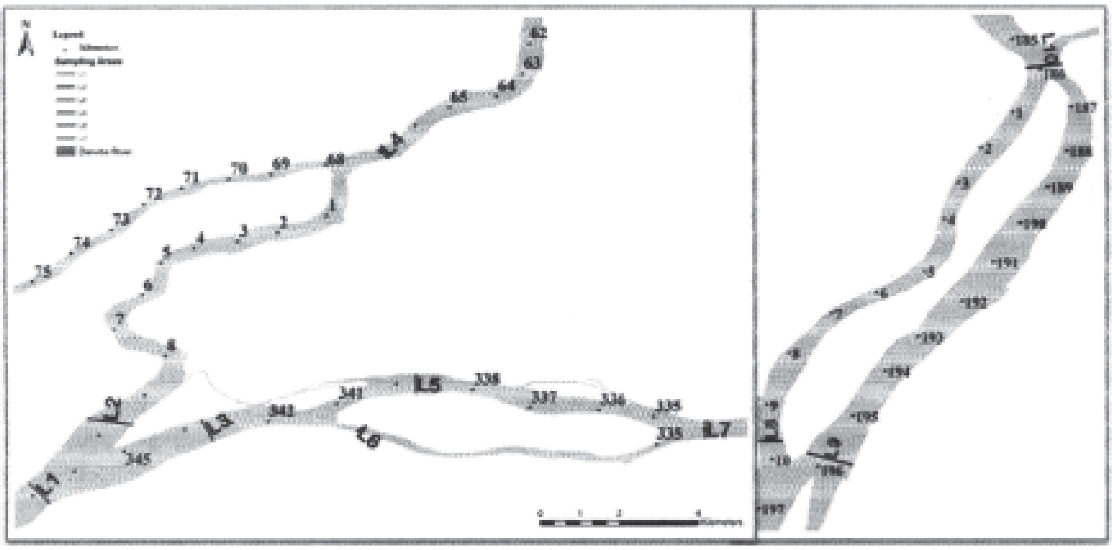


Fig. 1. Map of study area with sampling locations [15]

from the center of the river from 3 different depths (0.5 m, 1.5 m and 3 m). For sampling, polyethylene bottles were used, cleaned in advance with nitric acid solution and then with ultrapure water (deionized water). Water samples were stored at 4 °C and transported to the laboratory, where they were divided into smaller samples. Each 1 liter sample was then brought to *p*H < 2 by addition of high-purity (65%) nitric acid to prevent hydrolysis [10, 12].

Heavy metals analysis

The concentration of metals in the water has been determined by using an electrothermal atomic absorption spectrometry (Thermo M5) with specific lamp for each metal. After plotting the calibration curves, the concentration of metals in each sample was determined, applying correction against a blank, and the final result consisted in the average concentration from the analysis of three replicate subsamples [16].

Heavy Metal Pollution Index

The first calculated index was the heavy metal pollution index (HPI). This represents a method for assessing the water quality providing information about the composite influence of each metal to overall water pollution [17]. The heavy metal pollution index is an effective tool to describe the surface water pollution by combining several parameters to reach a certain value that can be compared with the critical value to assess the level of pollution load. Generally, the critical pollution index value is 100 [18].

The calculation of the HPI has three stages. In the first stage (1) each metal was assigned a weightage (W_i), being calculated as the value inversely proportional to the recommended standard for each metal [4, 18]. The second step (2) involved the calculation of the quality rating (Q_i) for each metal. Finally, these sub-indices were summed in the overall index (3).

$$W_i = \frac{k}{S_i} \quad (1)$$

$$Q_i = \sum_{i=1}^{n} \frac{\{M_i(-)I_i\}}{(S_i - I_i)} \; x \; 100 \quad (2)$$

$$HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \quad (3)$$

were:

W_i is the unit weightage, S_i is the recommended standard for each heavy metal, *k* is the proportionality constant, Q_i is the sub-index of each heavy metal, *n* is the number of heavy metal considered, M_i is the monitored value of the ith parameter, *Ii* is the ideal value for ith parameter, *the sign (-)* indicates the numerical difference of the values, ignoring the algebraic sign.

