Spatial distribution of heavy metal contamination and ecological risk assessment in water from the Danube River

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Abstract: Heavy metals are considered dangerous contaminants due to the possibility of bioaccumulation and toxic effects on environment and human health. Six metals exhibiting a greater relevance to the aquatic ecosystem in terms of toxic effects (Cd, Cr, Cu, Zn, Ni and Pb) were analyzed from water samples collected monthly from ten sites, during May 2012 - April 2015. The levels of heavy metals in water samples were measured using atomic absorption spectrophotometry (AAS). Results obtained emphasized that the average concentrations of the studied metals from water have decreased as follows: Zn>Cu>Ni>Cr>Pb>Cd. Spatial distribution maps of studied heavy metals were performed using ArcView 9.3 software. Quantifying the risk of aquatic ecosystem exposure to heavy metal pollution was carried out based on ecological hazard quotient (HQ). Exposure to heavy metals in water pose no risk factor.

Key-Words: heavy metals, Danube River, ecological risk assessment, toxicity reference values, spatial distribution, statistical analyses

1 Introduction

The Danube River is the second largest river in Europe after Volga, flowing along 2857 km from Germany's Black Forest to its delta from the Black Sea [1], from which, 1072 km on the Romanian territory, representing the border with Serbia, Bulgaria, Republic of Moldova and Ukraine [2].

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 [3]. High levels of trace metals in aquatic systems have resulted from a number of land use activities including agriculture, urbanization, impoundments, mining, transportation, fossil fuels and industrial activities [1,4,5,6,7,8,9].

The quality of any body of surface water is a function of either or both natural influences and human activities [7,10]. Contaminants in water may come from upstream aqueous sources including waste sites, other anthropogenic sources, and background, exchange of materials between the surface water and contaminated sediments, or exchange of contaminants between the biota and the water column [11,12,13,14]. Without human influences, water quality would be determined by the weathering of bedrock minerals, by the atmospheric processes of evapotranspiration and the deposition of dust and salt by wind, by the natural leaching of organic matter and nutrients from soil, by hydrological factors that lead to runoff, and by biological processes within the aquatic environment that can alter the physical and chemical composition of water [7].

The ecological risk assessment process has several features that contribute to effective environmental decision making [15,16].

Trace metals can be harmful to aquatic organisms causing adverse effects on human health and the aquatic ecosystem [9,12,17]. Effects include low growth rates, impaired reproduction, and sometimes death [7].

The negative effect that heavy metals have on human and aquatic ecosystem health has been investigated in numerous studies and therefore, the assessment of their distribution in water and sediment has become a pressing issue, being particularly important in the study of heavy metal bioaccumulation processes in aquatic ecosystems. [18,19,20]. Accumulation of metals is a risk to the ecosystem and their concentrations can provide

information on the historical pollution of the studied areas.
Copper, for example, is highly toxic in aquatic environments and has effects in fish, invertebrates, and amphibians; lead is carcinogenic and it can be bioconcentrated from water, but does not bioaccumulate and tends to decrease with increasing trophic levels in freshwater habitats; Observed effects of nickel (a carcinogen and mutagen) in aquatic environments include tissue damage, genotoxicity, and growth reduction [21,22].

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 water 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. Water samples were collected at 50cm depth below the surface using 1 litre polyethylene bottles with screw caps. 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 (latitude, longitude)	
		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
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
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
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
S5	Danube km 338	44°12'22.62"N 27°39'11.60"E	44°12'12.62"N 27°39'10.87"E
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
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

Sections	River km	Geographical coordinates (latitude, longitude)	
		Left bank	Right bank
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
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
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

Laboratory Analysis of heavy metals

Sampling, processing and preservation of evidence was done taking into account national and international standards. Water sample was digested with hydrochloric acid 37% (Merck) and nitric acid 65% (Merck) on a thermostatic hot plate. The remaining solution was transferred to a 100 ml volumetric flask, diluted to the mark and mixed thoroughly. The quantitative determination of metals was performed using an atomic absorption spectrophotometer (Solaar M5) with a mixture of air and acetylene for flame combustion.

