

# APPLICATION OF POLLUTION INDICES FOR EVALUATION OF LONG-TERM ACCUMULATION OF HEAVY METALS IN LAKE MODRAC IN BOSNIA AND HERCEGOVINA

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**Abstract:** In this study the results of a 15-year long monitoring survey on heavy metals in water at Lake Modrac were assessed using pollution indices of heavy metals, such as Heavy metal pollution index HPI, Heavy metal evaluation index HEI and the Degree of contamination  $C_D$ . The results of the survey on heavy metal pollution of sediment conducted in 2015 were used as input data for the following pollution indices: Concentration factor  $C_F^i$ , Pollution load index PLI, Enrichment factor EF, Index of geo-accumulation  $I_{geo}^i$ , Ecological risk factor  $E_r^i$ , Potential ecological risk index to the water-body, RI. The results showed a good correlation and the lake sediment was characterized as polluted. Enrichment factors and indices of geo-accumulation of heavy metals were indicated as very high enriched in the sediment, and have been identified as an anthropogenic source of pollution. Cumulative presence in the sediment is assessed through the pollution index, RI, and has been assessed as moderate ecological risk to the lake water-body. The application of pollution indices presents a valuable tool in assessing the long-term pollution status of Lake Modrac.

**Keywords:** Heavy metals, pollution index, natural waters, sediment pollution, pollution status, ecological risk to water-body.

## Introduction

Lake Modrac is the largest artificial hydro-accumulation in Bosnia and Herzegovina, which plays a vital role in the economic life of Tuzla Canton. The catchment area of the lake is around 1189 km<sup>2</sup>. There is a large number of towns and settlements in the catchment area, as well as industrial capacities and coal mines located nearby the lake, which largely contribute to its pollution because of the discharging of wastewaters and coal slurry directly into the waters. Lake Modrac has several purposes; provision of drinking water for the population of Tuzla canton, provision of industrial water to industries, flood protection and electricity production (The Heinrich Böll Foundation study, 2013).

Lake Modrac is under the process of excessive sedimentation and the volume was reduced by  $13 \times 10^6$  or 13.3 %, and the average depth decreased from approximately 5,7 to 5,2 m over a 50-year period, reducing the aphotic zone and making the lake susceptible to eutrophication, with the apparent deterioration of water quality. It is estimated that an average flux into the catchment was 342.000 m<sup>3</sup>, and the total volume of sediments in the lake can be estimated to be  $16,42 \times 10^6$  m<sup>3</sup>. (IHTM 1999-2012). The lake sediment is composed of soil, coal dust and organic and inorganic substances. Sediment presents the sink for heavy metals in the catchment, and it integrates the long-term pollution in the lake. Unfortunately, there is no regular monitoring scheme of Lake Modrac sediment nor sampling on regular basis. In year 2015 investigations of sediment quality were realized and are used in this study to assess the overall long-term pollution of Lake Modrac (The Project for Master Plan for Remediation, 2015). The quality of lake water has been regularly monitored by an authorized laboratory (IHTM study 1999-2012).

The purpose of this study is to assess the change of pollution status of lake water and sediment with application of adequate pollution indices computed based on the average annual heavy metals concentrations from four sampling sites, and to evaluate the potential ecological risk to the water-body. Heavy metals present a considerable environmental concern due to their toxicity, non-biodegradable properties and ac-

cumulative effect (Wang, 2010). The monitoring of sediment pollution presents an accurate indicator for the monitoring of contaminants in the lake aquatic environment.

## Methodology

### STUDY AREA AND SAMPLING

Lake Modrac is the largest artificial hydro-accumulation in B&H constructed 50 years ago when the dam on Spreča River was built. In addition to Spreča River, Turija River is another large watercourse flowing directly into the lake (Tu), as showed on Fig.1, where the sampling sites are presented.

