Spatial distribution of heavy metal contamination in surface sediments from the Danube River

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Abstract: Heavy metal pollution of sediments may have significant effects on environment and human health. Evaluation of heavy metal contamination (Zn, Cu, Ni, Pb, Cd, Cr) of 758 samples of surface sediments collected from the Danube River between Km 347 and Km 182 during May 2012 - April 2015 has been studied to represent the spatial distribution of heavy metals in sediments. The average concentrations of the studied metals have decreased in the following order: Zn>Cr>Cu>Ni>Pb>Cd. Their spatial distribution was analyzed using multivariate statistics. From the statistical analysis, significant correlations between Cu and Zn are highlighted, suggesting similar sources or similar geochemical processes that control the occurrence of these metals in sediments.

Key-Words: heavy metals, Danube River, contamination of sediments, sediment quality assessment, spatial distribution, statistical analyses

1 Introduction

The Danube is one of the largest rivers on the planet: it is the 21st-longest river, it has the 25th-largest river basin (817,000 km^2) [1] and it is the second longest river in Europe, flowing along 2857 km from Germany's Black Forest to its delta on the Black Sea [2].
Heavy metals in the environment originate from various sources: industrial activities, transportation, fossil fuels, agriculture, urbanization and other human activities [2,3,4,5]. Release of heavy metals in large quantities into the natural environment creates problems due to their persistence. Heavy metals are stable and persistent contaminants for environment because they do not degrade and destroy.

They can accumulate in the food chain causing adverse effects on human health and the aquatic ecosystem disturbing the food chain [6,7]. The drainage basin of the Danube has a long history of precious and base metal mining (Hungary, Serbia, Bulgaria and Romania), metal contaminants are released into the drainage basin of the Danube, part of these reaching the Danube Delta [8].

Sediments play a key role for assessment of aquatic environmental pollution and provide basic information for risk assessment of environmental health.
There are various studies that highlight the negative effect that heavy metals have on human health and aquatic ecosystems and therefore assessing their distribution in water and sediments has become a pressing problem being particularly important in the study of bioaccumulation processes of heavy metals in aquatic ecosystems [9,10]. The accumulation of metals in marine sediments is a risk for the ecosystem and the concentrations of these heavy metals can provide historical information about the pollution of areas.

2 Problem Formulation

In this study there were analyzed metals exhibiting a greater relevance to the environment in terms of toxic effects, namely: Cadmium (Cd), Chromium

(Cr), copper (Cu), lead (Pb), Nickel (Ni) and Zinc (Zn).
Samples of surface sediment were collected monthly from ten sites along the Danube River between Km 347 and Km 182 during May 2012 - (Fig. 1) April 2015, in order to assess the state of heavy metal pollution and represent the spatial distribution of the analyzed indicators.

Fig. 1. Sampling sections located along the lower part of Danube, Romania

The locations of sampling sections are shown in Table 1, and the sections were divided into two sectors: upstream (S1-S7) and downstream (S8-S10). Samples were collected on both sides of the Danube and traces of heavy metals were analyzed for Cu, Cr, Ni, Zn, Pb and Cd. Sediment samples were collected from 5-10 cm in the river in plastic bottles rinsed with acid. All samples have been kept cold in freezers at 4° C during the transport, and the analysis was performed immediately after receiving the samples in the laboratory.

Table 1. Sampling site location

Sections	River km	Geographical coordinates (Stereo 70 projection)	
		Left bank	Right bank
S1	Danube km 348	X: 703099, Y: 300605	X: 703443, Y: 300081
S2	Bala Branch km 9.4	X: 705857, Y: 303463	X: 706153, Y: 303289
S3	Danube km 344.8	X: 706148, Y: 302665	X: 706571, Y: 302083
S4	Borcea Branch km65	X: 711494, Y: 311355	X: 711691, Y: 310970
S5	Danube km 338	X: 712166, Y: 304201	X: 712160, Y: 303892
S6	Epurasu Branch km 1.8	X: 714810, Y: 302528	X: 714876, Y: 302298
S7	Danube km 334.3	X: 716166, Y: 303426	X: 716199, Y: 302955
S8	Caleia Branch km 8.9	X: 728525, Y: 402185	X: 728862, Y: 402104
S9	Danube km 186.5	X: 733012, Y: 409238	X: 733208, Y: 409370
S10	Danube km 182,6	X: 731126, Y: 412272	X: 731656, Y: 412342

Laboratory Analysis of heavy metals
Sediment samples
Sampling, processing and preservation of evidence was done taking into account national and international standards. 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 samples were digested using aqua-regia (1:3, v/v, 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).

