

Evaluation of heavy metal contamination through indexes analysis. Case studies: Plumbuita and Circului Lakes, Bucharest (Romania)

Petra Ionescu, Ecaterina Marcu, Violeta-Monica Radu,
Irina Elena Ciobotaru, Carmen Tociu

National Institute for Research and Development in Environmental Protection, 294 Spl. Independentei, 6th District, 06003, Bucharest, Romania. Corresponding author: P. Ionescu, ionescupetra2012@yahoo.ro

Abstract. In the last years, the population growth and urbanization development together with the lack of adequate infrastructure development have raised serious questions regarding the release of various contaminants in the surface waters such as lakes. Among the contaminants present in the environment, heavy metals present a particular interest due to their toxic effects on human health. The objective of this work was to assess the water quality in relation to the heavy metal content (cadmium, chromium, copper, lead and nickel) according to national regulation by using heavy metal pollution indices: Heavy metal Pollution Index (HPI) and Metal Index (MI) in two lakes located in Bucharest (Plumbuita Lake and Circului Lake). To establish interdependencies between heavy metals analyzed and to identify the nature and potential sources of pollution, group Cluster Analysis has been applied. Evaluation of heavy metals in the lake water is of environmental and health concerns and needs attention.

Key Words: heavy metals, pollution, Plumbuita Lake, Circului Lake.

Introduction. At the global level numerous studies have been performed, showing that most bodies of fresh water are polluted, leading to a decrease in their drinkability. Water quality monitoring is a useful tool not only to assess the impact of pollution sources, but also to ensure the efficient management of water resources and protection of aquatic life, water being the most important natural resource available to date (Radu et al 2016a).

Along rivers, lakes are important ecosystems because the survival of many organisms depends on freshwater and many people benefit from "goods and services" such as drinking water, food (fishing), irrigation, industrial and recreational activities (Bhateria & Jain 2016; Radu et al 2016b).

The main source of water quality degradation is the contamination by downloading toxic chemicals. When water quality is affected by the presence of different types of pollutants, water can play a major role in the emergence of many types of infectious diseases (caused by viruses, parasites and bacteria), non-infectious diseases like nitrate intoxication and poisoning with metals such as lead, mercury, cadmium, arsenic, therefore reducing their effects on human health is of particular importance for the modern society (Deák et al 2015; Tociu et al 2016).

The contamination of aquatic ecosystems with inorganic pollutants such as heavy metals become of great concern for the environment and for the sustainable use of water (Resetar-Deac & Diacu 2015). As a result of toxic effects, the persistence and tendency of heavy metals to bioaccumulate in the aquatic environment cause numerous health problems (Fua et al 2014; Li et al 2016).

The uncontrolled development of constructions near rivers and lakes, the indiscriminate use of fertilizers and pesticides in the agriculture, together with the lack of adequate infrastructure represented a potential risk of harm to surface water quality and loss of biodiversity (Agrawal et al 2010; Ioja et al 2010; Carstea et al 2013).

In Romania, in the Bucharest area, an increase of the urbanization has been found in the recent years, so that industrial areas within the city or the suburbs have been replaced by large shopping centers and residential areas, leading to impaired water quality of the lakes in the north and east part of Bucharest (Ioja et al 2010).

Most of the urban ecosystem of Bucharest is crossed by the Colentina River, represented by the 15 lakes along its course, with 10 lakes (Străulești, Grivița, Baneasa, Herastrau, Floreasca, Tei, Plumbuita, Fundeni, Pantelimon I and Pantelimon II) being located in the Municipality of Bucharest and with only 5 lakes (Buftea, Buciumeni, Mogosoia, Chitila, Cernica) being located in Ilfov county (Stănescu 2011).

Among the inland lakes situated in the Bucharest area, one of the artificial lakes emerged by excavation is the Circului Lake. Unfortunately, because of the human activities especially the excessive construction in the area whose foundation affect springs that supply the lake, in the last decade a slight decrease in the water level of this lake has been observed (Gogu et al 2015).