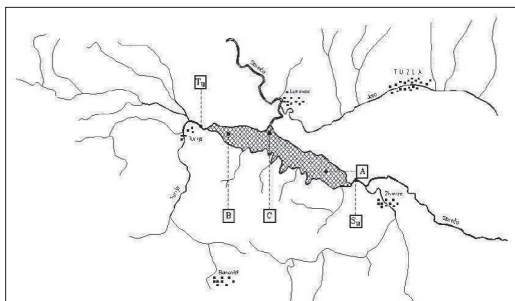


Figure 1. Map of Lake Modrac with sampling sites

The monitoring of lake water quality is realized by an authorized laboratory (IHTM) in accordance with the monitoring plan adopted by the Ministry for environmental protection of Tuzla canton. Lake water samples were collected from four monitoring sites, presented above on Figure 1. All samples were taken from three depths in water column (0,2; 2,0; 5,0 m) and physical and chemical analyses were performed in accordance with standard methods (APHA, 2005). The annual average concentrations from four monitoring sites were used as input data for computing of heavy metal pollution indices for lake water and sediment. The determination of heavy metals in water column and sediment was carried out in accordance with standard methods with AAS -Perkin Elmer and ICP –OES - Perkin Elmer (EPA, 2001).

### POLLUTION INDICES

Pollution indices applied for assessing heavy metal contamination can be classified into three categories (Caeiro et al., 2005): contamination indices, background enrichment indices and ecological risk indices.

### LAKE WATER POLLUTION INDICES

Based on the average annual heavy metal concentrations, the following pollution indices for lake water were computed: Heavy metal pollution index HPI, Heavy metal evaluation index HEI and the Degree of contamination  $C_d$ .

Heavy metal pollution index (HPI) was proposed by Pr.asad and Bose (2001), and it represents the total quality of water with respect to heavy metals. HPI is a rating method that considers the composite influence of individual heavy metal on the overall metal quality (Reza, 2010). Average annual concentrations of eight heavy metals were used for HPI determination for each year. HPI-index was developed by assigning a rating or weighthage  $W_i$  for each chosen parameter. The rating system is an arbitrarily value between 0 to 1 and its selection depends upon the importance of individual quality considerations, or it can be defined as inversely proportional to the standard permissible value (Mohan 1996); (Edet et al., 2002). The values of HPI for studied metals for each year are determined in accordance with the expression given below:

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

where  $Q_i$  is the sub-index of the  $i$ -th parameter;  $W_i$  is the unit weightage of the  $i$ -th parameter and  $n$  is the number of parameters considered. The sub-index  $Q_i$  is calculated by:

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

where  $M_i$ ,  $I_i$  and  $S_i$  are: monitored value of heavy metal, ideal and standard values of the  $i$ -th parameter, respectively. Critical limit for HPI, proposed by Prasad and Bose (2001) is 100.

Heavy metal evaluation index - HEI represents an overall water quality with respect to heavy metals, and is computed as (Edet 2002):

$$\text{HEI} = \sum_{i=1}^m \frac{H_c}{H_{mac}} \quad (3)$$

where  $H_c$  is the monitored value of the  $i$ -th parameter and  $H_{mac}$ , the maximum admissible concentrations of the  $i$ -th parameter. Critical values for HEI index are adopted as follows:  $\text{HEI} < 10$  for low pollution;  $\text{HEI} = 10 \div 20$  for medium pollution and  $\text{HEI} > 20$  for high pollution.

Degree of contamination -  $C_d$  summarises the combined effects of several quality parameters, it is computed as follows (Al-Ami et al., 1987):

$$C_d = \sum_{i=1}^n C_{fi} \quad (4) \text{ where } C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1 \quad (5)$$

where,  $C_{fi}$ ;  $C_{Ai}$  and  $C_{Ni}$  represent contamination factor, analytical value and upper permissible concentration of the component, respectively. Critical values for the Degree of contamination, which are used to estimate the extent of metal pollution in lake water, are as follows:  $C_d < 1$  for low pollution;  $C_d = 1 \div 3$  for medium pollution and  $C_d > 3$  for high pollution.

