

Danube River Basin Waters on Romanian Territory: Chemical Status Assessment Based on Priority Substances Data Analysis

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Framework Directive (2000/60/EC) (WFD) sets out a series of legal measures at European level against surface waters chemical pollution. The EU-list, annex of the WFD, contains those substances that present a significant risk to human health via aquatic environment, known as priority substances. In the last ten years, the Danube water quality has improved significantly. Instead, heavy metals concentrations in the tributaries waters sometimes were found to be rather highest and the chemical status is not in-line with the WFD requirements. Therefore, the Danube River Basin (DRB) waters quality showed a significant variability in terms of priority substances due to the diverse human activities, especially mining activities. This research paper aims to assess the chemical status of the DRB waters located on Romania territory regarding six heavy metals: Pb, Cd, Ni, Cr, Cu, and Zn by analysing water and sediment samples collected from different areas (south-west and north-west of Romania). Based on the obtained results by evaluating the quality elements, the water chemical status of DRB achieved a good chemical status for 74% of water samples and 55% of sediment samples. Also, the basic statistic and multivariate analysis were used to explore the relationship between the concentration values obtained for priority substances to underlying the water quality assessment.

Keywords: Water Framework Directive; Danube River Basin waters; priority substances; heavy metals

The human activities play a vital role in order to protect the aquatic environment, first of all, by respecting the water politics, often known as hydropolitics. Thereby, compliance with these policies is directly related to human development [1, 2]. The most important instrument of European environmental legislation that focuses on understanding and ensuring sustainable water governance still remains the Water Framework Directive 60/2000/CE (WFD) until its upcoming review in 2019. [3-7]. The WFD specifies the establishment of the ecological status or/and chemical status of the surface waters category that not meet the environmental objectives. The chemical status is based on the water and sediment quality standards of certain indicators that have been identified as of significant risk to or via the aquatic environment [8].

Industrial activities, especially the mining, have become a global concern due to the local and regional degradation of life quality by polluting the water, degrading the fertile land and lowering the air quality. Issues as the polymetallic tailing dumps and mining wastewater from the mining processes, can lead to depletion of natural resources and therefore require special attention in the context of sustainable management [9-12]. It is known that the Romanian mining industry has a long tradition in this field and the environmental issues still exists [13]. Actually, various alternatives to transform industrial wastes in secondary raw materials are studied in the context of the issue of natural resource depletion [14].

The surface waters studied in this paper belong to the Danube River Basin (DRB), that is the second largest and the most important basin in Europe [15]. The Romanian Danube River section is the general wastewater collector from the all countries it crosses until it flows into the Black Sea. [16]. Cadmium and lead were considered as the most serious inorganic microcontaminants in the Danube River Basin. The pollution of the Danube River and its major

tributaries by nickel and zinc was found to be rather low, excepting in the lower Danube section. For zinc the noncompliance with the target value in the lower Danube was not very frequent, the limit was exceeded by 20 - 100%. Nickel concentrations in the whole Danube River did not go over the target limit during 1996 -2000 [17]. In this context and because the Danube is an important transportation corridor for Europe, this paper deals with chemical status assessment of the DRB waters located on Romanian territory in terms of priority substances-heavy metals (HM).

Experimental part

To obtain the data, the following activities were pursued: the selection of the surface waters that are part of the DRB located on Romanian territory; collection, preservation and handling of water and sediment samples; laboratory analysis on collected water and sediment samples; the selection of the elements and quality standards of national legislation in force for establishing the chemical status of monitored surface water; the selection of the statistical methods which have been used for water quality assessment.

