Statistical Analysis of Heavy Metals Concentration in Water and Sediments in the Lower Part of the Danube River – Romanian Section

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The Danube River is a transboundary water body traversing many populated areas along its course and therefore is highly vulnerable to heavy metal pollution due to urbanization and industrialization. In this study, sixteen sites were sampled along the Danube River between Km 347 and Km 182 during September 2012 – August 2014 for assessment of heavy metal pollution status. Water and bottom sediment samples were collected monthly from left and right bank of the Danube and were determined the temperature, the pH and four heavy metals: Cu, Cr, Ni and Zn, by AAS technique. Total metals concentrations of water ranged between 0.05-13.63 µg/L for Cr, 0.41-49.84 µg/L for Cu, 0.02-32.0 µg/L for Ni and 0.20-93.50 µg/L for Zn. Meanwhile, for sediment, it ranged between 23.53-46.64 mg/kg for Cr, 21.02-42.35 mg/kg for Cu, 26.23-38.47 mg/kg for Ni and 78.66-106.22 mg/kg for Zn. These data revealed that metal concentration levels in the sediments surpassed corresponding levels in flowing water. To complete the monitoring process, statistical analyses were performed using software package Minitab 16 and JMP 9 (SAS). Pearson correlation coefficient revealed a strong relationship between Cr-Ni (0.881), Cu-Ni (0.879) and Cr-Cu (0.829) for water samples and Cu-Zn (0.772) for sediments.

Keywords: *Danube River, heavy metals, sediments, statistical analysis*

The Danube River is the longest river in the European Union and Europe's second longest river after Volga [1] and its lower part is on Romanian territory [2]. The Danube River that crosses Romania at its southern part flows into the Black sea. This important river, serves as a resource for various water uses and therefore, environmental quality of the Danube River basin is under great pressure due to a diverse range of human activities [3-6].

Heavy metals are known to constitute highly persistent environmental pollutants [7-11] and non-biodegradable and they can be bio-accumulated through the biologic chains: soil–plant–food and seawater–marine organism–food [12]. All heavy metals present in surface waters occur in the form of colloids, particulates and dissolved phases, although dissolved concentrations are generally low compared to their levels in the underlying associated sediments. Also, determining the total content of heavy metals in the sediment may be useful for the characterization of pollution intensity [13-15]. In this context, the contamination of Danube River sediments with heavy metals is a very old problem; earlier studies have revealed some hot-spots along the Danube [3, 16].

The aim of this work was to show that statistical analysis can provide a scientific basis for monitoring the heavy metals evolution in time and space in water and sediment and for controlling a non-point source of contamination produced by human activities. This was done by monitoring the levels of total heavy metals (Cu, Cr, Ni and Zn) in the water and sediment samples taken along the lower part of the Danube River.

Experimental part

Sampling and pretreatment

Sixteen sites were sampled along the Danube River between Km 347 and Km 182 during September 2012 – August 2014 (fig. 1). The sampling sections location are shown in table 1 and sections were grouped in three sectors: upstream (S1-S12), middle (S13-S14) and downstream (S15-S16). Water and sediment samples were collected monthly from sections S1, S2, S3, S4, S15, S16 and quarterly from S5 to S14. Samples were collected from both left and right bank of the Danube and were analysed for four trace metals: Ni, Cu, Cr and Zn. The pH and temperature were measured in the field. Water samples were collected at the depth of 50cm below the surface using 1L polyethylene bottles with screw caps. The samples of the first 5-10cm of the river deposits were collected in polythene bags using antirust scoop. All samples were kept in cooling boxes, at 4°C, during transportation, and the analyses were performed immediately after receiving the samples in the laboratory.

The collected sediment samples were air-dried, large particles were hand-picked and the rest were ground to powdery form. The fraction <63 mm was used for the analysis of the metals.

Laboratory analysis of heavy metals

Water samples

The collected water samples were digested with 1:1 (v/v) HNO_3:$HClO_4$ (nitric acid 65% and hydrochloric acid 37%, both Merck) until was ascertained a complete digestion through a gentle boiling on a thermostated hot plate. The digested samples were cooled down, quantitatively transferred to a 100 mL volumetric flask and made up to the mark with distilled water and mixed thoroughly. A blank determination was carried out also.