#### SEDIMENT POLLUTION INDICES

The pollution of Lake Modrac sediment with seven heavy metals is assessed based on computed values of the following pollution indices: Contamination factor  $C_f^i$ , Ecological risk factor  $E_r^i$ , Enrichment factor EF, Index of geo-accumulation  $I_{geo}$ , Pollution load index PLI, Potential ecological risk for water body RI. Contamination factor,  $C_f^i$ , is computed from the equation below (Hakanson 1980):

$$C_f^i = \frac{C_{0-1}^i}{C_n^i} \quad (6)$$

where,  $C_{0-1}^i$  is the mean content of the metal  $i$  from at least 5 sample sites and  $C_n^i$  is the pre-industrial reference level for metal  $i$ . The heavy metal pollution is expressed with critical values of contamination factors as follows:  $C_f^i < 1$  for low contamination;  $1 \leq C_f^i < 3$  for moderate contamination;  $3 \leq C_f^i < 6$  as considerable contamination and  $C_f^i \geq 6$  for very high contamination. Concentration factor,  $C_F^i$ , presents the modification of pollution index Contamination factor,  $C_f^i$ . This pollution index is computed as follows

$$C_F^i = C_i / C_{ni} \quad (7)$$

where  $C_i$  presents the content of metal in consideration, (instead of mean content from at least 5 sample sites as defined by Contamination factor) and  $C_{ni}$  is the reference value – baseline level or national criteria for metal in consideration  $C_i$  (US EPA, 1997). The critical values for pollution assessment expressed with this index are the same as given above with Contamination factor. The Pollution load index - PLI is defined by Tomlinson (1980) as follows:

$$PLI = (C_{F1} \times C_{F2} \times C_{F3} \times C_{F4} \times C_{F5} \times C_{F6} \times C_{F7})^{1/n} \quad (8)$$

where  $C_F$  is the Concentration factor for each examined metal and  $n$  represents the number of heavy metals. If the critical value of PLI is higher than 1 ( $PLI > 1$ ), it is estimated that the sediment is polluted by heavy metals (Dumcius et al., 2011). The Enrichment factor, EF, of metals, presents the pollution index and very useful indicator reflecting the status and degree of environmental contamination with heavy metals. EF is calculated using the method proposed by Buat-Menard (1979) and Sinex-Helz (1981) as follows:

$$EF = (C_i/Fe)_{\text{sample}} / (C_{\text{bck}}/Fe)_{\text{background}} \quad (9)$$

It is expressed by the natural background value of heavy metal to Fe ratio. Iron was chosen as the element of normalization because natural sources (1,5%) vastly dominate its input (Tippie, 1984). Critical values for pollution, expressed with EF values, are if enrichment factor is in the range  $2 < EF < 40$ . The Index of geo-accumulation,  $I_{\text{geo}}$ , serves to assess the contamination by comparing current and pre-industrial heavy metals concentrations. Background concentrations of heavy metals in the earth's crust were used as reference values implicating the pre-industrial environment. An index of geo-accumulation ( $I_{\text{geo}}$ ) was originally defined by Müller in 1969. In order to determine and define metal contamination in sediments by comparing current concentrations with pre-industrial levels, the index of geo-accumulation can be calculated as follows:

$$I_{\text{geo}} = \log_2 \left[ \frac{C_i}{(1,5 C_{ri})} \right] \quad (10)$$

where;  $C_i$  - measured concentration of the examined metal  $i$  in the sediment;  $C_{ri}$  - geochemical background concentration or reference value of the metal  $i$ . The factor 1,5 is used because of possible variations in background values for a given metal in the environment as well as very small anthropogenic influences. The Ecological risk factor,  $E_r^i$ , quantitatively expresses the potential ecological risk of a given metal, suggested by Hakanson, (1980) and it is computed for each metal in the sediment from the equation:

$$E_r^i = T_r^i \cdot C_f^i \quad (11)$$

where  $T_r^i$  is toxic response,  $C_f^i$  - concentration factor.

The methodology is based on the assumption that the sensitivity of the aquatic system depends on its productivity. Critical values for ecological risk factors that are suggested by Hakanson (1980), are in the range from 40 for low potential ecological risk to 320 for very high risk. The Potential ecological risk index for the water body, RI, is introduced to assess the ecological risk degree of heavy metals in soil or sediments, which was originally proposed by Hakanson (1980) and widely used. The value of RI can be calculated using the following equations:

$$RI = \sum E_{ri} \quad (12) \quad E_r^i = T_r^i C_f^i \quad (13) \quad C_f^i = \frac{C_o^i}{C_R^i} \quad (14)$$

where, RI stands for the sum of potential risk of individual heavy metal;  $E_r^i$  - represents the potential risk of individual heavy metal;  $T_r^i$  - is the toxic response factor for given heavy metal;  $C_f^i$  - is the contamination coefficient;  $C_o^i$  - represents the present concentration of heavy metals in sediments;  $C_R^i$  - is the pre-industrial record of heavy metal concentration in sediment. Based on the Hakanson approach, four critical values of RI are defined.