Studied area

The studied surface waters belonging to Somes-Tisa and Banat catchment areas on the Northwest and Southwest regions of Romania. Regarding the waters of Somes-Tisa catchment area, were studied: Somes, Tur, Tur, Batarci, Stramba, Socea, Tarna Mare from Satu Mare County and Lapus from Maramures County. The Bo'neag waters from Caras-Severin County were studied, which belong to the Banat catchment area and is the direct affluent of the Danube, having the confluence with the river in the vicinity of the Moldova Veche settlement. Also, was taken into consideration the Lower Danube water near

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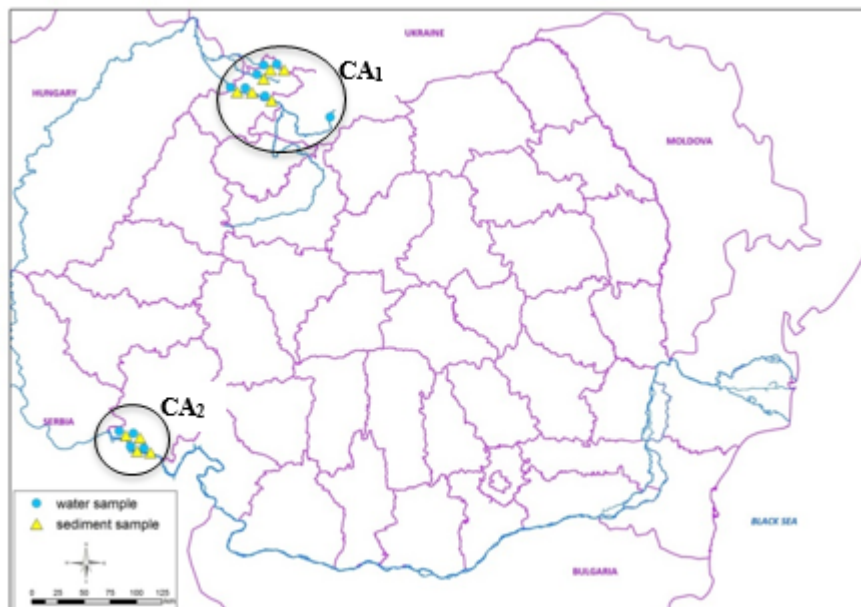


Fig. 1. Identification of DRB catchment areas on Romanian territory to which monitored surface waters belong

the left bank between Coronini and Pojejena, which delimits the southern extremity of the Banat catchment area. The two selected areas were noted CA₁ and CA₂ and can be viewed in figure1.

Sample collection, preservation and handling

The sampling it is an important procedure due to the systematic errors that can appear and tend to influence the measurement. In order to avoid any difficulties on the fieldwork and to carry out in good conditions the water and sediment sampling campaigns, as well as their analysis in optimal conditions, the selected areas were thoroughly studied in advance, mainly taking into account the access to each surface water at the sampling point, water depth and velocity, also the weather conditions. A total of 40 water samples and 20 sediment samples from the two studied areas (CA₁; CA₂) were taken during 2017.

In-situ measurements were performed for temperature, turbidity, pH, flow, depth, conductivity, etc. using a multiparameter sensor Eureka Manta 2 (fig. 2). The sample and equipment transport were carried out with the INCDPM AutoLab - *National Institute for Research and Development in Environmental Protection* mobile laboratory - used to monitor water and soil quality indicators (fig. 2). Prior to field dispatch, the multiparameter sensor was calibrated and the sampling recipients were checked in order to meet the sampling requirements specified in SR EN ISO 5667-6:2017 [18] and SR ISO 5667-12:2001 [19] standards. To identify correctly and easily the samples, the recipient was labeled and dated. Each recipient perfectly clean, made of polyethylene with a screw / cap stopper and hermetically sealed was used to ensure an optimum transport. Once in the laboratory, all samples were subjected to the procedures for determining the HM indicators.

Monitored parameter and laboratory analytical method

Six priority substances were selected for this study: Pb, Cd, Ni, Cr, Cu, and Zn. The method used for the HM determination was flame atomic absorption spectrometry using a high-resolution continuum source AAS spectrometer (contrAA 700, Analytik Jena, Germany).

The water samples with low organic content and low turbidity were acidified using concentrated HNO₃. In the case of samples with high organic content or high turbidity, acid digestion was performed using concentrated HNO₃ in an open system. 100 mL of water samples and 10 mL HNO₃ were introduced in a glass beaker and heated on a hot plate until the complete digestion of the sample avoiding complete evaporation. After digestion, the samples were filtered and brought to 100 mL with HNO₃ solution ~0.5% (v/v).