Table 2 summarizes the benchmarks used for I_i and S_i according to class I and III of quality provided by the national legislation [19].

Metal Index

The second index used for the evaluation of water quality is the Metal Index (MI). The MI represents the sum of the ratio between the analyzed parameters and their corresponding national standard values. It has a wide application and it is used as an indicator of the quality of surface water, as well as of drinking water. For the evaluation of the Metal Index in the selected locations, the following formula has been used (4):

$$MI = \sum_{i=1}^{n} \frac{C_i}{(MAC)_i} \quad (4)$$

were:

MAC is maximum allowable concentration and C_i is mean concentration of each heavy metal.

For this work the MAC has been used according to 311/2004 Law [20]. Based on the obtained MI values, the watercourses are classified into different classes (table 3).

The Heavy Metal Pollution Index and the Metal Index represent two useful tools for the assessment of the global level of pollution of surface waters with respect to heavy metal charge [21].

Table 2
STANDARD USED FOR HPI COMPUTATION BASED ON M.O. 161/2006

Heavy metal (μg/L)	*Ideal value, I_i (μg/L)*	*Highest permitted value, S_i (μg/L)*	*Unit weightage, W_i*
Cr	25	100	0.01
Cu	20	50	0.02
Cd	0.5	2	0.50
Zn	100	500	0.002
Ni	10	50	0.02
Pb	5	25	0.04

Class	*MI*	*Characteristics*
I	< 0.3	Very pure
II	0.3 - 1.0	Pure
III	1.0 - 2.0	Slightly affected
IV	2.0 - 4.0	Moderately affected
V	4.0 - 6.0	Strongly affected
VI	> 6.0	Seriously affected

Table 3
WATER QUALITY CLASSIFICATION USING MI [12, 18, 21]

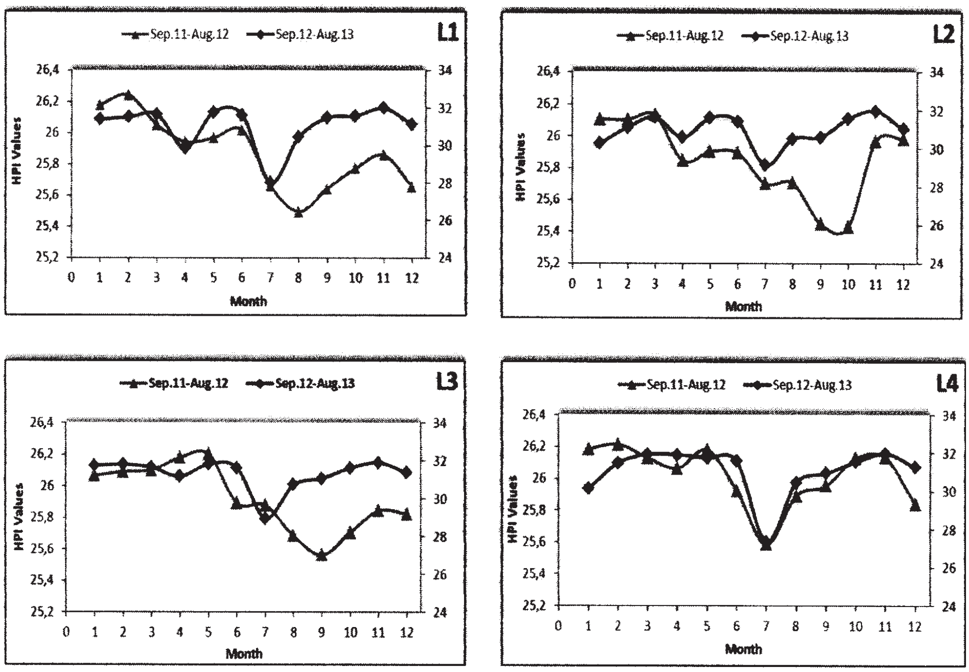


Fig. 2. Annual comparison of HPI values in L1-L4 locations (km 347 - km 343)

Results and discussions

For the calculation of the HPI and MI, the average concentrations of the determined metals have been used (Cu, Cr, Zn, Pb, Ni and Cd).

