Carpathian Journal of Earth and Environmental Sciences, July 2017, Vol. 12, No. 2, p. 437 - 445

ECOLOGICAL RISK ASSESSMENT OF HEAVY METALS IN SURFACE SEDIMENTS FROM THE DANUBE RIVER

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Abstract: Surface sediment samples were collected monthly from ten sites along the Danube River between Km 347 and Km 182, during May 2012 – August 2014, in order to assess heavy metal pollution status and adverse biological effects. Concentrations of six elements (Cu, Cr, Ni, Zn, Pb and Cd) were determined using AAS technique. Statistical analyses were performed using the following software package: Minitab 16 and JMP 9 (SAS). The general profile of mean metal concentration in sediments for the study area was Zn>Cr>Cu>Ni>Pb>Cd. Pearson correlation coefficient revealed a strong relationship between Cu-Zn, Ni-Zn and Cd-Zn. The contamination factor (CF), geoaccumulation index (Igeo), pollution load index (PLI) and potential ecological risk index (RI) - calculated using adapted background concentrations of heavy metals - were used to assess the ecological risk associated with the studied heavy metals in surface sediments. Also, the measured concentrations of heavy metals were compared with sediment quality guidelines values (TEL - threshold effect level and PEL - probable effect level). The obtained data showed that in all sampling sections the mean concentrations of Cu and Ni ranged between TEL and PEL references values and therefore, Cu and Ni in sediments may cause harmful biological effects on aquatic life.

Keywords: contamination factor, Danube River, heavy metals, sediment quality assessment, statistical analyses, potential ecological risk index (RI)

1. INTRODUCTION

In the past few decades, heavy metals contamination in aquatic environments has become of a major concern due to their toxicity, persistence and subsequent bioaccumulation in aquatic organisms (Matache et al., 2013; Öğlü et al., 2015), resulting in potential long-term implication on human health and ecosystem (Fernandes et al., 2007; Abdel-Baki et al., 2011; Smal et al., 2015). Heavy metals in aquatic environment are distributed between aqueous phase and suspended particles and, usually, tend to be accumulated in sediments (Uluturhan et al., 2011; Findik & Turan, 2012; Varol & Şen, 2012; Iordache et al., 2015). For this reason, sediments are regarded as the potential reservoir for heavy metals, but also, under different physical and chemical conditions, as potential secondary source of heavy metals pollution for the river water (Bekteshi & Myrtaj, 2014; Mititelu et al., 2012). Furthermore, sediments play an important role in determining the pollution patterns of aquatic systems, reflecting the history of pollution and providing a record of catchment inputs into aquatic ecosystems (Farkas et al., 2007).

The Danube River, the most important European River crosses many populated areas along its course and therefore it is highly vulnerable to heavy metal pollution due to urbanization and industrialization. The economic development in the Danube region brought not only improvement of life quality, but also a threat to environment and river (Enache, 2008). Extensive agriculture, increase of industrial activities, growing municipal communities represents potential sources of pollution and could have a negative impact on functions of the river and water quality (Enache, 2008). Some undertaken studies have revealed serious contamination of the Danube River with heavy metals, including copper and nickel (Gavrilescu, 2011; Crivineanu et al., 2012). The European Water Framework Directive 2000/60/EC (WFD), the most significant and complex legislative instrument in the field of water policy, develops the concept of ecological quality status for the assessment of water quality - based on the physical-chemical, hydro-morphologic and biological quality elements. One of the most important aims of WFD is the protection and improvement of the status for all European water bodies to the level of "good ecological and chemical status". In order to meet the objectives of the WFD, Romania and the other states from Danube Basin cooperate under the coordination of the International Commission for the Protection of the Danube River (ICPDR) for achieving a Unitary Management Plan for the Danube corridor (www.icpdr.org). Such environmental management strategies need to be accomplished by an increasing international effort for characterizing the current ecological and chemical status along the entire Danube River (including sediments and biota) (Milenkovic et al., 2005, Vrana et al., 2014) as well as by the assessment of aquatic ecosystems evolution trends (Grabić et al., 2016).