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.

Sediment quality assessment was performed considering sediment quality guidelines in Romania - Order of the Ministry of Environmental and Water No 161/2006 for the Approval of the Norm Concerning the Reference Objectives for the Surface Water Quality Classification (including Quality Standards for Sediments), Official Journal of Romania, Part 1, No 511 bis), transposed from European Water Framework Directive 2000/60/EC.

3 Problem Solution

3.1. Descriptive statistics

Statistical processing of analytical data and setting up the database to achieve GIS maps is an essential phase of sediment quality assessment. Descriptive statistical analysis was carried out using Microsoft Office Excel 2010.

Six indicators of the basic statistics were computed in this paper, based on the total number of concentrations - 4548, meaning 758 for each metal (Table 2). There were compared the minimum and maximum values to assess the spread of the data. In this case, it has been observed that a greater spread in the data was for Zn, Cr and Cu. On the other hand, the variation in the data, considering the mean value (CoefVar) indicates that Pb has the greatest spread in the data, followed by Cr and Cu. *Table 2* presents an overview of the heavy metals in sediment samples investigated.

Table 2. Main indicators of basic statistics for heavy metals' concentration in surface sediment samples of the Danube River (mg/kg)

Variable	Mean	StDev	CoefVar	Sum	Minimum	Maximum	Order 161/2006; WFD Limits [11, 12]	Samples which exceeded CMA* (%)
Cd	0.35	0.16	44.90	262.52	0.02	1.33	0.8	0.27
Cr	41.15	20.77	50.47	31193.62	1.45	93.03	100	-
Cu	36.94	17.52	47.42	27998.63	2.65	126.52	40	14.65
Pb	20.32	12.59	61.97	15400.41	0.42	83.40	85	-
Zn	97.32	27.31	28.06	73768.74	28.29	217.43	150	1.46
Ni	36.71	10.97	29.87	27829.21	10.08	79.87	35	27.05

CMA* - maximum permissible concentration (Order 161/2006, WFD, 2000)

The general profile of mean metal concentration in sediments for the study area was Zn>Cr>Cu>Ni>Pb>Cd. For sediment quality assessment, results are compared to the maximum permissible concentrations mentioned in Order 161/2006, WFD, 2000.

In the study area, the ranges of heavy metals in sediments were as follows: 0.02-1.33 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; 28.29-217.43 mg/kg for Zn; 10.08-79.87 mg/kg for Ni. Similar range of elements' concentrations in the Danube sediment samples was reported in the results obtained in the third Joint Danube Survey Expedition 3 (Joint Danube Survey 3 Final Report [13].

Regarding nickel, there were most overruns (27.05%) of the maximum permissible concentration followed by copper (14.65%), zinc (1.46%) and cadmium (0.27%). Metals such as: chromium and lead were analyzed with the lowest concentrations in sediment samples, their value being between 1.85 and 93.03 mg/kg for chromium and 0.42-83.40 for lead, values which didn't exceed the maximum permissible limit.

The differences between the two banks of the Danube (right bank – RB; left bank - LB) for each metal were shown in Figure 2 for the mean, minimum and maximum values. For the mean value, the differences do not exceed 3.0%. For the minimum values of Cd, the left bank concentration found in the surface sediment exceeds with 50%

that of the right bank, but for Pb, they are equal. For the maximum values, the difference was found above 20.0%, only for Cd.