The sediment samples were dried at ambient temperature, milled and sieved through a 63 µm-sieve (fig. 3). 0.5 g of sediment were digested with aqua regia (3 mL concentrated HNO₃ and 9 mL concentrated HCl) on a sand bath. After the digestion, the sediment samples were filtered and brought to 100 mL with HNO₃ solution ~0.5% (v/v).

Both water and sediment samples were analysed as prepared or after proper dilution (if needed).

The detection limits were 0.0080 mg/L (1.6 mg/kg for sediment) for Pb, 0.0010 mg/L (0.2 mg/kg for sediment) for Cd, 0.0040 mg/L (0.8 mg/kg for sediment) for Ni, 0.0100 mg/L (2 mg/kg for sediment) for Cr, 0.0080 mg/L (1.6 mg/kg) for Cu, and 0.0020 mg/L (0.4 mg/kg for sediment) for Zn.

Quality control. A representative spike concentration was selected for each HM to be measured. Using stock standards, a quality control check sample were prepared.



Fig. 2. INCDPM AutoLab. In-situ measurements and the sediment collection procedure from rivers



Fig. 3. Different types of sediment sample prepared for analysis (fine and coarse fractions)

Variable assessment

In this paper, the legislative reference for establishing the chemical status of monitored surface water is the Order no. 161/2006 [20]. This Ministerial Order (MO 161/2006) is the Romanian normative act that partial ensures transposition/implementation of WFD [20]. To assess the chemical status, the MO 161/2006 provides two states: *good chemical status* - compliance with the quality standards and *bad chemical status* - overcoming the quality standards [20]. For the considered water quality variables - HM, in Table 1 are presented the standards, both for water and sediment.

The use of statistics in environmental assessments has become an increasingly common practice in the research studies to draw valid conclusions [21]. The quantitative analysis of the obtained data was done using statistical methods. Thus, for the basic features description, basic statistics were performed, which provided simple data on each type of sample under analysis, i.e. the values of water and sediment concentrations. Pearson's correlation analysis was used to dataset obtained in order to certify the association among HM. Statistical data set analyses were performed with Minitab 17 software.

Results and discussions

Chemical status

According to the information provided by the literature, the ecological status, the ecological potential and the chemical status of DRB rivers in 2009 from a total of 681 assessed water bodies, a percent of 28% achieved a good ecological or ecological potential, and 64% of the water bodies achieved a good chemical status [22]. In this research study, for assessing the water quality status, the HM concentration levels obtained were compared to the standard levels. Table 3 presents the good chemical status achieved by the water bodies studied, in percent, based on the priority substances determination from water and sediment samples collected. Also, a visual identification of the sample points which achieved a good chemical status is showed in figure 4 and figure 5.

The analysis shows that, in the two studied areas CA1 and CA2, the pollution from industrial activities can pose a significant health threat caused by residential and agricultural uses, especially in areas where high parameters value were found. The copper levels in all the water samples were above the natural and maximum permissible concentration. Zinc concentration level for water is not standardized, but has been mapped by creating

Element	Unit		Quality Standard	
	Water	Sediment	Water	Sediment*
Cadmium	µg/L	mg/kg	1.0	0.8
Chromium	µg/L	mg/kg	2.5	100
Copper	µg/L	mg/kg	1.3	40
Nickel	µg/L	mg/kg	2.1	35
Lead	µg/L	mg/kg	1.7	85
Zinc	µg/L	mg/kg	-	150

*for fraction < 63 µm

Table 1
LEGAL CRITERIA FOR CONTROLLING THE SURFACE
WATER POLLUTION IN THE ROMANIA TERRITORY FROM
A VARIETY OF SOURCES [20]

Table 2
INTERPRETATION CRITERIA OF *r*'S AND *p*'S VALUES [5]