The objectives of the present study were to estimate the level of heavy metals contamination in Danube sediments, along Calarasi-Braila stretch, km 375 - km 175 and to assess the risk associated with the six heavy metals, by contamination factor (CF), geoaccumulation index (I_{geo}), pollution load index (PLI), potential ecological risk index (RI), as well as by comparing the measured concentrations to sediment quality guidelines *(SQGs)*.

2. EXPERIMENTAL

2.1. Sampling and Pre-treatment

The sampling sections were selected from an area belonging to the lower part of the Danube where construction works for improving the navigation conditions will be performed. These construction works could have a potential negative impact on water and sediment quality and also on biodiversity. Surface sediment samples (first 5-10cm layer of the river deposits) were collected monthly from ten sites along the Danube River between Km 347 and Km 182, during May 2012 – August 2014 (Fig. 1), in order to assess heavy metal pollution status and adverse biological effects.

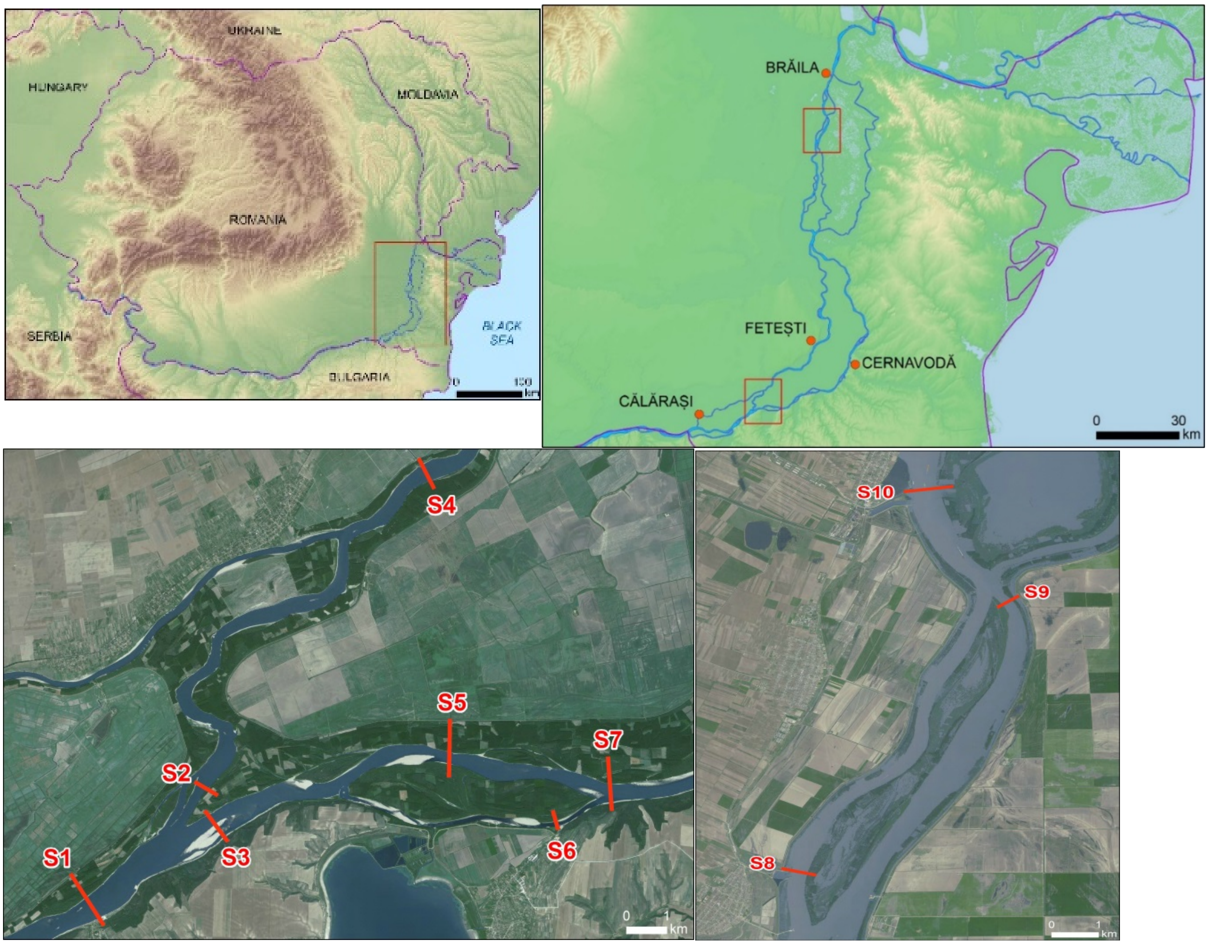


Figure 1. Sampling sections - Lower part of Danube, Romania

Table 1. Sampling site location

Sections	River km	Geographical coordinates (latitude, longitude)		Land use
		Left bank	Right bank	
S1	Danube km 348	44°10'35.63"N 27°32'18.44"E	44°10'18.31"N 27°32'33.18"E	Mix of residential, agricultural and rural
S2	Bala Branch km 9.4	44°12'05.33"N 27°34'26.60"E	44°11'59.39"N 27°34'39.67"E	Mix of residential, agricultural and rural
S3	Danube km 344.8	44°11'39.20"N 27°34'38.55"E	44°11'19.92"N 27°34'56.75"E	Mix of residential, agricultural and rural
S4	Borcea Branch km 65	44°16'14.93"N 27°38'51.90"E	44°16'02.26"N 27°39'00.21"E	Mix of residential, agricultural and rural
S5	Danube km 338	44°12'22.62"N 27°39'11.60"E	44°12'12.62"N 27°39'10.87"E	Mix of residential, agricultural and rural
S6	Epurasu Branch km 1.8	44°11'25.64"N 27°41'08.09"E	44°11'18.12"N 27°41'10.72"E	Rural
S7	Danube km 334.3	44°11'53.25"N 27°42'10.45"E	44°11'37.96"N 27°42'11.23"E	Rural