The levels of Cu, Cr, Ni and Zn in the processed samples were assessed by flame atomic absorption spectrophotometry using Solaar M5 instrument from Thermo manufacturer.

Sediment samples

The previously dried sediment was digested using aqua-regia (1:3 v/v HNO3: HCl). The acidified mixture was heated

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

Table 1
GEOGRAPHICAL COORDINATES OF SAMPLING SECTIONS ESTABLISHED BY GPS

Sections	*River km*	*Geographical coordinates (Stereo 70 projection)*	
		Left bank	*Right bank*
S1	347	X: 704192.42; Y: 301573.53	X: 704626.36; Y: 301023.59
S2	344+800	X: 706207; Y: 302653	X: 706541; Y: 302123
S3	338	X: 712137; Y: 304180	X: 712095; Y: 303961
S4	334	X: 716183; Y: 303399	X: 716203; Y: 302992
S5	329	X: 720451.35; Y: 305845.03	X: 720548.538; Y: 305605.206
S6	328	X: 721041.022; Y: 306799.956	X: 721311.497; Y: 306681.647
S7	327	X: 721595.666; Y: 307463.709	X: 721847.118; Y: 307256.092
S8	325+500	X: 722834.665; Y: 308247.778	X: 723140.09; Y: 307764.036
S9	323	X: 725714.663; Y: 309089.285	X: 725876.396; Y: 308909.581
S10	322+500	X: 725927.823; Y: 309343.894	X: 726159.338; Y: 309073.959
S11	321	X: 726870.085; Y: 310344.668	X: 727009.648; Y: 310154.213
S12	316	X: 731970.452; Y: 309898.102	X: 731810.752; Y:309398.039
S13	292	X: 744431.69; Y: 326795.928	X: 744616.869; Y: 326586.681
S14	290	X: 745298.187; Y: 328212.524	X: 745928; Y: 328212.524
S15	186+500	X: 733206; Y: 409362	X: 733019; Y: 409278
S16	182+500	X: 731157; Y: 412281	X: 731647; Y: 412308

to boiling point 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. Clear digestion solutions were then analysed for heavy metals content.

Quality control and assurance

Quality assurance procedures include the instrument calibration using certified standards and reagent blank. For these procedures were prepared for every 20 samples, both water and sediment, reagent blank and all concentrations obtained were below the detection limit. Analytical quality control was verified by the routine analysis of Certified Reference Materials - CRMs (CRM no. LGC6187 used for sediments; no. S-WW1 Batch 110 and no. S-WW2 Batch 109 CRMs used for water analysis). All acids used in this research had an analytical quality degree.

Statistical analysis

The statistical analysis was performed using Minitab 16 and JMP 9 (SAS) software package. This aims at finding some components that explain the major variation within experimental data. For cluster analysis were selected only sections sampled monthly (S1 – S4, S15, S16).

Results and discussions

Descriptive statistics

The physicochemical parameters of the water and sediments recorded in monitoried period in the Danube River showed that water temperature ranged from 1.1^{0}C to 25.6^{0}C. The *p*H was slightly basic, thus for the water samples ranged from 7.28 to 8.08 and for the sediments samples from 7.44 to 8.12.

According to the analytical data obtained for heavy metals (results were expressed for each metal in mg/kg of sediment and in μg/L of metal for water), a complete descriptive statistic summary of studied heavy metals in water and sediments is given in tables 2 and 3.

In the study area, the mean concentrations of studied heavy metals in water ranged between 0.52-1.21 μg/L for Cr, 3.06-5.20 μg/L for Cu, 1.61-2.78 μg/L for Ni and 10.60-16.45 μg/L for Zn (table 2). These mean concentrations of metals have classified the Danube water within the limits of first quality class of water, in accordance with the European Water Framework Directive 2000/60/EC (WFD). However, in sections S1 – S4, the maximum concentrations of Cu and Ni exceeded the values of 30 and 25 μg/L respectively, water limits stipulated within the WFD. Although the level of heavy metals in water is low, there is the risk that aquatic plants aquatic to uptake and accumulate significant amounts of heavy metals and, consequently, to transferred them to herbivorous fish species and aquatic invertebrates, thus entering in aquatic food chains and posing an ecotoxicological risk to species on higher trophic levels [17].