To compare the pollution load and to assess the water quality of the ten selected locations, the HPI were separately calculated for each location.

For the first 4 selected locations, stretching from km 347 to km 343 (fig. 2) the annual HPI variation for the 2 monitoring years has been plotted. For these graphs, the values for the first monitoring period are on the main axis, and the values for the second period are on the secondary axis. Following the monitoring, similar variations between the two monitoring periods have been recorded. The HPI values were below critical pollution index value of 100 for entire monitoring period. Slightly higher HPI values for the second monitoring period have also been found. Maximal HPI values between the 2nd and 5th month and minimal HPI values between the 7th and 10th month for both periods were also recorded.

For the locations situated between km 340 - km 334 (fig. 3) and locations between km 197 - km 195 (fig. 4), similar variations between the two monitoring periods with HPI values below critical pollution index of 100 have been recorded. For the sampling locations L5, L6, L7 maximal HPI values were recorded between the 1st and 4th month, and minimal HPI values were recorded between the 7th and 8th month for both periods were also recorded.

For the sampling locations L8, L9 and L10 the maximal HPI values were recorded in the 2nd and the 3rd month of monitoring and minimal HPI values were recorded between months 6th and 9th for both periods.

The second index used for the evaluation of water quality is the Metal Index. Figure 5.a illustrates the observed evolution of the metal index values for the first five locations (L1-L5) and figure 5.b the next 5 locations (L6-L10) in the monitoring period. In table 4 are shown the annual averages obtained for MI monitored locations.

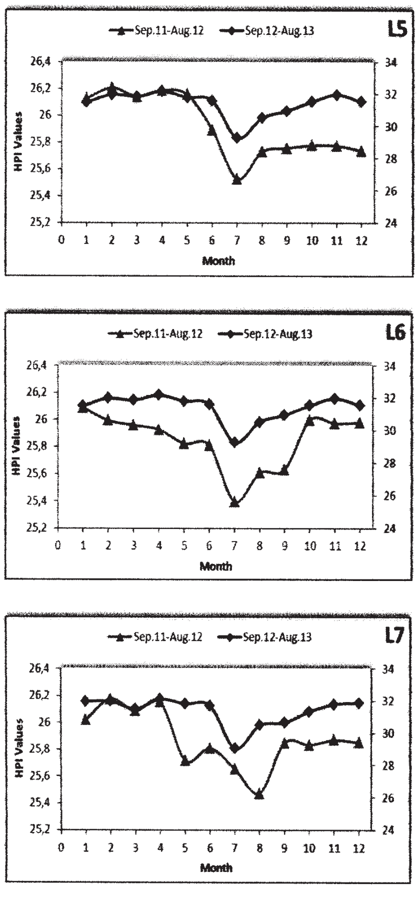


Fig. 3. Annual comparison of HPI values in L5-L7 locations (km 340 - km 334)