The objectives of the research paper were to: (1) determine concentrations of the metals: cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni) and lead (Pb) in water from the Plumbuita Lake and Circului Lake; (2) to assess the surface water quality in relation to the heavy metal content according to national regulation through indexes analysis; (3) to apply Cluster Analysis method for establishing the interdependence relationships between the analysed heavy metals and for identification of potential sources of pollution. The results of this study may become prospectives for the decision maker to improve protection procedures for the lakes against potential serious risks.

Material and Method. To assess the concentrations of heavy metals in the levels of aquatic ecosystems located in crowded urban areas, from the Bucharest area, 2 lakes have been selected for analysis: Plumbuita and Circului. For this purpose, 3 sampling sites have been established for Plumbuita Lake (L1, L2 and L3) and 2 sampling sites for Circului Lake (L4 and L5) from which water samples were collected in March 2015 (ISO 5667-4 2000) (Figure 1).

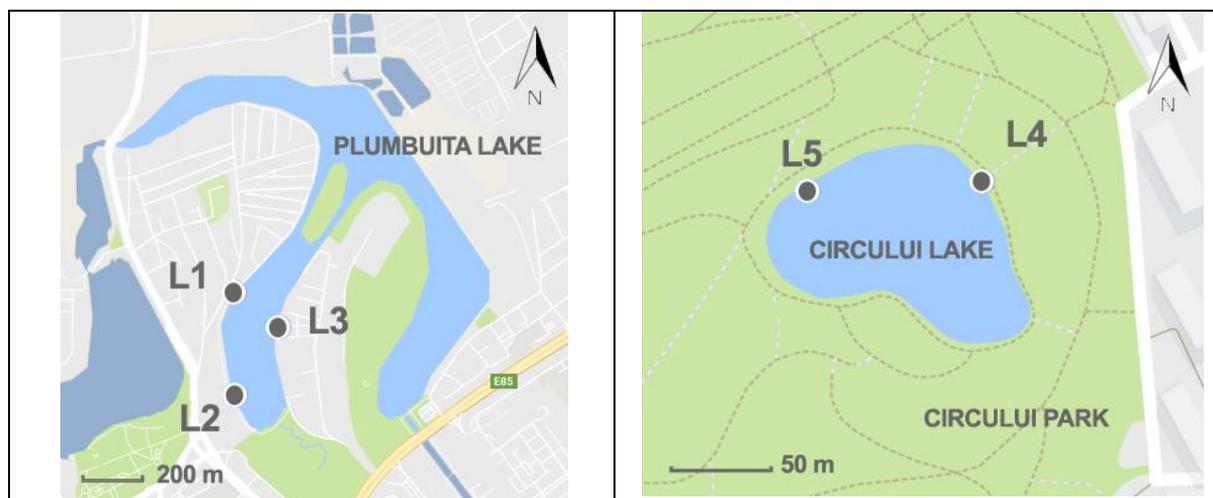


Figure 1. Sampling locations in the Plumbuita and Circului Lakes, Bucharest (Romania)

For sampling, polyethylene bottles were used, cleaned in advance with nitric acid solution and then with ultrapure water (deionized water). Samples were stored at 4°C and transported to the laboratory. Each 1 liter water sample was then brought to pH < 2 by addition of high-purity (65%) nitric acid to prevent hydrolysis (ISO 8288 2001; ISO 15586 2004). For determining the heavy metals (Cd, Cr, Cu, Ni and Pb), a High-Resolution Continuum Source atomic absorption spectrometer - ContrAA 700 was used.

Heavy Metal Pollution Index. To get an overview on the state of heavy metal pollution of both urban aquatic ecosystems, the first calculated index was the Heavy Metal Pollution Index (HPI).