S8	Caleia Branch km 8.9	45°04'56.17"N 27°54'06.61"E	45°04'53.16"N 27°54'21.88"E	Mix of residential, agricultural and rural
S9	Danube km 186.5	45°08'39.15"N 27°57'43.51"E	45°08'43.19"N 27°57'52.69"E	Mix of residential, agricultural and rural
S10	Danube km 182.6	45°10'19.60"N 27°56'22.34"E	45°10'21.23"N 27°56'46.71"E	Mix of residential, agricultural and rural

The sampling section locations are shown in table 1 and sections were grouped in two sectors: upstream sector (S1-S7) – located in the area of construction works and downstream sector (S8-S10) – located downstream from construction works area. Samples were collected from both left and right banks of the Danube and they were analysed for six trace metals: Cu, Cr, Ni, Zn, Pb and Cd. Samples of the first 5-10cm of the river deposits were collected in acid rinsed polyethylene bottles. All samples were kept in cooling boxes, at 4^{o}C during transportation, and the analyses were performed immediately after receiving the samples in the laboratory.

2.2. Laboratory Analysis of heavy metals

2.2.1. Sediment samples

The collected sediment samples were air-dried, large particles were hand-picked and the rest was ground to powder. The fraction <63 μm was used for analyzing metals.

Dry sediment was digested using aqua-regia (1:3 HNO_3: HCl). The acidified mixture was mineralized in microwave digestion system and then cooled to room temperature. The acidified mixture was filtered and distilled water was added to the filtrate in a volumetric flask up to 50 mL mark. Digestion solutions were then analyzed for heavy metals content using atomic absorption spectrophotometry (Solaar M5).

2.2.2. Quality control and assurance

Quality control was ensured by using procedural blanks and standards. For these procedures, reagent blank was prepared for every 20 sediment samples and all concentrations obtained were below the detection limit. All acids used in this study were of analytical grade quality control. Method validity was controlled by certified reference material digested together with samples.