## Results and discussion

### HEAVY METALS IN LAKE MODRAC WATER

The annual average heavy metal concentrations in Lake Modrac water on four locations for three years in the period between 2000 to 2015 are given in Table 1.

**Table 1.** Annual average concentrations of heavy metals in Lake Modrac water (mg/l) for period year 2000-2015 (IHTM study1999-2015)

Metals	Year 2000-2015		
	2000	2000	2015
Cu	0.004	0.007	0.009
Zn	0.015	0.022	0.055
Al	0.110	0.350 <sup>+</sup>	0.370 <sup>+</sup>
Pb	0.0035	0.030 <sup>+</sup>	0.122 <sup>+</sup>
Cr	0.005	0.019	0.065 <sup>+</sup>
Fe	0.170	0.700 <sup>+</sup>	0.800 <sup>+</sup>
Mn	0.045	0.055 <sup>+</sup>	0.060 <sup>+</sup>
Ni	0.009	0.024 <sup>+</sup>	0.029 <sup>+</sup>

Concentrations of heavy metals which are above maximum permissible concentrations (MPC) according to EPA standards (EPA, 1987), are marked with „+“ in Table 1. There is an evident increase of heavy metal concentrations over the 15 year period in the lake water, especially of Al, Pb, Cr, Fe, Mn and Ni, which exceed the maximum permissible concentrations defined by EPA. This increase is characterized by the following order:  $Fe > Al > Pb > Cr > Mn > Zn > Ni > Cu$ .

The following pollution indices for lake water are computed: Heavy metal pollution index HPI, Heavy metal evaluation index HEI and the Degree of contamination  $C_d$ . The concentration limits, i.e., the standard permissible value ( $S_i$ ) and the highest desirable value ( $I_i$ ) for each metal were taken from WHO standards and are given in Table 2 (WHO standards 2004).

**Table 2.** Standard values of MAC,  $I$ ,  $S_i$  and  $W$  (mg/l), for determination of HPI values

	MAC mg/l	$I$ mg/l	$S$ mg/l	$W$ mg/l
Cu	1.0	2.0	1.0	1
Fe	0.2	0.2	0.3	3.33
Pb	0.015	0.01	0.1	10
Zn	5.0	3.0	5.0	0.2
Ni	0.02	0.02	0.02	50
Cr	0.05	0.05	0.05	20
Mn	0.05	0.5	0.1	10
Al	0.2	0.2	0.25	4

The values of HPI for studied metals for each year are determined based on the equations (1) and (2). The critical limit for HPI, proposed by Prasad and Bose (2001) is 100. The values for HPI were com-

puted using equation (3). The degrees of contamination for lake water,  $C_D$ , are computed based on the equations (4) and (5). Computed values for metal pollution indices HPI, HEI and  $C_D$  for the water column of Lake Modrac for the period year 2000 to 2015 are given in Table 3, as well as assessment of the pollution status based on critical values for each pollution index.

**Table 3.** Heavy metals' pollution indices for Lake Modrac water for the period year 2000 to 2015

Pollution indices	Year		
	2000	2010	2015
HPI	48.83 <i>Not polluted</i>	84.7 <i>Medium-high pollution</i>	147.27 <i>High pollution</i>
$C_d$	-4.759 <i>Low pollution</i>	1.427 <i>Medium pollution</i>	8.935 <i>High pollution</i>
HEI	3.09 <i>Low pollution</i>	10.941 <i>Medium pollution</i>	19.5 <i>High pollution</i>

The assessment of pollution with heavy metals of Lake Modrac water, based on computed values of pollution indices, shows an increasing pollution trend in the 15 year period. Since all three indices reflect the cumulative effect of eight metals to the pollution status, good correlation of pollution status assessment with application of heavy metal pollution indices was achieved indicating the low pollution status until year 2000, to medium pollution status in the period year 2000 to year 2010 and high pollution in year 2015.