The mean concentrations of Cr and Zn in sediments were lower than the limits prescribed by WFD. In the case of Ni, the mean concentrations exceeded the 35.0 mg/kg WFD sediment limit at sampling sections S3, S4 and S7. The exceeding of maximum limit for Ni in the Danube sediments was reported also in earlier studies [18-20] and seems to reflect its background concentrations in

Table 2

DESCRIPTIVE STATISTIC OF METAL CONCENTRATIONS IN WATER SAMPLES IN THE SELECTED SECTIONS OF DANUBE RIVER

Section		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16
Cr	Mean	1,13	1,09	1,12	**1,21**	0,77	0,71	0,64	0,63	0,61	0,63	0,69	0,64	0,52	0,60	1,13	0,93
	StDev*	1,91	1,64	1,66	2,14	0,62	0,54	0,43	0,39	0,28	0,33	0,38	0,48	0,28	0,47	1,00	0,73
	CoefVar**	169,81	150,26	148,52	177,48	80,57	76,52	67,56	61,89	46,14	52,97	55,37	75,76	54,72	79,32	88,19	78,89
	Minimum	0,21	0,21	0,24	0,17	0,05	0,25	0,19	0,30	0,23	0,25	0,27	0,10	0,05	0,17	0,10	0,22
	Median	0,56	0,60	0,61	0,59	0,60	0,55	0,59	0,50	0,58	0,50	0,55	0,50	0,42	0,54	0,69	0,72
	Maximum	11,47	10,87	10,90	13,63	2,19	2,36	2,01	1,57	1,05	1,30	1,44	1,96	1,05	2,17	5,13	4,16
Cu	Mean	4,14	4,12	4,18	4,79	3,52	3,49	3,92	3,26	3,43	3,14	3,27	3,29	3,06	3,51	**5,20**	4,08
	StDev*	6,19	5,76	5,23	7,69	1,90	1,78	2,73	1,74	1,71	1,58	1,56	1,76	1,33	1,88	6,01	1,98
	CoefVar**	149,33	139,91	125,07	160,61	53,93	50,89	69,65	53,25	50,02	50,38	47,74	53,34	43,30	53,61	115,48	48,66
	Minimum	0,44	0,46	0,43	0,41	0,68	0,67	0,59	0,62	0,63	0,62	0,68	0,75	0,96	0,72	0,48	0,55
	Median	3,03	3,05	3,19	3,60	3,35	3,37	3,64	3,36	3,71	3,30	3,05	3,03	3,02	3,39	3,68	3,83
	Maximum	40,00	42,68	34,31	49,84	6,81	5,87	11,35	6,24	6,57	5,35	5,53	6,26	5,28	6,23	26,34	7,84
Zn	Mean	12,50	11,95	12,18	13,14	15,62	15,94	16,40	15,12	16,07	14,03	15,76	15,11	15,76	**16,45**	11,28	10,60
	StDev*	15,89	15,05	14,91	17,73	18,16	18,80	16,69	15,13	17,99	17,68	19,33	16,95	17,87	18,86	12,50	12,61
	CoefVar**	127,12	125,97	122,41	134,94	116,27	118,00	101,75	100,11	111,94	126,02	122,60	112,21	113,43	114,68	110,87	118,96
	Minimum	1,30	0,40	0,90	1,20	1,70	1,20	1,40	1,90	1,40	0,70	0,20	1,30	1,00	1,60	1,30	0,70
	Median	6,85	6,30	7,10	7,20	6,00	7,30	10,00	10,60	8,50	5,50	6,80	8,50	9,00	8,50	6,50	7,16
	Maximum	67,80	71,30	66,10	93,50	53,42	54,11	48,63	45,20	52,74	47,26	53,42	53,42	51,37	52,74	58,00	58,00
Ni	Mean	**2,78**	2,50	2,44	2,60	1,75	1,76	1,96	1,70	1,84	1,63	1,90	1,62	1,78	1,61	2,57	2,38
	StDev*	4,63	4,02	4,06	4,07	0,67	0,98	1,17	0,94	1,12	0,94	0,92	1,11	0,74	0,79	1,43	1,09
	CoefVar**	166,86	161,05	165,94	156,84	38,32	55,58	59,35	55,28	60,79	57,23	48,67	68,45	41,67	49,18	55,70	45,78
	Minimum	0,57	0,57	0,29	0,57	0,66	0,08	0,02	0,23	0,12	0,12	0,21	0,33	0,42	0,51	0,90	0,97
	Median	1,76	1,64	1,73	1,73	1,52	1,78	1,94	1,88	1,73	1,58	2,12	1,21	1,98	1,56	2,16	2,06
	Maximum	32,00	30,62	30,50	25,67	2,96	3,53	4,04	3,19	3,94	3,71	3,13	3,72	2,98	3,04	7,58	7,22