2.2.3. Assessment methodology

The ecological risk associated with the studied heavy metals in surface sediments was assessed using a pollution status index contamination factor (CF), geoaccumulation index (I_{geo}), potential ecological risk index (RI) and pollution load index (PLI) calculated using adapted background concentrations of heavy metals, as well as by comparing the measured concentrations to sediment quality guidelines (Threshold Effect Level – TEL and Probable Effect Level – PEL). The background values play an important role in the interpretation of geochemical data (Wang et al., 2014). The following background values of Cu, Cr, Cd, Pb, Ni and Zn were used: 35; 30; 0.25; 25; 10 and 130 mg/kg, respectively (Woitke et al., 2003). The *geoaccumulation index* (I_{geo}) is defined by (Formula 1):

$$I_{geo} = log_2\left(\frac{Cn}{K\times Bn}\right) \quad (1)$$

where: Cn is the measured concentration of heavy metals in sediment;

Bn is the geochemical background value and K – constant, which is usually defined as 1.5

Based on the I_{geo} value, Müller (1969) has distinguished 7 classes: I_{geo} value of < 0, practically unpolluted (class 0); 0–1, unpolluted to moderately polluted (class 1); 1–2, moderately polluted (class 2); 2–3, moderately to heavily polluted (class 3); 3-4 heavily polluted (class 4); 4-5 heavy to extremely polluted (class 5) and > 5 very strongly polluted (class 6).

The *contamination factor* (CF) is computed using (Formula 2):

$$CF = \frac{C_{heavy\ metal}}{C_{background}} \quad (2)$$

Contamination levels were classified based on their intensities on a scale ranging from 1 to 6: 0=none, 1=none to medium, 2=moderate, 3=moderately to strong, 4=strongly polluted, 5=strong to very strong, 6=very strong (Hakanson, 1980).

Pollution load index (PLI) was determined as the n^{th} root of the multiplications of the concentrations CF (Formula 3):

$$PLI = (CF_1 \times CF_2 \times \ldots \times CF_n)^{1/n} \ (3)$$

where, „n" is the number of metals, CF_i (i=1,n) is contamination factor for every metal.

The values of PLI > 1 show that heavy metal pollution exists, whereas PLI < 1 indicates no heavy metal pollution (Tomlinson et al., 1980).

The *potential ecological risk index* (RI) was introduced by Hakanson (1980) to assess the risk of heavy metal pollution of sediments, according to the toxicity of metals and the response of environment.

RI is calculated using (Formula 4):

$$C_f^i = \frac{C_i}{C_n^i} \quad E_r^i = T_r^i \cdot C_f^i \quad RI = \sum_i^m E_r^i \ (4)$$

Where: C_f^i is the monomial contamination factors

E_r^i is the potential ecological risk factor of each heavy metal

T_r^i is the toxic-response factor of heavy metal i

The T_r^i values of for each element are: Cu=5, Zn=1, Cr=2, Ni=5, Pb=5 and Cd=30. RI is the potential ecological risk caused by the overall contamination. There are four categories of RI value: RI <150, low ecological risk for the sediment; 150≤ RI <300, moderate ecological risk for the sediment; 300≤ Ri <600, considerable ecological risk for sediment; RI ≥600, very high ecological risk for the sediment.

2.2.4. Sediment quality guidelines (SQGs)

Sediment quality assessment guidelines (SQGs) comprise two assessment levels and they are very useful in terms of revealing sediment contamination by comparing the sediment concentration to the corresponding quality guideline (MacDonald et al., 2000). The TEL (Threshold Effect Level) defines the concentration below which adverse biological effects rarely occur and PEL (Probable Effect Level) represents a concentration above which adverse effects are expected to occur over a wider range of organisms (Hroncová et al., 2014; MacDonald et al., 2000; Goldyn et al., 2015; Sun et al., 2011; Zahra et al., 2014).

