Assessing the Contamination of the Dambovita River Through Heavy Metal Indices

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Abstract. The continuous population growth, which leads to increased social and economic development, affects the quality and quantity of the freshwater resources, both directly through changes in landscapes and pollution caused by industrialization, urbanization, and agriculture, as well as indirectly through climate change pressures (such as higher air temperature, drought, frequent extreme precipitation events). Within this study, the heavy metal contamination of Dambovita River was assessed, as it is the main drinking water source for the city of Bucharest. Thus, surface water samples and sediments were collected from four sampling sites along the Dambovita River within two campaigns, in order to assess the seasonal fluctuations. The heavy metal pollution index (HPI) together with the metal index (MI) of the collected water samples were calculated for cadmium, nickel and lead, for each sampling site. Additionally, in order to establish the potential ecological risk index, the contamination factors and potential ecological risk factors were assessed considering each of the monitored heavy metals (Cd, Ni and Pb). The results showed that the HPI values were below the critical pollution index value of 100, along with MI values below 1. Also, the sediment analyses further confirmed that all the sampling sites can be classified with low to medium levels of potential ecological risk.

1. Introduction

Water, one of the most important natural resource, is under continuous pressures generated by the combination of both naturally occurring conditions and anthropogenic activities. This leads to the continuous variation of the chemical composition hindering the water quality monitoring [1, 2]. One of the most frequent issues in water management is the contamination with hazardous substances, among which heavy metals can affect the aquatic organisms and also human health due to their capacity to accumulate in quantities exceeding the allowable thresholds [3, 4]. Therefore, the identification and quantification of heavy metal contamination sources, extent and persistence (highlighted by seasonal variations) are relevant in establishing proper amelioration solutions. A useful tool in assessing the long term water quality trends are the quality indices.

In this context, several indices were used by researchers to analyze both water quality and long-term sediments contamination, such as heavy metal pollution index, metal quality index, arithmetic weighted water quality index, multi-parametric quality index, and potential ecological risk index [1, 5-8].

Among these, the heavy metal pollution index (HPI) is the most frequently used by researchers, as it rates the total quality of water with respect to the cumulated influence of individual heavy metals,
providing an overview on the overall pollution generated by heavy metals [9]. Another index used for establishing the general quality of surface waters is the metal index (MI). This index analyzes the potential cumulative impact of hazardous substances, namely heavy metals, on the human health [10].

Additionally, as heavy metals are integrated in the organic matter of the sediments, the potential ecological risk index (RI) can assess the combined pollution risk to an ecological system [11]. RI considers various factors, such as synergy between analyzed heavy metals, toxicity level, heavy metals concentration and ecological sensitivity of heavy metals [12].

Although the assessment of each individual index is relevant for highlighting the water quality status, it should be conducted together with other analysis tools (indices) in order to comprehend the overall status of the analyzed water bodies.

Therefore, in the context of increased industrialization and urbanization in Bucharest, the purpose of the present study was to analyze the Dambovita River water quality using heavy metal indices, highlighting the possible water contamination which could provide further support to competent authorities in managing the valuable water resources.

2. Materials and methods

2.1. Sampling

Water and sediment samples were collected in two campaigns (summer - C1 and autumn - C2) from four locations on the Dambovita River, as it can be seen in Figure 1. The samples were collected in polyethylene containers, and subsequently transported in the laboratory for further processing. Water samples were preserved by using high purity nitric acid (69%) at a pH < 2 until further analysis. The obtained sediment samples were initially dried at room temperature, and subsequently crushed, sieved, digested and analysed.

Figure 1. Sampling locations on the Dambovita River.

The concentrations of Cd, Ni and Pb were determined using a HighResolution Continuum Source atomic absorption spectrometer (ContrAA 700, Analytik Jena, Germany). Water samples were analysed using the graphite furnace technique, applying a method similar to ISO 15586/2003, and the sediment samples were analysed using the flame technique.
2.2. Methods

2.2.1. Heavy Metal Pollution Index. HPI was calculated using the weighted arithmetic quality mean method (13), which implies to first establish a rating scale for each selected metal giving it a weight and subsequent selection of the pollution parameter on which the index is to be based.

The rating scale ranges between zero and one, being equal to an inversely proportional value to the recommended standard of each analyzed heavy metal [5].