* StDev - standard deviation of concentration ** CoefVar – coefficient of variation

Table 3

DESCRIPTIVE STATISTIC OF METAL CONCENTRATIONS IN SEDIMENT SAMPLES IN THE SELECTED SECTIONS OF DANUBE RIVER

Section		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16
Cr	Mean	42,28	42,77	**44,72**	40,46	33,12	36,69	37,42	32,10	27,12	30,47	28,83	29,77	32,16	24,89	43,76	41,71
	StDev*	21,19	20,61	18,93	19,83	17,11	20,56	19,86	22,01	9,64	18,82	13,71	17,78	20,91	13,91	20,30	21,50
	CoefVar**	50,12	48,18	42,34	49,01	51,66	56,03	53,08	68,56	35,56	61,79	47,55	59,73	65,02	55,87	46,39	51,54
	Minimum	4,09	7,51	10,56	4,36	8,52	8,45	15,36	5,13	7,36	7,15	10,11	7,16	8,35	4,16	8,51	2,24
	Median	37,94	40,66	42,83	41,58	34,12	34,28	38,03	33,09	31,10	26,97	28,86	31,45	26,91	27,30	41,97	40,63
	Maximum	86,81	90,87	90,14	89,98	68,04	74,43	82,37	72,11	36,56	69,50	60,92	59,00	76,78	41,35	80,66	89,66
Cu	Mean	38,56	37,27	38,76	**40,98**	34,39	26,43	31,61	31,42	24,85	27,73	30,69	34,12	35,96	30,03	26,16	25,58
	StDev*	17,14	16,38	17,31	16,96	14,96	6,46	12,52	13,32	9,20	8,29	17,37	10,28	15,49	15,06	10,85	11,02
	CoefVar**	44,45	43,97	44,66	41,38	43,50	24,44	39,59	42,40	37,01	29,90	56,60	30,12	43,09	50,17	41,49	43,08
	Minimum	13,68	11,06	11,82	10,40	21,54	20,45	6,42	12,98	11,54	15,13	3,32	17,55	20,30	3,93	5,12	6,69
	Median	34,92	34,30	36,72	35,86	27,50	24,01	33,26	31,70	25,31	30,99	31,27	32,66	33,28	34,86	27,15	25,73
	Maximum	84,41	80,17	93,14	94,51	69,67	38,85	51,04	54,08	36,35	35,06	67,12	58,51	65,22	50,85	52,67	56,39
Zn	Mean	98,37	95,63	103,39	105,46	100,85	95,72	98,71	**106,35**	89,33	88,87	97,55	103,90	104,72	92,85	89,83	83,99
	StDev*	29,29	24,99	29,52	24,85	19,72	17,83	26,69	29,53	24,89	20,49	29,03	23,87	20,42	22,11	22,24	29,98
	CoefVar**	29,77	26,14	28,55	23,56	19,55	18,63	27,04	27,77	27,86	23,06	29,75	22,97	19,50	23,81	24,76	35,69
	Minimum	54,78	28,29	63,89	66,63	56,05	60,27	60,96	62,04	60,59	60,19	54,22	70,87	75,21	55,05	38,40	31,45
	Median	91,10	93,29	95,28	99,91	101,71	96,63	98,51	111,83	81,56	83,45	97,28	97,41	106,73	104,59	89,13	82,08
	Maximum	203,52	142,34	206,99	179,30	134,61	128,84	143,29	141,37	126,03	126,46	136,22	146,83	136,22	120,48	135,49	176,21
Ni	Mean	33,83	32,54	**40,11**	35,83	34,73	32,46	35,10	34,60	32,26	27,48	30,40	34,08	34,28	33,89	33,49	31,70
	StDev*	9,65	8,30	10,53	7,32	7,08	5,04	7,59	6,16	4,03	4,69	5,33	8,38	5,84	9,24	7,24	9,90
	CoefVar**	28,53	25,52	26,25	20,43	20,38	15,52	21,62	17,79	12,49	17,08	17,55	24,63	17,05	27,27	21,63	31,23
	Minimum	11,93	15,48	16,82	22,81	20,73	22,53	24,35	24,72	25,31	20,82	21,78	27,35	21,54	16,18	14,39	10,79
	Median	32,23	32,48	41,44	34,23	34,43	33,00	36,44	35,31	32,81	27,88	30,60	31,27	33,24	37,61	33,70	32,80
	Maximum	61,30	52,37	63,61	56,97	48,50	38,92	48,44	41,77	38,47	34,19	36,64	56,31	41,00	46,03	47,60	54,08