#### HEAVY METALS IN LAKE MODRAC SEDIMENT

Heavy metals are introduced into the sediment of Lake Modrac via several pathways, including discharging of polluted industrial waters, coal mines slurries, wastewater streams from agricultural activities, municipal wastewaters, as well as by atmospheric deposition (The Heinrich Boll Foundation study, 2013). The only extensive study of sediment pollution was realised within the latest study in year 2015. Average annual heavy metal concentrations in the sediment from four sites given on Figure 1, are shown in Table 4.

**Table 4.** Average annual concentrations of heavy metals in the sediment of Lake Modrac ( year 2015)

Metal	Average concentration (mg/kg)	EPA, Sediment quality guidelines (1997)
Cd	1.32	<i>Moderately polluted</i>
Pb	27.29	<i>Not polluted</i>
Cr	185.04	<i>Heavily polluted</i>
Cu	37.0	<i>Moderately polluted</i>
Ni	260.63	<i>Heavily polluted</i>
Zn	117.69	<i>Moderately polluted</i>
Mn	809.57	<i>Heavily polluted</i>

Average annual concentrations of Ni, Mn and Cr indicate heavy pollution levels, while average concentrations of Cd, Cu and Zn indicate moderate pollution levels. Values of annual average concentrations of heavy metals given in Table 4 are used as input data in computing the following pollution indices for lake sediment: Concentration factor  $C_F^i$ ; Ecological risk factor  $E_r^i$ ; Enrichment factor EF; Index of geo-accumulation  $I_{geo}$ ; Pollution load index PLI and Potential ecological risk for water body, RI. Pollution index

Concentration factor,  $C_F^i$ , is computed from equation (7). The results of assessment of pollution with heavy metals of Lake Modrac based on the Concentration factor pollution indices are given in Table 5.

**Table 5.** Concentration factors,  $C_F^i$ , for heavy metals in Lake Modrac sediment

Metal	Concentration factor, $C_F$	Critical values for pollution
<b>Cd</b>	4.4	<i>Considerable contamination</i>
<b>Pb</b>	1.365	<i>Moderate contamination</i>
<b>Cr</b>	4.96	<i>Considerable contamination</i>
<b>Cu</b>	1.036	<i>Moderate contamination</i>
<b>Ni</b>	3.48	<i>Considerable contamination</i>
<b>Zn</b>	1.239	<i>Moderate contamination</i>
<b>Mn</b>	1.011	<i>Moderate contamination</i>

Based on  $C_F$  values, lake sediment can be considered as polluted with metals in the following order: Cd>Ni>Cr>Pb>Zn>Mn>Cu. Pollution load index, PLI, is computed using equation (8), where values of concentration factors,  $C_{Fp}$ , from Table 5 were used. The calculated value of Pollution load index for Lake Modrac sediment, is PLI= 1.67, what is higher than 1, which is the critical value for heavy metal sediment pollution. It can be concluded that the lake sediment is polluted with heavy metals. The pollution index Enrichment factor, EF, is calculated using equation (9). Critical pollution values for EF are as follows: EF< 2 depletion to mineral, 2≤EF<5 moderate enrichment, 5≤EF<20 significant enrichment, 20≤EF<40 very high enrichment and EF>40 for extremely high enrichment. Calculated values for enrichment factors for heavy metals in Lake Modrac sediment are given in Table 6.

**Table 6.** Enrichment factors (EF) for heavy metals in Lake Modrac sediment

Metal	Enrichment factors EF	Assessment of Pollution
<b>Cd</b>	26.35	<i>Very high enrichment</i>
<b>Pb</b>	25.73	
<b>Cr</b>	25.89	
<b>Cu</b>	25.00	
<b>Ni</b>	26.10	
<b>Zn</b>	25.62	
<b>Mn</b>	23.08	

The pollution index EF is widely used approach to characterize the degree of anthropogenic pollution to establish enrichment ratios (Wang,2010). If the EF value for a certain heavy metal is greater than 1, it indicates that the metal is more abundant in the sample relative to that found in Earth's crust, which is a clear indication of metal accumulation.