2.2.5. Statistical analysis

Statistical analyses were performed using Minitab 16 and JMP 9 (SAS) software package. Data for studied heavy metals were analyzed using descriptive statistic. Pearson correlation coefficient was used to reveal relationship between sediment heavy metal values. Also, cluster analysis was used to group the studied heavy metals into clusters on the basis of similarities/dissimilarities between different groups.

3. RESULTS AND DISCUSSION

3.1. Descriptive statistics

In Table 2 there is presented a complete descriptive statistic summary of studied heavy metals. In the study area, the ranges of heavy metals in sediments were as follows: 0.07-1.33 mg/kg for Cd; 1.45-93.03 mg/kg for Cr; 2.65-126.52 mg/kg for Cu; 0.42-83.40 mg/kg for Pb; 31.45-206.99 mg/kg for Zn; 10.08-79.87 mg/kg for Ni. Similar range of elements concentrations in the Danube sediments samples was reported in the results obtained in the third Joint Danube Survey Expedition 3 (Joint Danube Survey 3 Final Report. ICPDR, 2015).

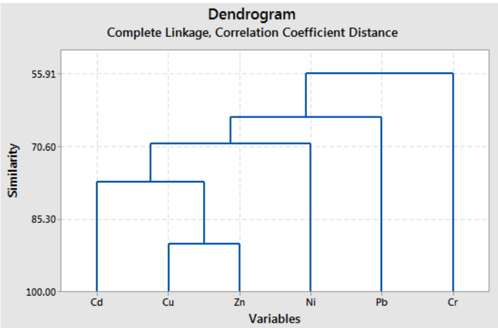
Pearson's correlation analysis was applied to test the relationships between the studied heavy metals (Table 3). Pearson coefficient and cluster analysis revealed a strong relationship between Cu-Zn (0.809) and a moderate correlation between Ni-Zn (0.664) and Cd-Zn (0.629). Crnković et al., (2016) have also reveled significant correlation between Cu, Cd, Zn and Pb in sediment samples collected from Danube right bank, between 1077 and 956 river Km, using multi-criteria cluster analysis. These significant and positive correlations between heavy metals possibly reflect the same or similar sources of input, mutual dependence and/or identical behaviour during the transport (Sedgwick, 2012). Furthermore, according to literature, the associations and interactions between heavy metals are important, as they determine potential toxicity to organisms in aquatic ecosystems (Vuković et al, 2014; Luoma, 1983).

Table 2. Descriptive statistic of heavy metals concentrations in Danube sediments samples (mg/kg)