* StDev - standard deviation of concentration ** CoefVar – coefficient of variation

sediments. The mean concentrations of Cu exceeded the 40 mg/kg WFD sediment limit only in sampling sections S4. Moreover, the maximum levels of Cu and Ni were exceeded the WFD sediments limits in all sampling sections, except sections S9 and S10 for Cu, and S10 for Ni; the maximum levels of Zn were exceeded the WFD sediments limit in sections S1, S3, S4 and S16 (table 3). The increased concentrations of heavy metals in sediments might be attributed mainly to the metal retentions capacity of sediments as well as urbanizations and industrialization activities along Danube River and may pose a hazard to the aquatic biota [21].

The calculation of the coefficient of variation (CV) for water revealed that for Cr, Cu and Ni, the CV value were higher than 80% in the section S1 – S4 and S15. In case of Zn, the CV values are higher than 100% in all section. For sediment, the coefficient of variation (CV) ranged between 15.52 and 68.56.

Average concentrations of analysed heavy metals from each sampling section decreased in the order presented in tables 4 and 5. Spatial distribution of heavy metals, both water and sediments, showed no longitudinal patterns along the Danube River, between Km 347 - 182. However, based on the data of published studies [3, 22], in the Danube sediments, it was observed a general increase in the levels of Pb along the course of the Danube River, especially from Km 1500 - 130.

In statistics, the Pearson correlation coefficient (Pearson's r) is a measure of the linear correlation between two variables, giving a value between +1 and -1 inclusive, where 1 is total positive correlation, 0 is no correlation, and -1 is total negative correlation [23].

The correlative relationships between heavy metals were analysed and presented in tables 6 and 7. A high positive correlation between Cr-Ni, Cu-Ni and Cr-Cu in water samples was revealed (table 6). For sediments samples, it was obtained a strong relationship between Cu-Zn and Ni-Zn (table 7). In agreement with the literature [24-25], if the correlation coefficient between the heavy metal factors is positive, these factors might have similar sources of input, mutual dependence and identical behaviour during the transport. Furthermore, associations between heavy metals

Table 4

SAMPLING SECTIONS ORDERED BY DECREASING MEAN CONCENTRATIONS – WATER

Cr	S4	S15	S1	S3	S2	S16	S5	S6	S11	S7	S12	S10	S8	S9	S14	S13
Cu	S15	S4	S3	S1	S2	S16	S7	S5	S14	S6	S9	S12	S11	S8	S10	S13
Zn	S14	S7	S9	S6	S11	S13	S5	S8	S12	S10	S4	S1	S3	S2	S15	S16
Ni	S1	S4	S15	S2	S3	S16	S7	S11	S9	S13	S6	S5	S8	S10	S12	S14

Table 5

SAMPLING SECTIONS ORDERED BY DECREASING MEAN CONCENTRATIONS – SEDIMENTS

Cr	S3	S15	S2	S1	S16	S4	S7	S6	S5	S13	S8	S10	S12	S11	S9	S14
Cu	S4	S3	S1	S2	S13	S5	S12	S7	S8	S11	S14	S10	S6	S15	S16	S9
Zn	S8	S4	S13	S12	S3	S5	S7	S1	S11	S6	S2	S14	S15	S9	S10	S16
Ni	S3	S4	S7	S5	S8	S13	S12	S14	S1	S15	S2	S6	S9	S16	S11	S10