The results of this study show that enrichment factors for all studied heavy metals characterize a very high accumulation in the lake sediment, as given in Table 6, what corresponds to the pollution status *very high enrichment* according to the critical values for enrichment factors, EF, what indicates the high degree of anthropogenic pollution. Industrial and agricultural activities, coal mining, as well as municipal

sewage are predominantly responsible for significant heavy metal inputs into the Lake Modrac. In accordance with the EF values accumulation of metals in the lake sediment is characterized with the following order: Cd>Ni>Cr>Pb>Zn>Cu>Mn.

Following the method of Hernandez (2003), by re-arranging the formula for Enrichment factor, EF, accumulated heavy metals from anthropogenic origin can be estimated as follows :

$$M_{\text{lithogenic}} = M_{\text{sample}} \times \left( \frac{M}{EF} \right)_{\text{sediment}} \tag{15}$$

$$M_{\text{antropogenic}} = M_{\text{total}} - M_{\text{lithogenic}} \tag{16}$$

where  $M_{\text{lithogenic}}$  and  $M_{\text{antropogenic}}$  represent enrichment due to lithogenic and antropogenic source respectively. Concentration of heavy metals in the sediment of Lake Modrac with respect to estimated origin are given in Table 7.

**Table 7.** Origin of accumulated heavy metals in Lake Modrac sediment

Metal	$M_{\text{lithogenic}}$ mg/kg	$M_{\text{antropogenic}}$ mg/kg	$M_{\text{total}}$ mg/kg
<b>Cd</b>	0.0049	1.27	1.32
<b>Pb</b>	1.053	26.23	27.29
<b>Cr</b>	7.02	178.02	185.04
<b>Cu</b>	1.431	35.57	37.0
<b>Ni</b>	10.125	250.5	260.63
<b>Zn</b>	4.59	113.1	117.69
<b>Mn</b>	31.185	778.4	809.57

It can be concluded that all accumulated heavy metals originate from the antropogenic source of pollution. The Index of geo-accumulation,  $I_{\text{geo}}$ , is calculated from equation (10). The geo-accumulation scale consists of seven grades (0-6) defining pollution levels ranging from unpolluted to highly polluted, as given in Table 8 (Muller 1969).

**Table 8.** Geo-accumulation index scale (Martin 1979)

$I_{\text{geo}}$ Grades	$I_{\text{geo}}$ Class	Sediment Quality
<b>0</b>	$I_{\text{geo}} \leq 0$	<i>Uncontaminated</i>
<b>1</b>	$0 < I_{\text{geo}} \leq 1$	<i>Uncontaminated to moderately contaminated</i>
<b>2</b>	$1 < I_{\text{geo}} \leq 2$	<i>Moderately contaminated</i>
<b>3</b>	$2 < I_{\text{geo}} \leq 3$	<i>Moderately to heavily contaminated</i>
<b>4</b>	$3 < I_{\text{geo}} \leq 4$	<i>Heavily contaminated</i>
<b>5</b>	$4 < I_{\text{geo}} \leq 5$	<i>Heavily to extremely contaminated</i>
<b>6</b>	$5 < I_{\text{geo}}$	<i>Extremely contaminated</i>

The degree of pollution of the lake sediment is assessed on the basis of values of geo-accumulation indices,  $I_{\text{geo}}$ . As background concentrations for metals, world shale concentrations, were used (Turekian, 1961). Indices of geo-accumulation are given in Table 9.



**Table 9.** Pollution indices of geo-accumulation ( $I_{geo}$ ) for heavy metals in Lake Modrac sediment

Metal	$I_{geo}$	Critical values for pollution
Cd	1.815	<i>Moderately polluted</i>
Pb	0.850	<i>Moderately polluted</i>
Cr	0.900	<i>Moderately polluted</i>
Cu	-0.350	<i>Unpolluted</i>
Ni	1.350	<i>Moderately polluted</i>
Zn	0.550	<i>Moderately polluted</i>
Mn	0.490	<i>Modrately polluted</i>