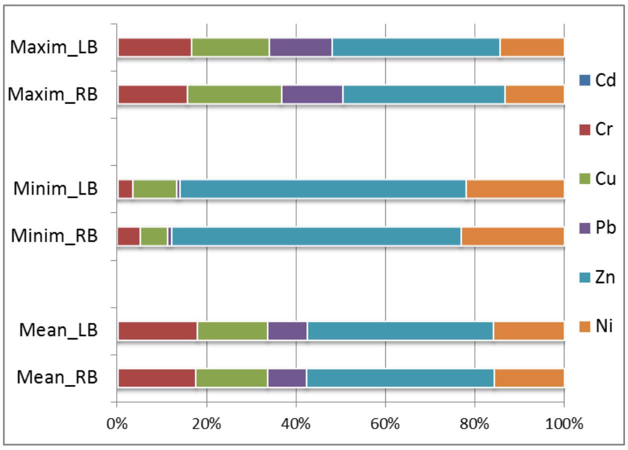

Fig.2. The mean, minimum and maximum values of heavy metals in sediments

The relationship between the concentrations of these six heavy metals was shown by performing correlation analysis (Table 3). The Pearson's *r* coefficient values obtained reveals that only seven pairs of heavy metals have a high correlation (Cd-Cu; Cd-Zn; Cu-Pb; Cu-Zn; Cu-Ni; Pb-Zn and Zn-Ni), four pairs of heavy metals have a medium correlation (Cd-Pb; Cd-Ni; Cr-Cu and Pb-Ni) and four pairs of heavy metals have a low correlation (Cd-Cr; Cr-Pb; Cr-Zn and Cr-Ni).
The strongest correlation was found between Cu-Zn with *r*=0.796 and the lower, between Cd-Cr with *r*=0.170. It was observed that between all variables there is a positive linear relationship according to the bivariate correlation coefficient obtained.

Tabel 3. Pearson correlation (*r* value) of the heavy metals' concentration in the Danube surface sediment

	Cd	Cr	Cu	Pb	Zn
Cr	0.170				
Cu	0.537	0.303			
Pb	0.313	0.180	0.559		
Zn	0.573	0.254	0.796	0.505	
Ni	0.384	0.284	0.589	0.407	0.642

3.2 Multivariate statistics

Multivariate statistics was used to assess the sources and distribution of heavy metals in sediments. The principal component analysis (PCA) is considered the basis of the multivariate data analysis and it was first formulated by Pearson in statistics, followed by Fisher and MacKenzie. PC was widely applied to reduce original variables of the contaminants and analyze their sources [14, 15]. However, the PCA estimates the correlation structure of the variables used [*15*.]. The number of the resulting principal component - PC (in this case, the number is 6) is always equal to the variables' number introduced (heavy metals' concentration value). The PCA's number must have the eigenvalues greater than 1, in order to be taken into account. Therefore, from the six PCs computed, only PC1 was selected to explain the variation in data and it is shown in Table 4. PC1 has variance 3.2869 (equal to the largest eigenvalue) and it accounts for 0.548 (54.8%) of the total variation in data. PC1 showed positive factor loadings for Cu, Zn and Ni. Probably, the non-point discharges have controlled the distribution of Cu, Zn and Ni in river sediment.

Table 4. Factor analysis of heavy metals in surface sediment of the Lower Danube

Variable	PC1	Eigenanalysis of the Covariance Matrix		
		Eigenvalue	*Proportion*	*Cumulative*
Cd	0.378	3,2869	0,548	0,548
Cr	0.230			
Cu	0.491			
Pb	0.374			
Zn	0.493			
Ni	0.423			

Cluster analysis

In the last decades, the clustering techniques have often been applied to a wide variety of research issues [10, 16, 17]. The complete linkage method was used to determine the distance in different clusters, of the two closest metals based on concentration values found in surface sediment. Five clusters result from the diagram as it can be seen in Figure 3. The highest similarity level was found between Cu-Zn with a ratio of 89.81 and the lowest between Cr and the rest five heavy metals with a ratio of 58.48.

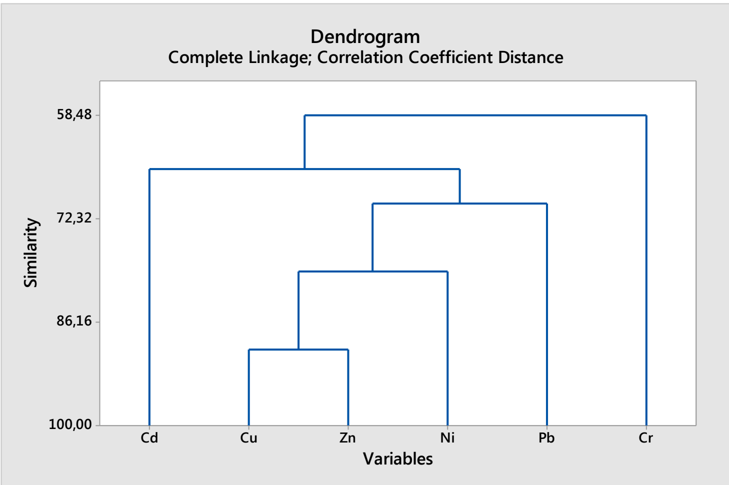

Fig.3. Tree diagram of the complete linkage method for the heavy metals' concentration in surface sediment of the Danube River