Quality control and assurance

Quality control was ensured by using procedural blanks and standards. For these procedures, reagent blank was prepared for every 20 water 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.

Water quality assessments were performed considering 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, (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 water quality assessment. Six indicators of the basic statistics were computed in this paper, based on the total number of concentrations – 11400, meaning 1900 for each metal for water (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, Cu and Ni. On the other hand, the variation in the data, considering the mean value (CoefVar) indicates that Zn has the greatest spread in the data, followed by Cd and Cr. *Table 2* presents an overview of the heavy metals in water samples investigated.

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

Variable	Mean	StDev	CoefVar	Sum	Minimum	Maximum	Order 161/2006; WFD,2000 Limits [23,24]
Cr	0.93	0.70	75.48	1769.94	0.08	6.45	25
Cu	3.64	1.70	46.62	6916.25	0.37	13.48	20
Zn	16.14	19.95	123.58	30656.62	0.40	79.59	100
Pb	0.91	0.66	72.83	1719.84	0.04	4.73	5.0
Cd	0.05	0.04	84.16	93.44	0.02	0.35	0.5
Ni	2.16	1.02	47.10	4104.69	0.29	13.19	20

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

In the study area, the ranges of heavy metals in water were as follows: 0.02-0.35 µg/L for Cd; 0.08-6.45 µg/L for Cr; 0.37-13.48 µg/L for Cu; 0.04-4.73 µg/L for Pb; 0.40-79.59 µg/L for Zn; 0.29-13.19 µg/L for Ni. Similar range of elements' concentrations in the Danube water samples was reported in the results obtained in the third Joint Danube Survey Expedition 3 [25].

3.3. Ecological Risk Caracterization

The aquatic environment strongly influence the health of aquatic organisms, such as phytoplankton, zooplankton, invertebrates, fish [26]. Assessing the risk of Danube aquatic ecosystem exposure to heavy metal pollution was carried out based on ecological hazard quotient (HQ). The risk was characterized by comparing the values of heavy metal concentrations determined in water and sediments with Toxicity Reference Values (TRV) developed by the USEPA [27].
The hazard quotients (HQ) of heavy metals were calculated as follows:

$$HQ_{heavy\ metals} = \frac{C_{exposure}}{TVR_{heavy\ metals}}$$

where:

$HQ_{heavy\ metals}$ – ecological hazard quotient for heavy metals;
$C_{exposure}$ – is the environmental monitoring concentration of an individual heavy metal
$TVR_{heavy\ metals}$ – toxicity reference value of a heavy metals

An assessment of the ecological hazard quotient (HQ) >1,0 for a heavy metal is a potential risk to aquatic ecosystems and HQ<1,0 indicates that the risk is relatively low to the exposure to a certain heavy metal.

Values of the ecological hazard quotient (HQ) are presented in Table 3 for average values of heavy metal concentrations determined in water and sediment samples taken from the Danube.

Table 3. Values of the ecological hazard quotient $(HQ)_{heavy\ metals}$ and toxicity reference value $TVR_{heavy\ metals}$ in water and surface sediment of the Lower Danube

Site	$HQ_{heavy\ metals}$					
	HQ_{Cr}	HQ_{Cu}	HQ_{Zn}	HQ_{Pb}	HQ_{Cd}	HQ_{Ni}
S1	0.075	0.398	0.160	0.344	0.026	0.037
S2	0.074	0.367	0.151	0.335	0.024	0.036
S3	0.069	0.358	0.152	0.320	0.024	0.034
S4	0.089	0.441	0.150	0.421	0.023	0.044
S5	0.077	0.384	0.167	0.338	0.025	0.035
S6	0.071	0.389	0.164	0.338	0.025	0.038
S7	0.074	0.386	0.164	0.356	0.025	0.036
S8	0.079	0.358	0.155	0.336	0.028	0.042
S9	0.085	0.374	0.157	0.349	0.026	0.044
S10	0.077	0.366	0.158	0.337	0.027	0.044
$TVR_{heavy\ metals}$	2.2	9.0	118	2.5	2.2	52

W=HQ $_{heavy\ metals}$ in water (μg/L); $HQ_{heavy\ metals}$ = ecological hazard quotient for heavy metals; $TVR_{heavy\ metals}$ = toxicity reference value of heavy metals [27].