Based on the mean values of  $I_{geo}$ , given in Table 9, it can be concluded that the sediment is moderately polluted with metals in the following order:  $Cd > Ni > Cr > Pb > Zn > Mn$ , except for Cu. Ecological risk factor,  $E_r^i$ , or Hakanson index, is computed from equation (11) and it is a diagnostic tool used to assess the potential ecological risk for water pollution control purposes. The methodology is based on the assumption that the sensitivity of the aquatic system depends on its productivity. Critical values for Ecological risk factors suggested by Hakanson (1980) are as follows:  $E_r^i < 40$  low potential ecological risk;  $40 \leq E_r^i < 80$  moderate potential ecological risk;  $80 < E_r^i < 160$  considerable potential ecological risk;  $160 < E_r^i < 320$  high potential ecological risk;  $E_r^i \geq 320$  very high ecological risk. Values for Concentration factors  $C_F^i$ , given in Table 5, and toxic responses,  $T_r^i$ , given in Table 2, are used to determine the Ecological risk factors,  $E_r^i$ , for heavy metals in the sediment, which are presented in Table 10.

**Table 10.** Ecological risk factors,  $E_r^i$ , for metals in Lake Modrac sediment

Metal	$E_r^i$	Critical values for pollution
Cd	132	<i>Considerable ecological risk</i>
Pb	4.14	<i>Low potential ecological risk</i>
Cr	6.38	
Cu	3.70	
Ni	17.50	
Zn	1.24	
Mn	1.01	

The values of Ecological risk factors for most heavy metals in the sediment are less than critical value, which is 40, what suggests that accumulated heavy metals present a low potential risk to the water body except for cadmium, which presents considerable ecological risk. The order of potential ecological risk of heavy metals in the lake sediment is as follows:  $Cd > Ni > Cr > Pb > Cu > Zn > Mn$ . The Potential ecological risk index for the water body, RI, is calculated using the equations (12), (13) and (14) and four categories of RI are defined, as presented in Table 11.

**Table 11.** Critical values for Potential ecological risk, RI, for heavy metals

RI- value	Grade of potential risk
RI < 100	Low risk
110 ≤ RI ≤ 250	Moderate risk
220 ≤ RI ≤ 400	Considerable risk
RI ≥ 440	Very high risk

The Potential risk for the water-body, RI, presents the sum of all values of Ecological risk factors for all examined heavy metal (Dumcius et al. 2011). The calculated value of Potential ecological risk index for Lake Modrac water-body is  $RI \cong 160$ , what indicates the moderate ecological risk from all examined heavy metals accumulated in the lake sediment.

## Conclusions

In this study, results of long-term (15 years) monitoring of heavy metals in Lake Modrac water were assessed with application of cumulative heavy metal pollution indices which are computed based on annual average concentrations of heavy metals in lake water and sediment on four monitoring sites. Lake water pollution indices indicated the low pollution status for the period until 2000, medium pollution for the period year 2000 to year 2010 and status of the high pollution for the period from year 2000 to year 2015. This increase is characterized with the following order:  $Fe > Al > Pb > Cr > Mn > Zn > Ni$ . The sediment can be characterized as polluted in accordance with the Concentration factor,  $C_p$ , pollution index and the Pollution load index, PLI. Enrichment factors for studied heavy metals indicated a very high enrichment in the sediment, as well as an anthropogenic source of pollution. The Index of geo-accumulation,  $I_{geo}$ , showed a good correlation with the enrichment indices. The contamination status of sediment can be defined as moderately polluted for most metals. The Ecological risk factors,  $E_r^i$ , for heavy metals in sediment suggest that each accumulated heavy metal presents a low potential ecological risk for the water-body. The Potential ecological risk index, RI, to the water-body was graded as moderate ecological risk from all examined heavy metals in the sediment. Application of heavy metal pollution indices presents a useful methodology and gives useful insights for seeking appropriate management strategies for decreasing heavy metal pollution, as well as to implement necessary measures in order to regulate the anthropogenic factors which play the key role in heavy metal pollution of Lake Modrac.