Value	Interpretation
<i>r</i>	
0.90 to 1.00 (−0.90 to −1.00)	Very high positive/negative correlation – VHP/NC
0.70 to 0.90 (−0.70 to −0.90)	High positive/negative correlation - HP/NC
0.50 to 0.70 (−0.50 to −0.70)	Moderate positive/negative correlation - MP/NC
0.30 to 0.50 (−0.30 to −0.50)	Low positive/negative correlation - LP/NC
0.00 to 0.30 (0.00 to −0.30)	Negligible correlation - NgC
<i>p</i> -value	
= 0.05 or < 0.05	Statistical significance correlation (95% confidence level)
= 0.01 or = (0.01- 0.001)	Highly significant correlation (99% confidence level)
= (0.001- 0.000)	Very high significance correlation (99% confidence level)
> 0.05	Insignificant correlation

Table 3
COMPARISON OF RESULTS OBTAINED FOR
WATER SAMPLES WITH THE LEGAL CRITERIA

Element	Percent (%)	
	Water	Sediment
Cadmium	88.46	20.00
Chromium	100.00	95.00
Copper	0.00	55.00
Nickel	80.77	85.00
Lead	73.08	85.00
Zinc	-	20.00

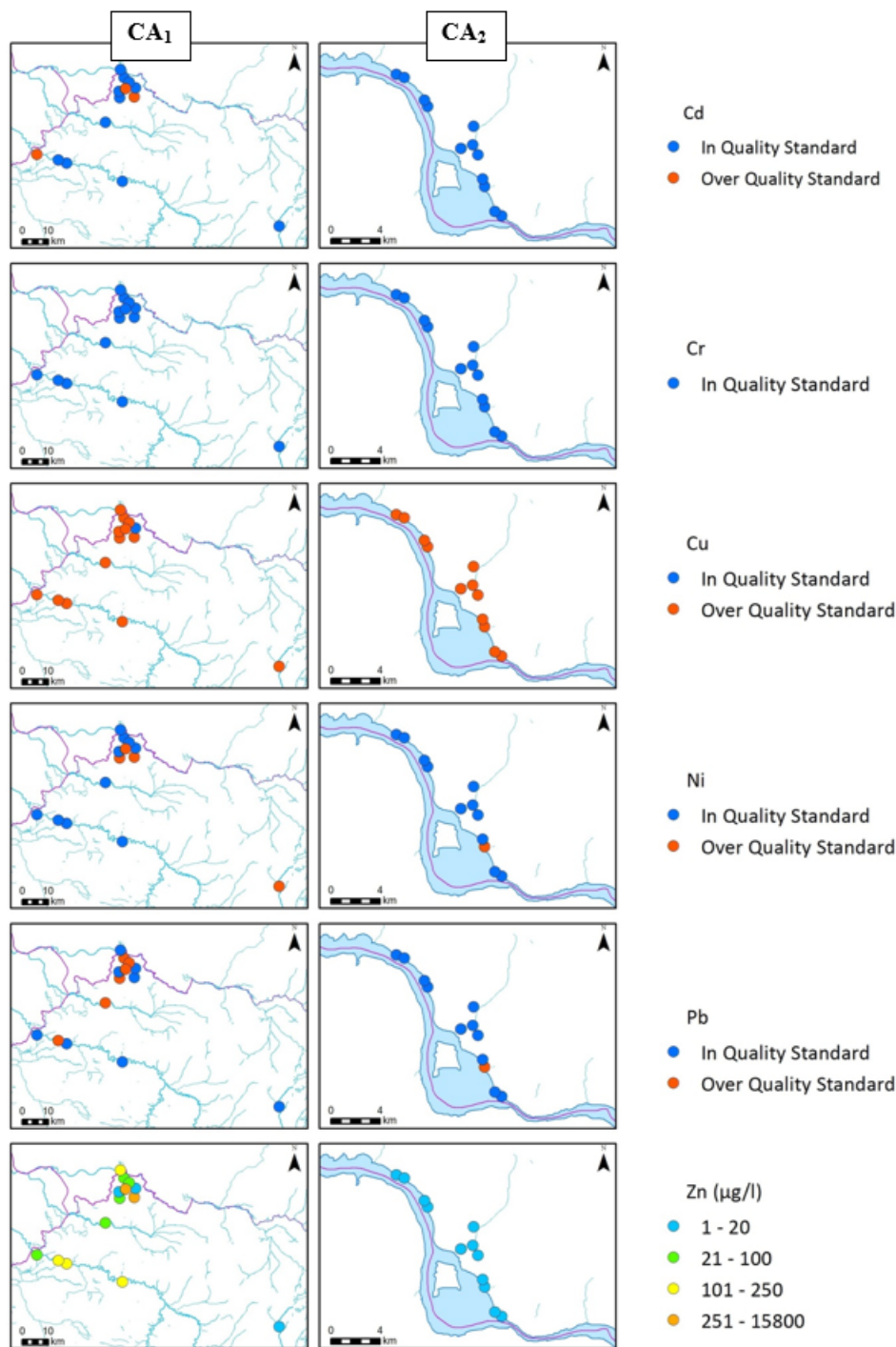


Fig. 4. Concentration levels obtained compared to legal criteria for water

intervals marked with different colours, as it is illustrated in Figure 4. Hence, the major difference between the first interval (1-20 µg/L Zn) and the last (251-15800 µg/L Zn) it is obvious. In the sediment samples, cadmium and zinc have the most concentration values above maximum quality standard.

Water quality statistical analysis

By displaying the Descriptive Statistics a summary of information for available data set was provided and are shown in Table 4. Were calculated the measures of central tendency (mean and median) to describe the whole set of the obtained data with a single value and, also, the measures of variability (variance, standard deviation, coefficient of variation) to observe if the values tend to cluster together or if they tend to be spread out. Analysing the minimum and maximum of each indicator, there was observed a very large difference between the two values

for both water samples and sediment samples. This indicates the presence of point sources of heavy metal pollution and that samples have been taken from different points. Based on the mean concentrations, the HM in the studied surface waters exhibited the following descending order: Zn > Cu > Ni > Pb > Cd > Cr – in the water samples; Zn > Cu > Pb > Cr > Ni > Cd – in the sediment samples. In another paper, was found that the general profile of the mean metals concentrations in sediments of the Danube River waters (between Km 347 and Km 182) as beeing Zn>Cr>Cu>Ni>Pb>Cd [23].

The linear relationship that exists between the HM variables in the collected samples, based on the concentration values, was checked with the Pearson product-moment correlation coefficient. Thereby, it was displayed the r (Pearson's correlation coefficient) and p -value (the value that indicates a significant correlation between the elements [5]) forming the Pearson's matrix showed in Table 5. Based on samples concentration values,