From the results shown in Table 3 one can observe that heavy metals from water pose no environmental risk to the aquatic ecosystem, the ecological hazard quotient recording values of HQ<1,0.

3.4 Spatial distribution of heavy metals in water

The spatial distribution of metal concentrations in water is important in order to understand the accumulation and geochemical distribution mechanisms of heavy metals in aquatic systems and to provide basic information for evaluating environmental health risks [28,29].
The GIS mapping technique was involved to create spatial distribution maps of total metal concentrations for six metals observed in the water samples from the Danube River. The software used for mapping and spatial analysis was ArcView 9.3.
Spatial distribution of heavy metals in water along the Danube River between Km 347 and Km 182 is shown in the following figures.

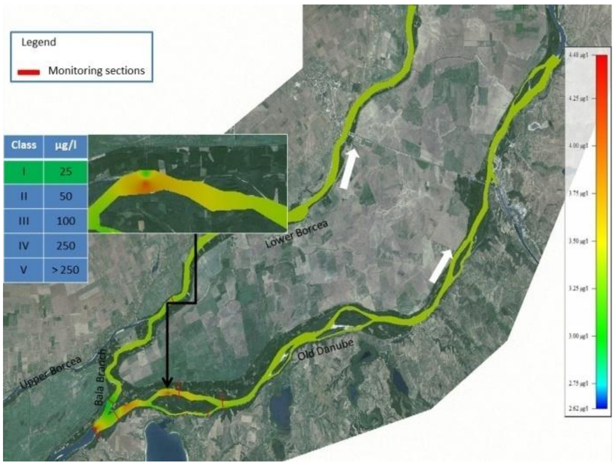

Fig.2. Spatial distribution of Cr in water [µg/L] - Danube River km 347 -182

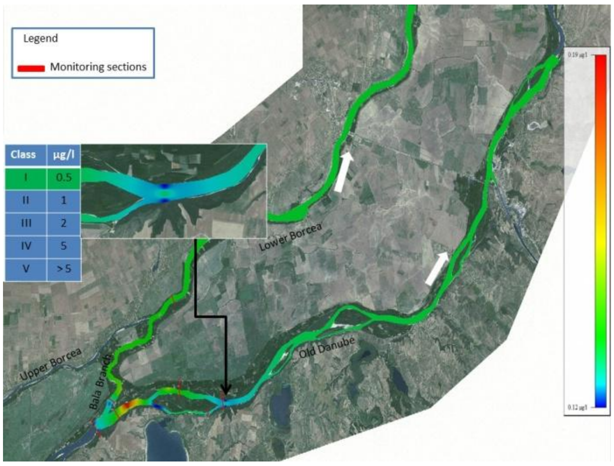

Fig.3. Spatial distribution of Cd in water [µg/L] - Danube River km 347 -182

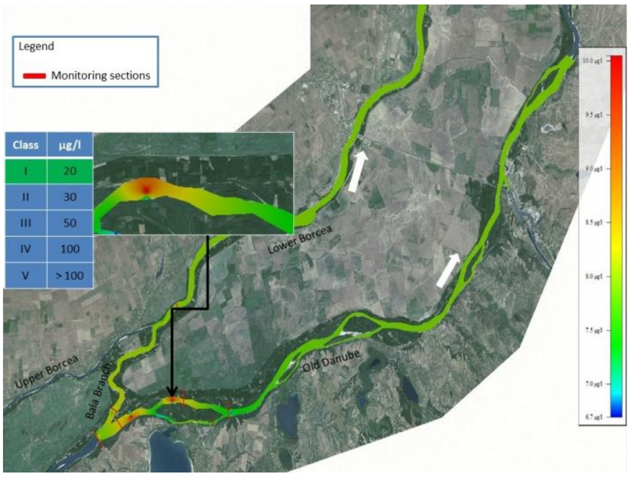

Fig.4. Spatial distribution of Cu in water [µg/L]- Danube River km 347 -182

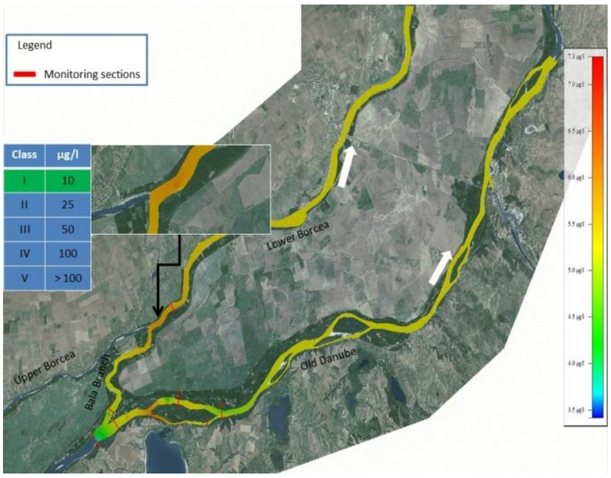

Fig.5. Spatial distribution of Ni in water [µg/L]- Danube River km 347 -182

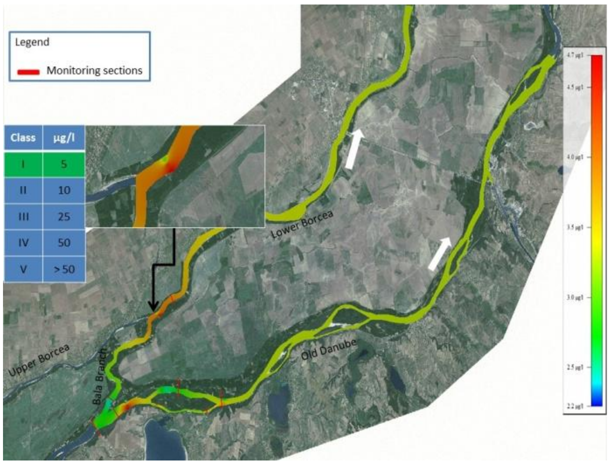

Fig.6. Spatial distribution of Pb in water [µg/L]- Danube River km 347 -182