## References

- Al-Ami, M., Al-Nikab, S., Ritha, N., Nouri, A., Al-Assina, A. (1987). Water quality index applied to the classification and zoning of Al-Jaysh coral. *Journal of Environmental Science and Health*, Vol.22, 305-319.
- APHA (2005) – Standard methods for examination of water and wastewater (21<sup>st</sup> ed.) Washington DC, American Public Health Association
- Backman, B., Bodis, D., Lahermo, P., Rapant, S. (1997). Application of groundwater contamination index in Finland and Slovakia. *Environmental Geology*, Vol.36 (1-2), 55-64.
- Birch, G. (2003). A scheme for assessing human impacts on coastal aquatic environments using sediments in: Woodcoffe, C.D., Furness, R.A. (ed). *Coastal GIS 2003*,
- Bruces, W.R, Wandan, L.F, Bell, R.G, Green, M.O., Kim J.P. (1996). Heavy metal and suspended sediment from a contaminated intertidal inlet. *Marine pollution Bulletin*, Vol.32, 812-822
- Buat-Menard. (1979). Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. *Earth and Planetary Science Letters*, Vol.42, 399-411
- Cabrera, F., Clemente, I., Barrientos, D. (1999). Heavy metal pollution of soils affected by the guadamar toxic flood. *The science of Total Environment*, Vol. 242, 117-129.
- Caeiro, S., Costa, M., Ramos, T. (2005). Assessing contamination in Sado Estuary Sediment. *Ecological Indicators*, Vol. 5, 151-169

- Dumcius, A., Paliulis, D., Kozłowska, J. (2011). Selection of investigation methods for heavy metal pollution on soil and sediments of water basins and river bottoms: a review. *Ekologija*, Vol. 57 (1), 30-38.
- IHTM. 2012. Istraživanja kvaliteta voda akumulacije Modrac za snabdjevanje pitkom vodom tuzlanske regije 1999-2012
- Edet, A., Offiong, O. (2002). Evaluation of water quality pollution indices for heavy metal contamination monitoring. *Geo. Journal*, Vol.57, 295-304
- EPA - Method 200.7 (2001). Determination of metals and trace elements in water and wastes by ICP - atomic emission spectroscopy, URL: [http://www.accustandard.com/assets/200\\_7.pdf](http://www.accustandard.com/assets/200_7.pdf) (15.06.2016)
- Hakanson, M., (1980). An ecological risk index for aquatic pollution control-a sedimentological approach. *Water research*, Vol. 14, 975-1001.
- Hernandez, L. et al (2003). Heavy metal distribution in some French forest soils; Evidence for atmosphere contamination, *The Science of Total Environment*, Vol. 312, 195-210.
- Mohan, S., Nithila, P., Reddy S. (1996). Estimation of heavy metal in drinking water and development of heavy metal pollution index, *J. Environ. Sci. Health*, Vol. 31, 283-289.
- Martin, J.M., Maybeck, M. (1979). Elemental mass of material balance carried by major world rivers. *Marine Chem*, Vol.7, 173-206.
- Muller, G., (1969). Index of geo-accumulation in sediments of Rhine River, *Geochemical J.*, Vol. 2, 108-118.
- Prasad, B., Bose, J.M. (2001). Evaluation of heavy metal pollution index for surface and spring water near a limestone mining area of the lower Himalayas. *Environmental Geology*, Vol. 41, 183-188
- Reza, R., Singh, G. (2010). Heavy metal contamination and its indexing approach for river water, *International Journal of Environmental Science Technology*, Vol. 7/4, 785-792
- Sinex, S., Helz, G. (1981). Regional geochemistry of trace elements in Chesapeake Bay sediments. *Environmental Geology*, Vol.3/6, 315-323.
- The Heinrich Boll Foundation, (2013). Study "Uticaj otpadnih voda iz rudnika uglja na akumulaciju Modrac"
- Tomlinson, D., Wilson, G., Haris, C., Jeffrey, D. (2008). The assessment of heavy metal levels in estuaries and formation of a pollution index. *Helgol Meeresunters*, Vol.33, 566-575.
- Institute for hydrotechnics Sarajevo. (2015). The Project for Master Plan for Remediation of Hotspots in B&H.
- Tippie, V., (1984). The estuary as a filter, *Academic Press New York*, 467-487.
- Turekian, K., Wedepohl, K. (1961). Distribution of the elements in some major units of the earth's crust, *American Geology Social Bulletin*, Vol. 72, 175-182.
- US EPA. (1997).. National Sediment Quality survey, Vol 1, EPA-823-R.97-006
- WHO, (2004). Guidelines for drinking water quality, 3<sup>rd</sup> ed., World Health Organization
- Wang, S., (2010). Fractionation of heavy metals in shallow marine sediments from Jinzhou Bay China. *Journal of Environmental Sciences*, Vol. 22/1, 23-31

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