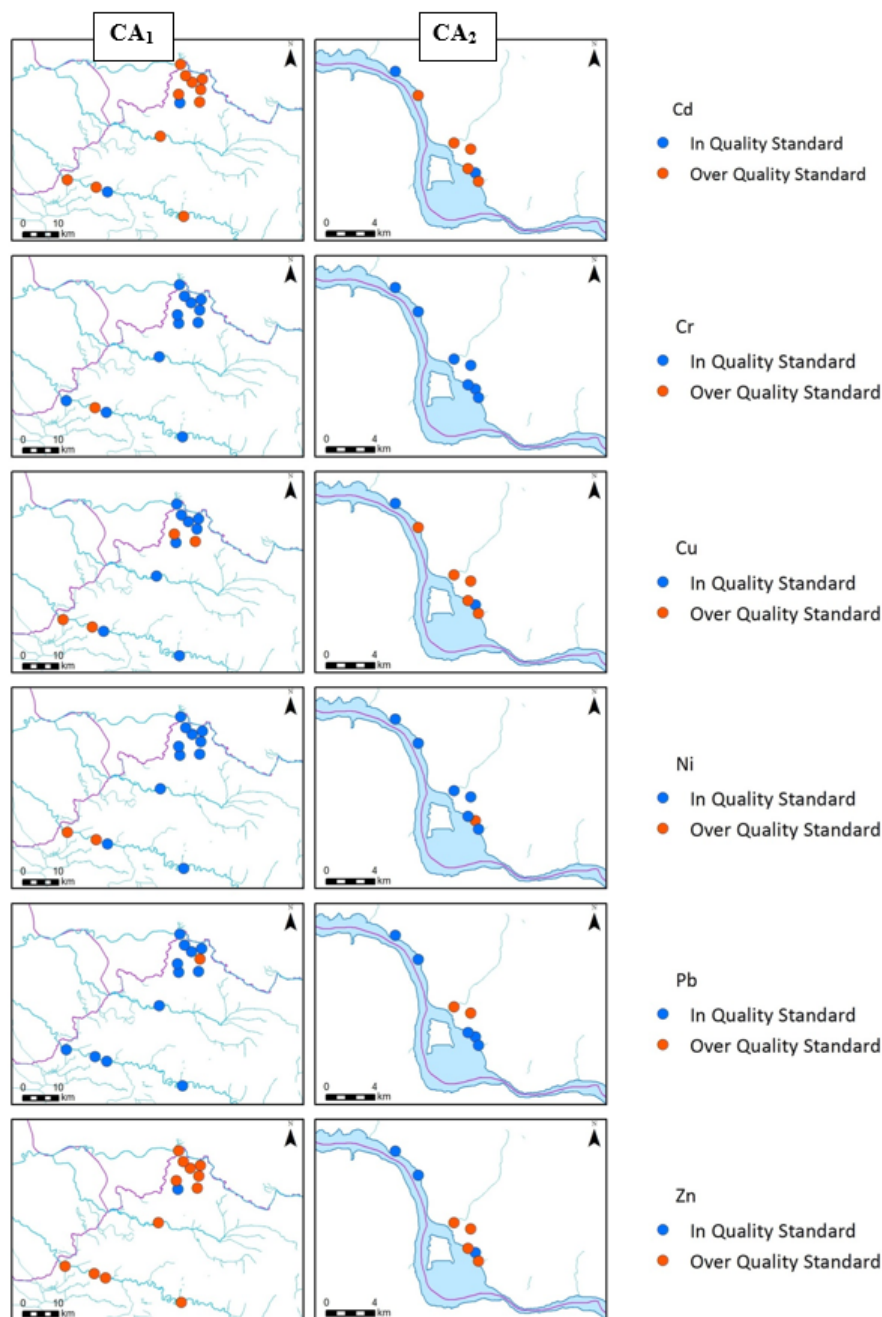


Fig. 5. Concentration levels obtained compared to legal criteria for sediment

Table 4
QUANTITATIVE DESCRIPTIONS OF THE WATER ($\mu\text{g/L}$) AND SEDIMENT (mg/kg) CONCENTRATION VALUES

Variable	Unit	Total Count	Mean	StDev	Variance	CoefVar	Min→Max	Median
<i>Cd</i>	$\mu\text{g/L}$	26	2.1	7.8	51.4	342.1	0.001 → 32.7	0.04
	mg/kg	20	1.6	0.8	0.7	51.9	0.3 → 2.9	1.4
<i>Cr</i>	$\mu\text{g/L}$	26	0.5	0.6	0.3	120.6	0.01 → 2.0	0.2
	mg/kg	20	49.8	104.5	10911.1	209.6	2.0 → 488.6	27.8
<i>Cu</i>	$\mu\text{g/L}$	26	16.3	35.6	1266.4	219.0	1.4 → 147.8	4.0
	mg/kg	20	191.7	392.3	153909.0	204.6	18.8 → 1570.2	37.7
<i>Ni</i>	$\mu\text{g/L}$	26	5.2	14.9	222.4	285.9	0.004 → 69.9	0.9
	mg/kg	20	23.9	14.5	210.4	60.7	4.0 → 61.9	23.7
<i>Pb</i>	$\mu\text{g/L}$	26	2.4	3.9	15.1	162.4	0.008 → 15.5	1.0
	mg/kg	20	116.1	286.1	81848.3	246.5	13.5 → 1315.0	51.2
<i>Zn</i>	$\mu\text{g/L}$	26	1249.0	4261.0	18156657.0	341.2	1.0 → 15772.0	9.0
	mg/kg	20	365.7	296.8	88106.4	81.2	56.1 → 1049.7	245.8