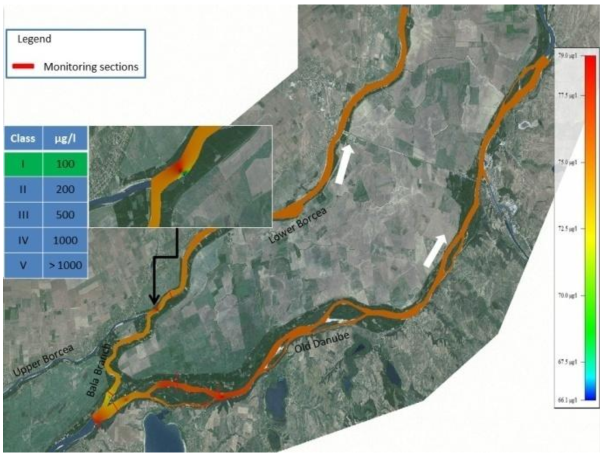

Fig.7. Spatial distribution of Zn in water [µg/L]- Danube River km 347 -182

Representation of heavy metal distribution maps determined from Danube water samples emphasizes the maximum values recorded for heavy metal concentrations, Zn respectively, in S1, S4, S7, S18 and S19 sections, Cu in S7, Cd in S1 and S20, Pb in S3, S4 and S7, Ni in S4 and Cr in S19 in water samples. 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.

5 Conclusion

This study represents the spatial distribution of heavy metal contamination of water in the Danube River. The profile of mean metal concentration in water for the study area was Zn>Cu>Ni>Cr>Pb>Cd; all the values recorded for these metals are within the limits allowed by aquatic environment protection law. Quantifying the exposure risk of aquatic ecosystem to heavy metal pollution based on ecological hazard quotient (HQ) emphasizes that exposure to heavy metals in water does not pose a risk to aquatic organisms.

This study supports the monitoring and control of the Danube metal pollution. Monitoring the exposure of aquatic ecosystems to heavy metal pollution and developing the GIS maps for their distribution will be a useful tool for authorities which are responsible for the sustainable management of natural resources in the process of evaluating the condition of aquatic environment.

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