3.3 Spatial distribution of heavy metals in sediments

The GIS mapping technique was involved to create spatial distribution maps of total metal concentrations for six metals observed in the sediment samples from the Danube River. The software used for mapping and spatial analysis was ArcView 9.3.

Spatial distribution of heavy metals in sediments along the Danube River between Km 347 and Km 182 is shown in the following figures.

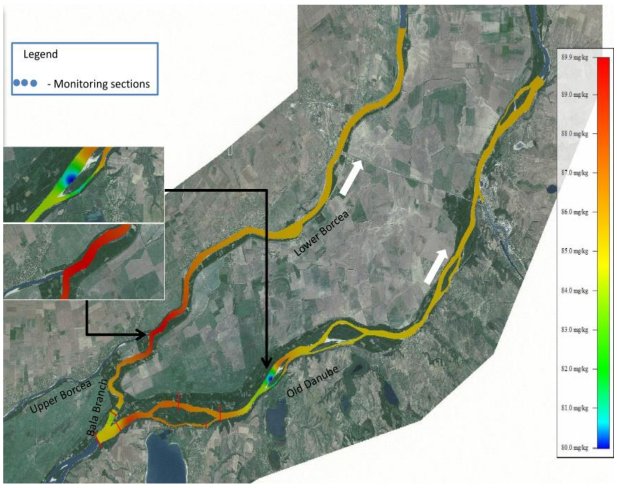

Fig.4. Spatial distribution of Cr in sediments [mg / kg] - Danube River km 347 -182

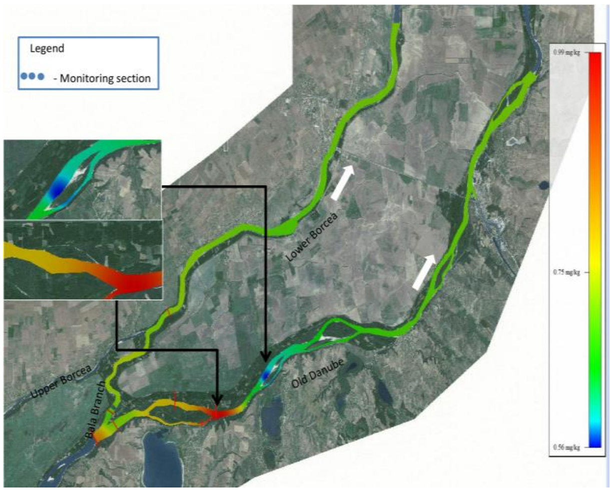

Fig.5. Spatial distribution of Cd in sediments [mg / kg] - Danube River km 347 -182

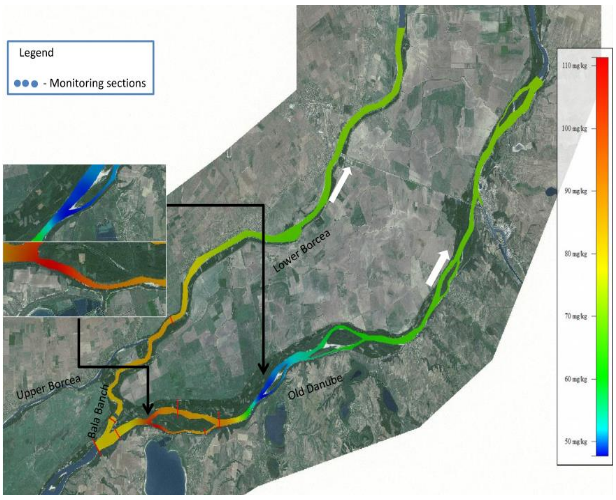

Fig.6. Spatial distribution of Cu in sediments [mg / kg]- Danube River km 347 -182