Table 6

PEARSON CORRELATION MATRIX FOR HEAVY METAL CONCENTRATION IN WATER

	Cr	Cu	Zn	Ni
Cr	1			
Cu	0.829	1		
Zn	0.413	0.510	1	
Ni	0.881	0.879	0.477	1

Table 7

PEARSON CORRELATION MATRIX FOR HEAVY METAL IN SURFACE SEDIMENTS

	Cr	Cu	Zn	Ni
Cr	1			
Cu	0.357	1		
Zn	0.306	0.772	1	
Ni	0.243	0.540	0.644	1

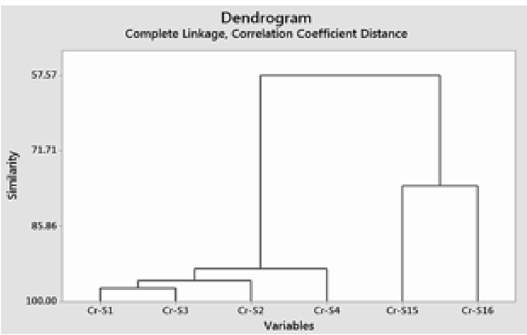
are important, as they determine the bioavailability and potential toxicity to organisms in aquatic ecosystems [26].

Cluster analysis of data

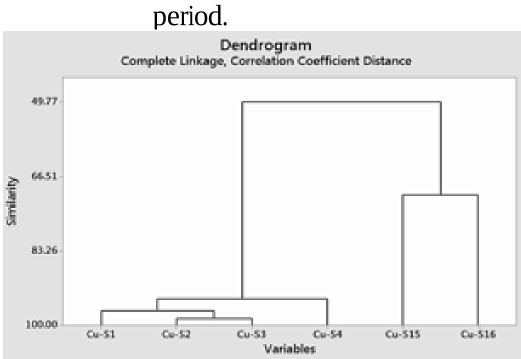
Cluster analysis or clustering is the most basic quantitative method for estimating similarities [27]. After it was carried out the hierarchical cluster analysis, the process was represented on a diagram known as a *dendrogram*. The diagrams illustrate which clusters have been joined at each stage of the analysis and the distance between clusters at the time of joining [28]. Cluster analysis grouped the studied sampling sections into clusters on the basis of similarities within a group and dissimilarities between different groups (figs.2 and 3).

Spatial cluster analysis of water sampling sections produced dendrograms with two groups (fig. 2). Cluster A comprised sections S1 – S4 (located upstream of study area) and cluster B contained sections S15 – S16 (located downstream of study area). Moreover, the sections from cluster A were grouped at high similarity percentage, about 90% for all studied heavy metals, which may indicate that the sections within the groups had similar natural backgrounds or/and were likely affected by common pollution sources.

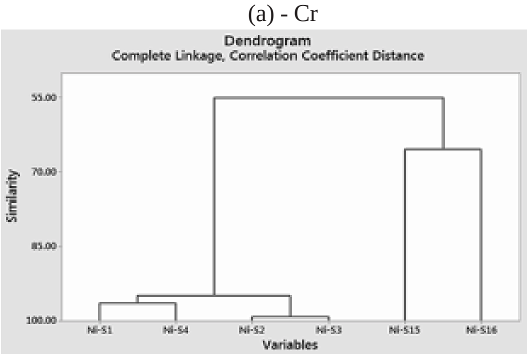
In case of sediments, it was observed that the grouping of sampling sections in clusters do not have the same pattern as in the case of water, respectively grouping the upstream and downstream sampling sections in two different clusters, except Cr (fig. 3). It is know that sediments are able to adsorb and retain significant amounts of toxic contaminants as heavy metals [29] from water column differently along the aquatic ecosystem. The adsorption capacity depends on many factors of the sediment-water system, including *p*H, temperature, cation exchange capacity, ionic strength, surface area, grain size, mineralogical properties, activity of the benthic organisms etc [31]. These might explain the dissimilarities between studied sections on the Danube River in the monitored period.