Element / Section	Cd	Cr	Cu	Pb	Zn	Ni
	Mean	Mean	Mean	Mean	Mean	Mean
	Min-Max StDev	Min-Max StDev	Min-Max StDev	Min-Max StDev	Min-Max StDev	Min-Max StDev
1	0.36	42.28	38.56	19.03	98.37	33.83
	0.13 - 0.87	4.09 - 86.81	13.68 -84.41	0.67 - 75.90	54.78 - 203.52	11.93 - 61.30
	0.15	21.19	17.14	13.48	29.29	9.65
2	0.36	44.52	37.67	19.23	96.06	34.76
	0.10 - 0.73	8.93 - 84.92	2.65 - 81.38	0.67 - 56.30	44.63 - 138.72	13.65 - 79.87
	0.16	20.48	15.09	10.87	23.52	10.89
3	0.35	42.77	37.27	18.61	95.63	32.54
	0.12 - 0.69	7.51 - 90.87	11.06 - 80.17	0.67 - 50.23	28.29-142.34	15.48 - 52.37
	0.14	20.61	16.38	12.22	24.99	8.30
4	0.35	46.16	37.40	19.41	98.05	37.39
	0.09 - 0.70	9.13 - 93.03	10.35 - 93.17	0.67 - 54.80	51.66-156.34	11.39 - 56.60
	0.16	21.80	20.19	13.69	27.75	8.75
5	0.35	44.72	38.76	22.61	103.39	40.11
	0.14 - 0.80	10.56 - 90.14	11.82 - 93.14	0.67 - 63.29	63.89 - 206.99	16.82 - 63.61
	0.16	18.93	17.31	15.64	29.52	10.53
6	0.43	44.08	48.15	23.84	111.65	37.92
	0.12 - 0.80	6.42 - 87.28	11.04 - 126.52	0.67 - 83.40	61.35 - 217.43	24.34 - 60.44
	0.15	21.42	22.72	14.96	28.81	7.63
7	0.40	40.46	40.98	24.38	105.46	35.83
	0.10 - 1.33	4.36 - 89.98	10.40 - 94.51	0.42 - 77.67	66.63 - 179.30	22.81 - 56.97
	0.19	19.83	16.96	16.93	24.85	7.32
8	0.24	42.33	24.81	13.07	83.68	32.03
	0.10 - 0.54	1.85 - 83.64	4.59 - 50.33	0.57 - 58.44	39.79 - 147.78	10.08 - 52.69
	0.10	21.63	10.82	10.11	23.26	9.17
9	0.26	43.76	26.16	13.42	89.83	33.49
	0.09 - 0.48	8.51 - 80.66	5.12 - 52.67	0.67 - 31.70	38.40 - 135.49	14.39 - 47.60
	0.11	20.30	10.85	6.77	22.24	7.24
10	0.25	41.71	25.58	13.84	83.99	31.70
	0.07 - 0.43	2.24 - 89.66	6.69 - 56.39	0.67 - 72.66	31.45 - 176.21	10.79 - 54.03
	0.10	21.50	11.02	10.60	29.98	9.90

Table 3. Pearson correlation matrix and dendrogram for heavy metal concentration in the Danube sediments

	Cd	Cr	Cu	Pb	Zn	Ni
Cd	1					
Cr	0.118	1				
Cu	0.558	0.361	1			
Pb	0.293	0.225	0.531	1		
Zn	0.629	0.311	0.809	0.495	1	
Ni	0.401	0.292	0.537	0.353	0.664	1



3.2. Sediment contamination status Igeo

Calculated geo - accumulation index (I_{geo}) for heavy metal concentrations in the Danube sediments ranged from -1.52 to 1.42 (Fig. 2.). The geo-accumulation index values showed that the Danube sediments were not polluted with Cu, Cr, Pb and Zn, but moderately polluted by Ni in all sampling sections. I_{geo} index in section S4 was 0.04 for Cr, suggesting that this section is unpolluted-moderately polluted by Cr. In sections S6 and S7, the values of I_{geo} for Cd were between 0 and 1, suggesting that these sections were designated as unpolluted-moderately polluted. This is in agreement with a risk assessment of heavy metals in the Danube sediment using enrichment factors, carried out by Woitke et al., (2003), revealing high concentrations of Cd, particularly in the lower part of Danube River downstream Iron Gates. Based on the I_{geo} classification, the degree of heavy metals pollution in the Danube surface sediments decreased in the following sequence: Ni>Cr>Cd>Cu>Pb>Zn.

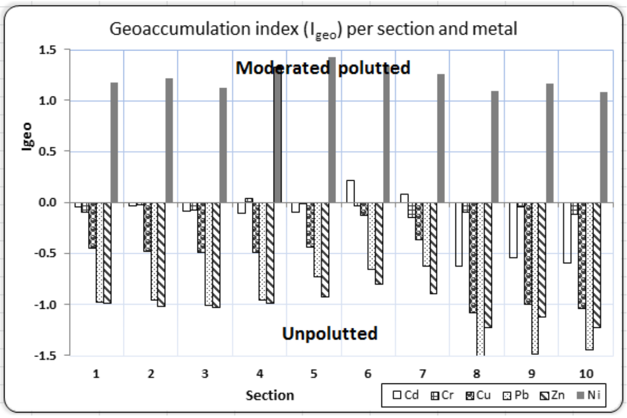


Figure 2. Geo-accumulation index in the Danube sediments

3.3. Contamination factor CF

The values of CF obtained in the Danube sediments are presented in figure 3. The CF values for Zn, Pb and Cu in sections S8, S9, S10 were lower than 1 and they were found at a low contamination level, while the contamination factor for Cr, Cd and Cu in sections S1-S7 reached moderate value. The contamination factor for Ni reached considerable values in all sampling sections. The sequence of CF values for studied heavy metals followed the order: Ni>Cr>Cd>Cu>Pb>Zn.