The calculation of HPI involves three steps: first, to each metal (Mi), a weight (Wi) is assigned, calculated as the value inversely proportional to the standard recommended for each metal; the second stage consists in calculation of the parameter (Qi) for each metal; in the final stage sub-indexes computed in a global index are summed (the critical value of metal pollution index is 100) (Reza et al 2010):

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

Table 1 shows the limit values specified by national legislation (Ministerial Order No. 161/2006) for quality Class I (I_i = ideal value) and quality Class III have been counted (S_i = maximum permissible value) (Ionescu et al 2015).

Table 1

Standard used for HPI computation based on M.O. 161/2006

$M_i (\mu\text{g L}^{-1})$	$I_i (\mu\text{g L}^{-1})$	$S_i (\mu\text{g L}^{-1})$	W_i
<i>Cd</i>	0.50	2	0.50
<i>Cr</i>	25	100	0.01
<i>Cu</i>	20	50	0.02
<i>Ni</i>	10	50	0.02
<i>Pb</i>	5	25	0.04

Metal Index. Another index used for evaluating the surface water quality and drinking water is the metal index (MI). To calculate this index, the possible effects of heavy metals on human health are taken into account (Caeiro et al 2005).

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

where MAC is the maximum allowable concentration and C_i is the concentration of each heavy metal. For this work the MAC value has been assigned according to national legislation (Ministerial Order No. 161/2006) for quality Class I.

According to the available data in the literature, depending on the MI values, water quality can be classified into six classes as shown in Table 2 (Caeiro et al 2005).

Table 2

Water quality classification using MI

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

Cluster analysis. Statistical analysis was performed using the statistical software package JMP 10 for windows for the cluster analysis (CA). Cluster analysis was performed both for establishing relations of similarity between the analyzed heavy metals and for the identification of the nature and sources of pollution.

Results and Discussion

Heavy metal pollution index. Heavy metal pollution index (HPI) was calculated separately for each of the five sampling locations taking into account the concentrations of heavy metals (Cd, Cu, Cr, Ni and Pb) determined in the water samples. Figure 2 presents the variation of heavy metal pollution index obtained in the established locations. Following the analysis it was observed that the HPI recorded the following variation in sampling locations: $L5 < L2 < L1 < L4 < L3$. For water samples taken from L3 and L4, values that easily exceed the limit of 100 were recorded. Following this study, higher HPI values for Plumbuita Lake were observed, compared to the values for Circului Lake.

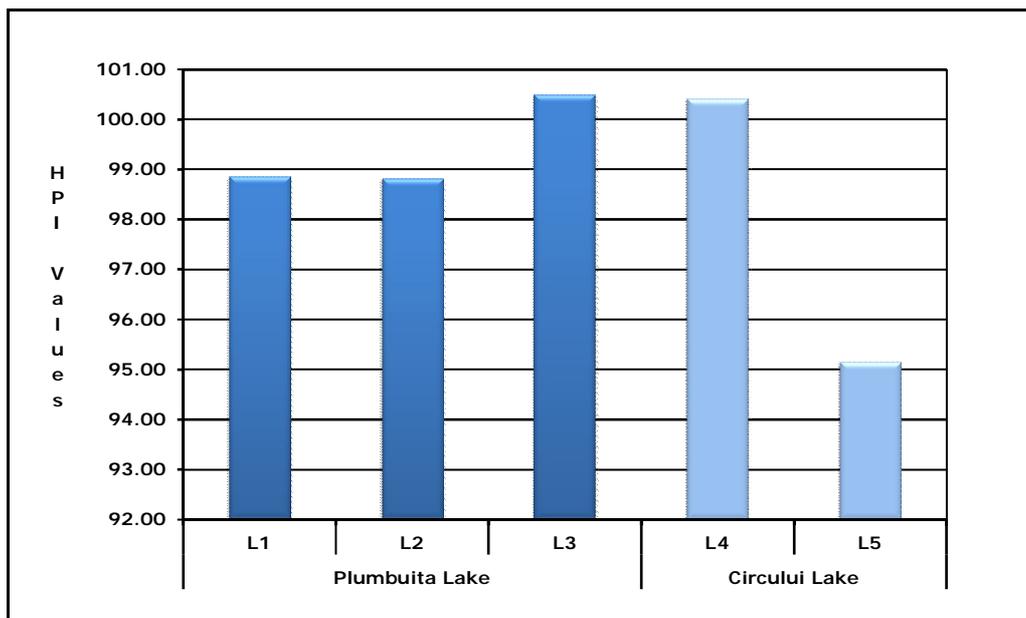


Figure 2. Dynamics of HPI variation in the 5 sampling locations.