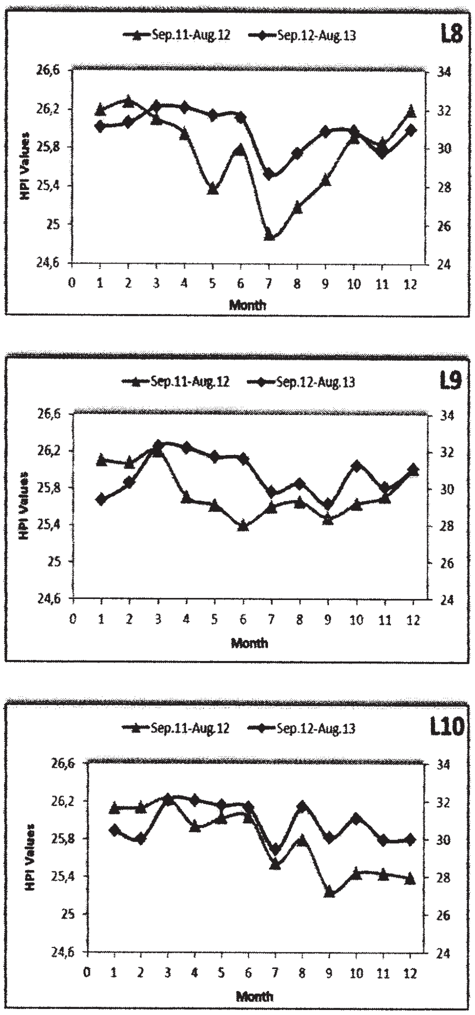
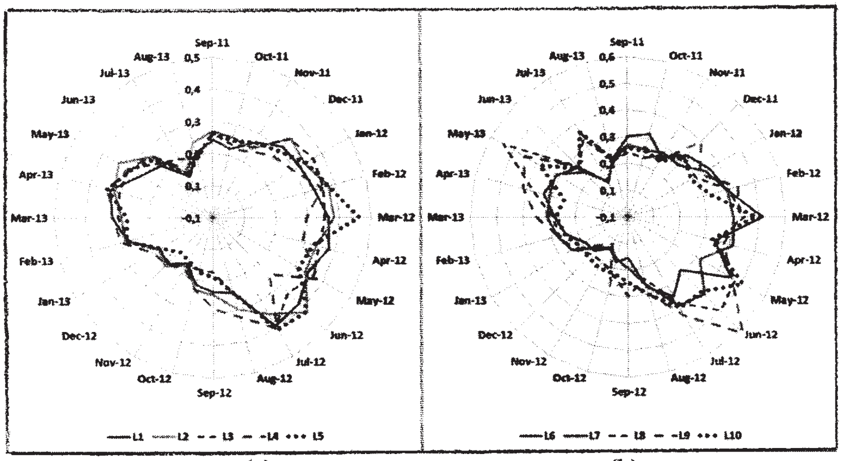


Fig. 4. Annual comparison of HPI values in L8-L10 locations (km 197 - km 195)



(a) (b)

Fig. 5. Monthly variation of MI in L1-L5 locations (a) and L6-L10 locations (b)

Table 4
ANNUAL MI VALUES RECORDED AT DIFFERENT SAMPLING LOCATIONS

Locations	*Mean MI*	
	Sep. 2011- Aug. 2012	*Sep. 2012 - Aug. 2013*
L1	0.27	0.18
L2	0.28	0.20
L3	0.27	0.18
L4	0.25	0.20
L5	0.28	0.17
L6	0.30	0.17
L7	0.28	0.18
L8	0.29	0.24
L9	0.33	0.23
L10	0.29	0.21

It is noted that in the first year of monitoring higher values for MI compared to the second year were registered, but water quality related to MI for both years is classified as very pure, except for location L9 for which the water quality is classified as "pure", not representing a matter of concern however.

Conclusions

Heavy metal pollution index (HPI) and Metal index (MI) have proved to be two effective tools for the Lower Danube water quality assessment using its heavy metal load.

All obtained values for HPI based on the mean concentration of the six heavy metals (Cu, Cr, Cd, Pb, Ni and Zn) for the Lower Danube River were below the limit of the critical pollution index of 100.

The two year comparison of the HPI has shown similar variations to all monitored areas as well as a slight decrease of heavy metal load that may have been linked to higher water flow for that period.

The highest value of 32.29 for HPI, reported during November 2012 was recorded in location L9, while the lowest value of 24.91 was recorded in March 2012 in location L8.

According to the MI classification, the water quality was between classes I - II with respect to heavy metal pollution.

The addition of these two heavy metal indexes to the global assessment of water quality can lead to a significant improvement of its accuracy, as they become a useful tool for the monitoring of water pollution level, and being also able to predict its tendency for the future.

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