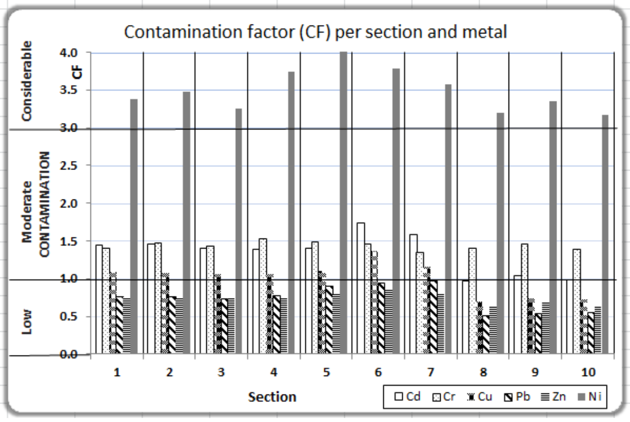


Figure 3. Contamination factor in the Danube sediments

3.4. The pollution load index

The pollution load index (PLI) represents the number of times by which the heavy metals level in the sediments exceeds the background concentration and gives a summative indication of the overall level of heavy metals toxicity in a particular sample (Barakat et al., 2012). The PLI calculated for the Danube sediment samples (Table 4) ranged from 1.01 to 1.49, values that indicated heavy metal pollution in the studied area. PLI values for the sampling sections followed the order: S6>S7>S5>S4>S2>S1>S3 >S9>S10>S8, with the highest values recorded in sections S5, S6 and S7, confirming the interpretation of the CFs.

Table 4. Pollution load index (PLI) and Ecological risk index (RI) for the Danube sediments

Section	Pollution load index-PLI	Ecological Risk Index-RI
1	1.28	73.28
2	1.29	73.99
3	1.25	71.07
4	1.31	73.56
5	1.37	75.74
6	1.49	86.55
7	1.39	79.64
8	1.01	54.65
9	1.06	57.84
10	1.02	55.33

3.5. Ecological risk – RI

In order to quantify the overall potential ecological risk of studied heavy metals in the Danube sediments, RI was calculated as the sum of the six risk factors (Table 4) and the contribution of individual heavy metals to overall potentially ecological risk was presented in (Fig. 4).

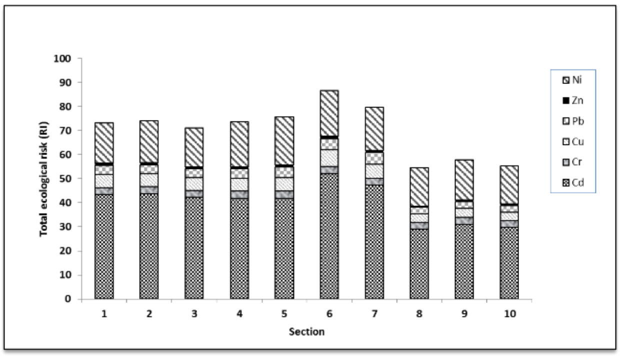


Figure 4. Contributions of different heavy metals to ecological risk (RI) in sampling sections of the Danube sediments

The RI values in all section were found to be < 150 and therefore sediments come under low ecological risk. Gati et al., (2016) found a similar low ecological risk (RI 94.8) for sediment samples collected from Danube Delta. In this study, the contribution to the total potential ecological risk of the Danube sediments revealed that Cd contributed with 40.24%, Ni contributed with 17.48%, Cu and Pb contributed with 5.08% and 3.75% respectively, while Cr was 2.89%. Results of geo-accumulation evaluation indicated that Cd was mainly at the