The HPI model is calculated using the following equation [5]:

\[
HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i}
\]  

Where: \( W_i \) represents the unit weight for each \( i \)th heavy metal, \( Q_i \) represents the sub-index for each \( i \)th heavy metal, and \( n \) represents the number of analyzed heavy metals [5]. This sub-index of the heavy metals is calculated by equation (2):

\[
Q_i = \frac{M_i - I_i}{S_i - I_i} \cdot 100
\]

Where: \( M_i \) represents the monitored value for each \( i \)th heavy metal, \( I_i \) represents the ideal value for each \( i \)th heavy metal, and \( S_i \) represents the recommended standard value for each \( i \)th heavy metal, in ppb [5].

Within this study, the recommended standard (\( S_i \)), and the desirable maximum value (\( I_i \)) considering each analyzed heavy metal were identified in the national legislation (Ministerial Order No. 161/2006), as quality Class III for the recommended standard (\( S_i \)) and quality Class I for the desirable maximum value (\( I_i \)).

Although Prasad and Bose have determined the critical pollution index value as being equal to 100 [13], within this study the obtained HPI values will be analyzed using the three classes scale established by Edet and Offiong (low for HPI values <15, medium for HPI values ranging between 15-30 and high for HPI values >30) [14].

2.2.2. Metal Index. This indicator estimates the water quality trend, by correlating the heavy metal concentration (\( C_i \)) to the maximum allowable concentration (MAC) of each analyzed heavy metal, as it can be determined from the following equation [10]:

\[
MI = \frac{\sum_{i=1}^{n} C_i}{(MAC)_i}
\]

The MAC values were selected from the regulatory document regarding the classification of surface water quality (Ministerial Order No. 161/2006). For MAC values lower than the analyzed heavy metal concentration, the water quality can be considered degraded. Thus, the obtained results will characterize the water quality as a MI value higher than 1 is a threshold of warning, while values lower than 0.3 highlight a very pure water [15].

2.2.3. Potential Ecological Risk Index. RI characterizes the potential ecological risks determined by the accumulation of heavy metals in sediments, being determined by the potential ecological risk factor (\( E_R \)) through the degree of contamination (\( C_D \)) and toxic-response factor (\( T_R \)) [7].

\[
RI = \sum_{i=1}^{n} E_R^i
\]

\[
E_R^i = T_R^i \cdot C_D^i
\]
\[ C^i_F = \frac{C^i_f}{C^i_d} \]  \hspace{1cm} (6)

Where: \( E^i_R \) represents the potential ecological risk index for each \( i \)th heavy metal, \( T^i_R \) represents the toxic response factor for each \( i \)th heavy metal, \( C^i_f \) represents the pollution coefficient for each \( i \)th heavy metal, \( C^i_d \) represents the measured concentration for each \( i \)th heavy metal in each sampling point; \( C^i_R \) represents the reference value, which can be considered the background value of each heavy metal in sediments [7]. The toxic response factors determined for Cd, Ni and Pb are 30, 5 and respectively 5 [8].

There are five grades of \( E^i_R \) and four grades of RI, as it can be seen in Table 1.

| \( E^i_R \) (risk) | Grades of \( E^i_R \) (risk) | RI | Grades of RI (risk) |
|---------------------|-------------------------------|-----|---------------------|
| <40                 | Low                           | <150| Low                 |
| 40-80               | Moderate                      | 150-300| Moderate        |
| 80-160              | Considerable                  | 300-600| Considerable      |
| 160-320             | High                          | \( \geq 600 \) | Very high        |
| \( \geq 320 \)      | Very high                     |     |                     |

3. Results and discussion

3.1. HPI determination

In order to determine HPI of the sampling points, the concentrations of Cd, Ni and Pb were determined, taking also into account the temporal variations of heavy metals in the Dambovita River with the sampling being performed in two campaigns. Table 2 presents the parameters used in this study to calculate HPI.

| Heavy metal | \( I_i, \mu g/L \) | \( S_i, \mu g/L \) | \( W_i \) |
|------------|------------------|------------------|--------|
| Cd         | 0.50             | 2.00             | 0.50   |
| Ni         | 10.00            | 50.00            | 0.02   |
| Pb         | 5.00             | 25.00            | 0.04   |

Figure 2 presents the HPI variation obtained for both campaigns in the sampling points. Although the individual concentration of heavy metals do not highlight a contamination risk, the HPI values place the analyzed water samples in the high class area of critical pollution index. The lowest HPI value (61.38) was observed at P3 sampling point (near the wastewater treatment plant from Glina) in the second campaign, while the highest HPI (80.60) was observed in the first campaign at P2 (approximately 400 m upstream the wastewater treatment plant from Glina). Although the overall water quality with respect to the heavy metals is alarming, all HPI values are lower than the critical value of 100. Following the analysis it can be highlighted that the HPI recorded the following variation in sampling locations: \( P3 < P4 < P2 < P1 \).