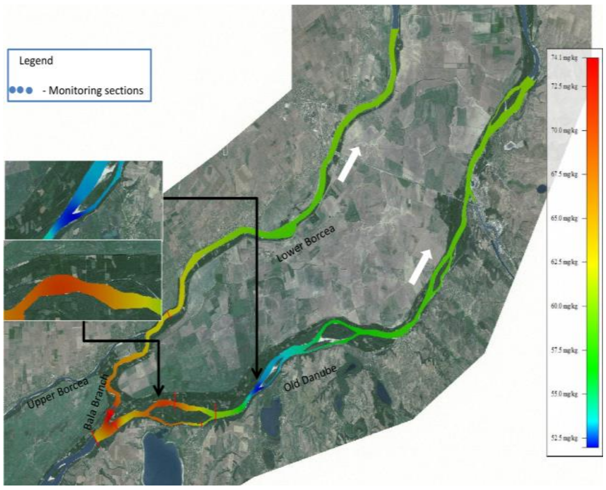

Fig.7. Spatial distribution of Ni in sediments [mg / kg]- Danube River km 347 -182

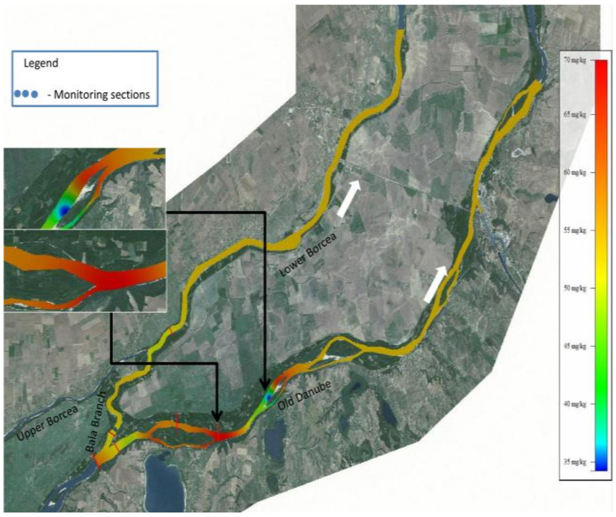

Fig.8. Spatial distribution of Pb in sediments [mg / kg]- Danube River km 347 -182

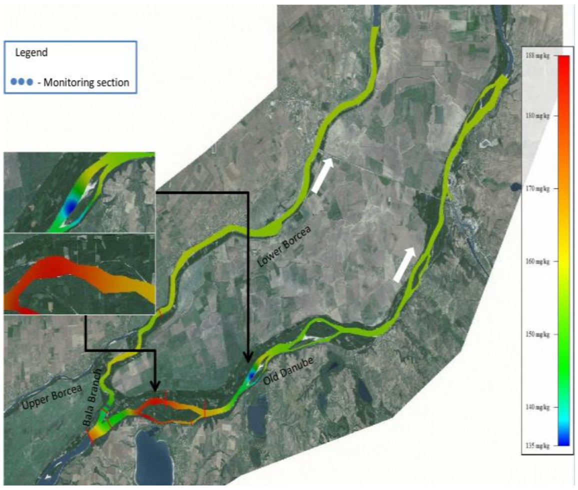

Fig.9. Spatial distribution of Zn in sediments [mg / kg]- Danube River km 347 -182

Determination of heavy metal levels and their spatial variations is essential for a better understanding of pollution sources and possible risks for the aquatic ecosystems.

4 Conclusion

This study represents the spatial distribution of heavy metal contamination of sediments in the Danube. The general profile of mean metal concentration in sediments for the study area was Zn>Cr>Cu>Ni>Pb>Cd, nickel recording the highest breaches of the maximum permissible concentration in 27.05% of sediment samples analyzed. Multivariate statistical analysis also revealed significant correlations between Cu and Zn, suggesting similar sources or similar geochemical processes that control the occurrence of these metals in sediments. It is important for heavy metals in sediments, especially Ni and Cu whose concentrations exceeded with over 10% the maximum allowable limits under the WFD, 2000, their monitoring to be carried out in the area studied. This study supports the monitoring and control of the Danube metal pollution. It will be a useful tool for authorities responsible for the sustainable management of natural resources.

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