Metal index. The second Index calculated to assess the water quality of the two urban aquatic ecosystems was the Metal Index (MI). Metal Index variation for the five sampling sites showed the following order: L4 < L5 < L3 < L1 < L2 (Figure 3). Similar to HPI, higher values of MI were observed in general for sampling locations on Lake Plumbuita compared to the values recorded for Circului Lake, but all values were below the limit value of class I quality as classified according to the MI values.

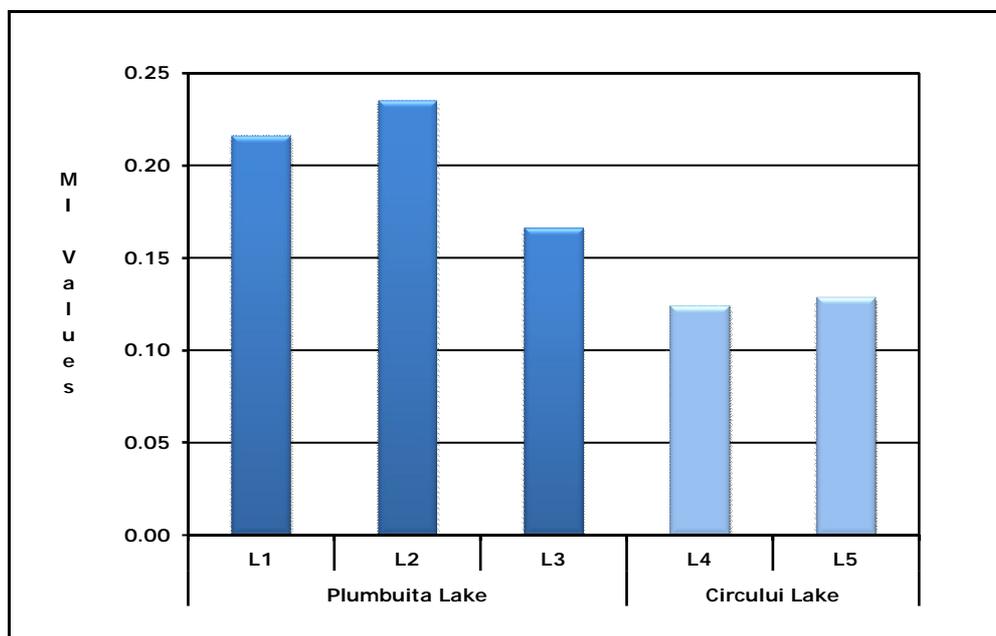


Figure 3. Dynamics of MI variation in the 5 sampling locations.

Cluster analysis. To establish interdependencies between the analyzed heavy metals and to identify the nature and sources of pollution, group cluster analysis was applied. Figure 4 presents the dendrogram obtained for water samples taken from Lake Plumbuita and Figure 5 dendrogram obtained for water samples taken from Circului Lake.

Following the analysis it was observed that for Plumbuita Lake (Figure 4) two independent clusters were identified: I (Cu - Ni) and II (Pb - Cr). Similar to this, for

Circului Lake, the independent highlighted clusters were: I (Cd - Pb) and II (Cu - Ni). These clusters indicate the possible presence of anthropogenic sources of pollution.