Table 5. Mean heavy metals concentrations in Danube sediments, TEL/PEL guideline values for heavy metals and Water Framework Directive 2000/60/EC (WFD) sediment limits (in mg/kg)

Heavy Metal	Sections										TEL*	PEL*	WFD** limits
	1	2	3	4	5	6	7	8	9	10			
Cd	0.36	0.36	0.35	0.35	0.35	0.43	0.40	0.24	0.26	0.25	0.68	4.21	0.8
Cr	42.28	44.52	42.77	46.16	44.72	44.08	40.46	42.33	43.76	41.71	52.3	160.4	100
Cu	38.56	37.67	37.27	37.40	38.76	48.15	40.98	24.81	26.16	25.58	18.7	108.2	40
Pb	19.03	19.23	18.61	19.41	22.61	23.84	24.38	13.07	13.42	13.84	30.2	112.2	85
Zn	98.37	96.06	95.63	98.05	103.39	111.65	105.46	83.68	89.83	83.99	124.0	271.0	150
Ni	33.83	34.76	32.54	37.39	40.11	37.92	35.83	32.03	33.49	31.70	15.9	42.8	35

*Canadian Sediment Quality Guidelines (2001); **Water Framework Directive 2000/60/EC (WFD) sediment limits (in mg/kg)

uncontaminated degree, excepting for sections S6 and S7. However, its contribution to overall ecological risk was important (40.24%), posing a considerable risk due to its high toxicity even at trace levels (El Bouraie et al., 2010).

3.6. Sediment quality guidelines (SQGs)

To achieve an assessment of sediment ecotoxicity, sediment quality guidelines in Romania (Order 161/2006 - for the Approval of the Norms on Reference Objectives for the Surface Water Quality Classification) and TEL/PEL values developed by MacDonald et al., (2000) have been used (Table 5). These consensus-based sediment quality guidelines evaluate the degree to which the sediment-associated heavy metal contamination status might adversely affect aquatic organisms in the study area (El Bouraie et al., 2010). Based on sediment quality guidelines in Romania, the results indicated that the mean concentrations of Cu exceeded the 40 mg/kg WFD sediment limit in sampling sections S6 and S7, which could be of concern for the health of the aquatic ecosystem. In the case of Ni, the concentration in the bottom sediment exceeded the 35.0 mg/kg WFD sediment limit in sampling sections S4 – S7. Some undertaken studies have revealed serious contamination of the Danube River with heavy metals, including copper and nickel (Pavlović et al., 2016).

Comparing the mean heavy metals concentrations to the TEL and PEL values, it was observed that Cu and Ni concentrations in all sampling sections ranged between TEL and PEL values. Based on this classification approach, those concentrations indicated that the adverse biological effects may occur rarely, occasionally and frequently for the broad range of biota (Goldyn et al., 2015). The mean concentrations of Cd, Cr, Pb and Zn in all sampling sections were less than TEL and PEL values.

4. CONCLUSIONS

The assessment methodology applied to the study area of the lower part of Danube River could be used along the entire Danube River for the management and planning of good water quality sustainability in the context of heavy metal pollution. In this study, the evaluation based on the TEL and PEL values showed that the concentrations of Cu and Ni are likely to result in adverse effects on sediment-dwelling organisms in all sampling sections. The results of CF index revealed that sediments was considerable polluted by Ni and moderately contaminated by Cd, Cr and Cu. Also, the results of this study provide valuable information on the heavy metals concentrations in the Danube sediments as a part of the increasing international effort for characterizing the current chemical status along the entire Danube River and highlight the necessity for drawing up more elaborate ecotoxicology studies in this area for assessment of aquatic ecosystems evolution trends.

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Received at: 02. 06. 2016
Revised at: 11. 01. 2017
Accepted for publication at: 09. 02. 2017
Published online at: 20. 02. 2017