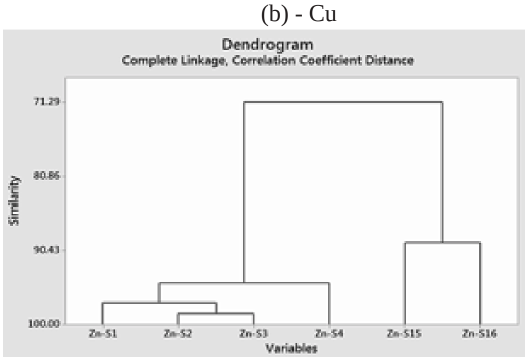
(a) - Cr



(b) - Cu



(c) - Ni



(d) - Zn

Fig. 2. Dendrograms of the water sampling sections from the Danube River

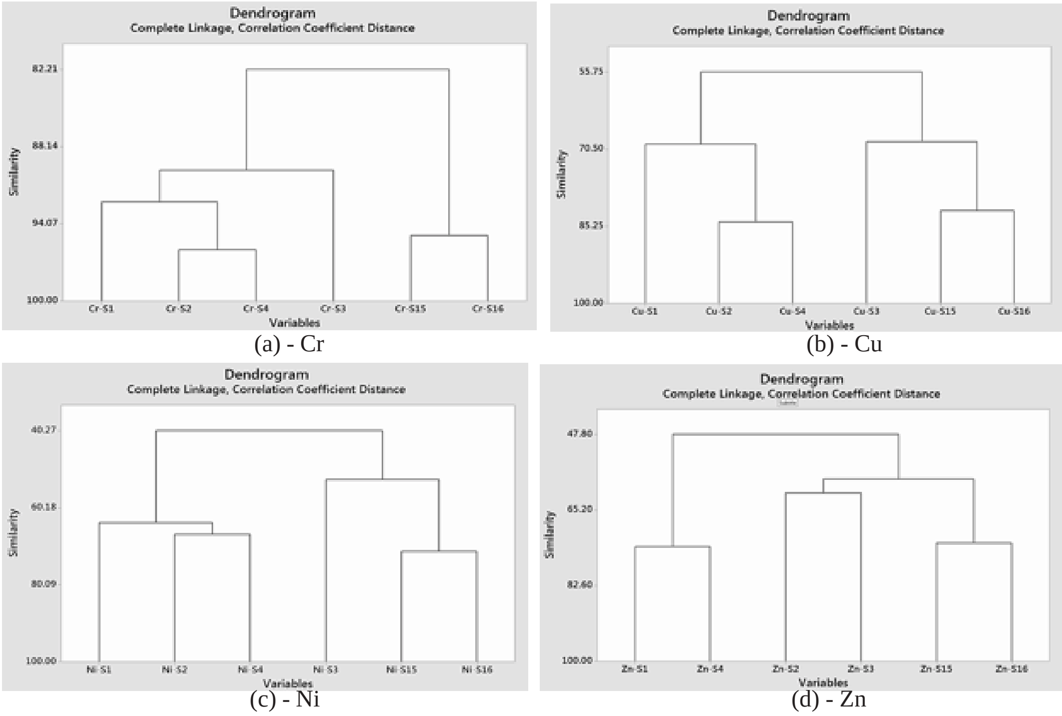


Fig. 3. Dendrograms of the sediments sampling sections from the Danube River

Conclusions

Lower concentrations than first quality class limits of the European Water Framework Directive 2000/60/EC for studied heavy metals were found for water samples and higher concentrations were found in sediments, for Ni and Cu.

Pearson correlation coefficient highlighted a strong relationship between Cr-Ni, Cu-Ni and Cr-Cu for water samples and Cu-Zn and Ni-Zn for sediments. Cluster analysis revealed that the grouping of sediments sampling sections in clusters do not have the same pattern as in the case of water, respectively grouping the upstream (S1, S2, S3, S4) and downstream (S15, S16) sampling sections in two different clusters, except Cr.

Spatial distribution of analyzed heavy metals in river water and sediments provides valuable information on studied sections along Danube River and these data could be used in the management strategies to protect aquatic ecosystems.

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