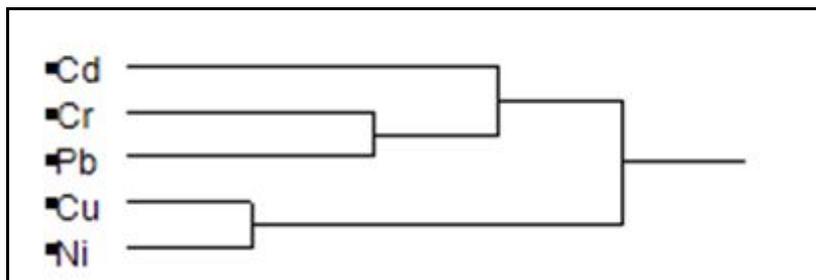


Figure 4. Dendrogram of heavy metals in water samples from Plumbuita Lake.

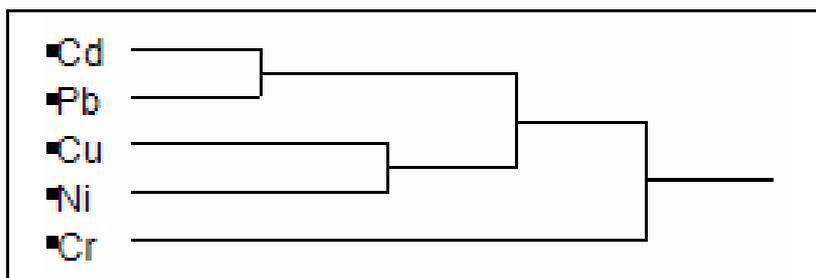


Figure 5. Dendrogram of heavy metals in water samples from Circului Lake.

Following this study, higher HPI values for Plumbuita Lake were observed, compared to the values for Circului Lake. Similar to HPI, higher values of MI were observed in general for sampling locations on Lake Plumbuita compared to the values recorded for Circului Lake, but all values were below the limit value of class I quality as classified according to the MI values. Following the analysis it was observed that for Plumbuita Lake two independent clusters were identified: I (Cu - Ni) and II (Pb - Cr). Similar to this, for Circului Lake, the independent highlighted clusters were: I (Cd - Pb) and II (Cu - Ni). These clusters indicate the possible presence of anthropogenic sources of pollution.

Conclusions. This study was carried out to provide information on heavy metal concentrations in water from the Plumbuita and Circului Lakes. Heavy metal pollution index (HPI) and Metal Index (MI) have proved to be two effective tools for the water quality assessment of these two lakes using their heavy metal load.

The values obtained for HPI based on concentrations of the five metals (Cd, Cr, Cu, Ni and Pb) registered slight exceedings of the critical value of 100 in the sampling location L3 of the Plumbuita Lake and L4 location of the Circului Lake.

According to the MI classification, the water quality recorded values within the class I with respect to heavy metal pollution. Application of Cluster Analysis for the values obtained showed trends of specific correlations for water samples heavy metal and common sources of pollution.

The study revealed the impact of various human activities on the quality of water. Although the water was not found to be critically polluted regarding heavy metal load, the situation still remains a matter of concern.

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Authors:

Petra Ionescu, National Institute for Research and Development in Environmental Protection, 294 Spl. Independentei, 6th District, 06003, Bucharest, Romania, e-mail: petraionescu2012@yahoo.ro

Ecaterina Marcu, National Institute for Research and Development in Environmental Protection, 294 Spl. Independentei, code 060031, Bucharest, Romania, e-mail: ecaterina.marcu@incdpm.ro

Violeta-Monica Radu, National Institute for Research and Development in Environmental Protection, 294 Spl. Independentei, 6th District, 06003, Bucharest, Romania, e-mail: radumonica33@yahoo.com

Irina Elena Ciobotaru, National Institute for Research and Development in Environmental Protection, 294 Spl. Independentei, 6th District, 06003, Bucharest, Romania, e-mail: irinaelenaciobotaru@yahoo.com

Carmen Tociu, National Institute for Research and Development in Environmental Protection, 294 Spl. Independentei, code 060031, Bucharest, Romania, e-mail: tociucarmen@yahoo.com

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