Table 5
PEARSON'S MATRIX FOR WATER AND SEDIMENT CONCENTRATION VALUES

<i>water</i> E*→ ↓	<i>Cd</i>	<i>Pb</i>	<i>Ni</i>	<i>Zn</i>	<i>Cr</i>	Coeff**	<i>Cd</i>	<i>Cu</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>	<i>sediment</i> ←E* ↓
<i>Pb</i>	0.585					<i>r</i>	0.154					<i>Cu</i>
	0.002					<i>p-value</i>	0.516					
<i>Ni</i>	0.809	0.284				<i>r</i>	0.030	0.008				<i>Ni</i>
	0.000	0.160				<i>p-value</i>	0.900	0.974				
<i>Zn</i>	0.956	0.459	0.944			<i>r</i>	-0.068	0.015	-0.329			<i>Pb</i>
	0.000	0.018	0.000			<i>p-value</i>	0.777	0.949	0.157			
<i>Cr</i>	-0.213	-0.202	-0.152	-0.206		<i>r</i>	0.828	0.013	-0.084	-0.124		<i>Zn</i>
	0.296	0.323	0.460	0.313		<i>p-value</i>	0.000	0.958	0.724	0.604		
<i>Cu</i>	0.779	0.663	0.593	0.706	-0.249	<i>r</i>	0.280	-0.065	0.720	-0.102	-0.072	<i>Cr</i>
	0.000	0.000	0.001	0.000	0.220	<i>p-value</i>	0.232	0.785	0.000	0.668	0.764	

*Element. ** Coefficient.

E*→ ↓	<i>Cd</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>	<i>Cr</i>
<i>Cu</i>	<i>HPC / NgC</i>	<i>MPC / NgC</i>	<i>MPC / NgC</i>	<i>HPC / NgC</i>	<i>NgC / NgC</i>
<i>Ni</i>	<i>HPC / NgC</i>				
<i>Pb</i>	<i>MPC / NgC</i>	<i>NgC / LNC</i>			
<i>Zn</i>	<i>VHPC / HPC</i>	<i>VHPC / NgC</i>	<i>LPC / NgC</i>		
<i>Cr</i>	<i>NgC / NgC</i>	<i>NgC / HPC</i>	<i>NgC / NgC</i>	<i>NgC / NgC</i>	

*Element.

Table 6
PEARSON'S CORRELATION COEFFICIENT
INTERPRETATION FOR WATER/SEDIMENT
CONCENTRATION VALUES

the resulting Pearson matrix shows a strongest statistically significant correlation between seven pairs of HM for water and two pairs of HM for sediment. It has been observed that the pair Cd-Zn reacts in the same way both for water and sediment and having a very high significance correlation. The negative correlation between the some pairs of HM shows that the amounts of the two HM in one pair vary in opposite directions (in surface water matrix, the amount of one HM increases, and for the other HM decreases). After the computation Pearson matrix, the *r* coefficient was interpreted according to Table 2 and it is shown in Table 6. The HM that presents a statistical significant correlation with each other in the studied surface waters, suggested a common pollution source such as mining activities. It is well known the fact that the deposition of fine grained materials and organic matter physically controls the abundance and distribution of metals in sediments at distance from the source [21].

Conclusions

The analysis performed highlights the importance of this type of research study. The information obtained revealed that the industrial activities (mining) causes ecosystem disturbance on long term. These disturbances leads to an evitable fall out of industrialization and today's civilization, but mining still remains one of the main global economic activities.

Also, the study proves the utility of statistical methods application and above all the analysis and interpretation of the complex water quality data sets. The methods used have made it possible to identify the polluted areas and the distribution of pollutants along the studied water bodies for a better understanding into the temporal and spatial

changes in water quality. On the basis of actual information on chemical status, may be improved the local governance for better environmental management. Hence, may be established new targets that can be included in the water analysis and planning tool (Management Plan), developed at the level of the entire Danube River Basin and which respects the Water Framework Directive requirements.

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