Besides the spatial variation, from figure 2 it can be noticed a temporal variation, as in the second campaign there were lower HPI values than in the first sampling campaign. This may be due to the diluting effect owing to the increase in precipitations.
The seasonal behavior of heavy metal persistence was also observed by Mondol et al. [16].

3.2. MI determination

In order to determine the MI values, first the MAC values were established for each heavy metal analyzed within this study. Accordingly, the maximum allowable concentration for Cd was 3 μg/L, for Ni was 20 μg/L and for Pb was 10 μg/L.

Figure 3 presents the MI for all sampling points. It can be seen that all selected sampling points along the Dambovita River have MI values well below the warning level, indicating pure and very pure water. A similar behavior was observed by Ionescu et al. when investigating the heavy metal contamination of two lakes from Bucharest [17]. Accordingly, the Metal Index spatial variation in the study area showed the following order: P1 < P2 < P4 < P3.

In terms of temporal variation, a slight increase of the MI values in the second campaign compared to the first one can be explained by many factors, such as bioaccumulation, dissolution of sediments, and complexes with organic matter [18].

3.3. RI determination

In order to establish the comprehensive potential ecological risk index (RI), the potential ecological risk index for Cd, Ni and Pb (E\text{a}) were initially calculated. The obtained results are presented in Table 3.
Table 3. RI computation in the four sampling points.

| Campaign | Sampling point | $E_R^{Cd}$ | $E_R^{Ni}$ | $E_R^{Pb}$ | RI    |
|----------|----------------|------------|------------|------------|-------|
| C1       | P1             | 7.17       | 5.76       | 1.20       | 14.12 |
|          | P2             | 144.14     | 7.37       | 15.73      | 167.23|
|          | P3             | 59.28      | 3.97       | 6.27       | 69.51 |
|          | P4             | 14.92      | 7.58       | 25.38      | 47.88 |
| C2       | P1             | 11.24      | 6.01       | 1.75       | 19.00 |
|          | P2             | 118.46     | 7.68       | 10.97      | 137.12|
|          | P3             | 76.40      | 11.96      | 16.71      | 105.07|
|          | P4             | 25.04      | 6.94       | 6.47       | 38.44 |

From Table 3 it can be noticed that the ecological risk index values of each analyzed heavy metal fluctuates with the sampling point. Accordingly, Cd analysis highlights a considerable potential ecological risk in the sampling point P2 and a moderate risk at P3, while the other heavy metals have low potential ecological risk in all sampling points. Therefore, the potential ecological risk arrays in the following order: $E_R^{Cd} > E_R^{Pb} > E_R^{Ni}$.

The RI values highlight the potential ecological risk levels along the Dambovita River. The corresponding ecological risk grades were generally low, except for the sampling point P2 which had a slight moderate grade.

4. Conclusions
The present paper established the baseline characterization of heavy metals along the Dambovita River. The overall status of water quality was evaluated considering three indices, heavy metal pollution index, metal index, and potential ecological risk index.

The HPI values showed spatial and temporal variations, highlighting the influence of both natural and anthropogenic factors on the heavy metal pollution (such as discharge from industrial and urban activities, increased precipitations). Although none of the samples presented higher values than the critical pollution index value of 100, all the samples had HPI values categorized in the high class, accentuating the need for further monitoring.

The MI values obtained in all the sampling points showed that the total trend assessment indicates the existence of pure water.

However, considering the sediments potential to accumulate heavy metals and the possibility of a subsequent release of heavy metals back into the water, the paper showed a considerable potential ecological risk of Cd upstream of the wastewater treatment plant, through the analysis of the potential ecological risk index.

Therefore, a continuous monitoring of the heavy metal indices should be performed for the Dambovita River, and if necessary suitable solutions should be identified in order to ameliorate any temporary excess.

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