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THE SECOND JOINT DANUBE SURVEY EXPEDITION – HAZARDOUS METALS AND METALS CONCENTRATION FROM DANUBE RIVER SEDIMENT

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abstract: The paper present the results obtained in the second Joint Danube Survey Expedition organized in 2007, regarding the metals and heavy metals analysis from sediment samples in this river.

key words: Water Framework Directive 2000/60/EC, sediment concentration of hazardous metals and ordinary metals

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Introduction

The Danube River was always the most important European River, providing the basic necessities for human life. From its source to mouth the Danube River and its tributaries serve as a resource for different water uses, like drinking water supply, industry and energy production, transport, irrigation in agricultural areas, waste water recipient etc.

The protection of the Danube became an issue over the past years. The economic development in the Danube region brought not only improvement of quality of life but also threat to the environment and to the river. Increase of industrial activities, extensive agriculture, growing municipal communities, all these are potential sources of pollution if not properly managed and can have negative impact on functions of the river, water quality, water uses.

The European Water Framework Directive 2000/60/EC [1] develops the concept of ecological quality status (EcoQ) for the assessment of the quality of water mass. The EcoQ is based upon the status of biological, hydro-morphologic and physical-chemical quality elements, with biological elements being especially important and supported by the others. The physical-chemical elements include general variables such as dissolved oxygen, nutrients etc) and specific pollutants. The former correspond to variable measured directly

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in the water. However, there is no indication about which matrices are to be sampled, or for which specific pollutants.

Sediments are considered to be important in the assessment of anthropogenic impacts. It is also well know that the sediment have an impact on the ecological quality. They are subject to transport, deposition and erosion, thus forming a dynamic part of the hydrological system.

The contamination of sediments with heavy metals is a very old problem; the Cousteau Report [2] has provided results from which the Iron Gates Reservoir was chacterized as a long term chemical bomb with concentrations of heavy metals exceeding 3-5 times the Elbe and Rhine specific concentrations. This problem was investigated by JDS 1 [3] were some hot – spots were detected in the same sites as during earlier surveys (Cousteau – Survey).

Experimental

Samples pretreatment

Homogenized and freeze-dried samples of sediments (fraction <63 µm) were provide in polypropylene bottles. Samples were stored at room temperature before they were analyzed. Sample pre-treatment is a step where heavy metals are extracted from solid state to aquatic state. Extraction of heavy metals followed the EPA 3051 method using the microwave digester.

Table 1 Equipments and methods used for trace elements and metals analysis.

Determinant	Unit	Equipment	Method
Cadmium (Cd)	µg/l	AAS – GF*	ISO 15586:2003[6]
Chromium (Cr)	µg/l	AAS - GF	ISO 15586:2003[6]
Copper (Cu)	µg/l	AAS - GF	ISO 15586:2003[6]
Lead (Pb)	µg/l	AAS - GF	ISO 15586:2003[6]
Nickel (Ni)	µg/l	AAS - GF	ISO 15586:2003[6]
Mercury (Hg)	µg/l	FIMS**	SR EN 1483:2003 [5]
Iron (Fe)	mg/l	AAS – F***	SR ISO 8288:2001
Manganese (Mn)	mg/l	AAS - F	SR ISO 8288:2001
Zinc (Zn)	mg/l	AAS - F	SR ISO 8288:2001

* AAS – GF – Atomic Absorption Spectrometry with graphite furnace [7]

** FIMS – Flow Injection Mercury System

*** AAS – F – Atomic Absorption Spectrometry with Flame

According with the procedure provided by ICPDR (International Commission for the Danube River Protection), trace elements and metals were mineralized as follow:

- for trace elements (Cd, Pb, Ni, Cu, Cr, Hg) all 172 samples were mineralized;
- for metals (Fe, Mn and Zn) samples from 25 sampling sites were mineralized as individual samples and the remaining sampling sites were mineralized as mixed samples (the same amount of dry sediment was taken from left and right site for the extraction).

Analytical quality control

To control the accuracy of the heavy metals results, at every 5 samples an certified reference material (CRM) ,which is river sediment LGC 6187 from monitoring station lagoon on the river Elbe ,close to the Czech – German border, was analyzed.

The extraction of heavy metals from sediment CRM followed the same procedure as for the samples with the difference that for the certified reference materials approximate 0.2-0.5 g of dry sediment were weighted into PTFE (Teflon vessel).

The results of quality control samples are summarized in Table 2. These results are referred to the weight of approximate 0.5 g.

Table 2 Heavy metals concentrations (overall mean ± uncertainty*) in certified reference material.

Metals	CRM LGC 6187 (mg/kg)		ICIM Results (mg/kg)	
	conc. (mg/kg)	Uncertainty*	(conc. mg/kg)	uncertainty**
Cd	2.7	0.3	1.79	0.3
Cu	83.6	4.1	85.46	11.9
Cr	84	9.4	86.15	9.94
Pb	77.2	4.5	86.61	16.62
Ni	34.7	1.7	38.94	8.91
Zn	439	26	480.51	27.08
Fe	23600	1500	23463.3	1910.12
Mn	1240	60	1222.1	145.52
Hg	1.4	0.1	1.27	0.31

* the uncertainty quoted is an expanded uncertainty with a coverage factor of 2, and approximates to the half width of the 95% confidence interval

** the uncertainty was calculated based on the our laboratory results as twice the standard deviation of the overall mean.

The above mentioned results indicate no significant difference between certified concentration results and the results obtained by our laboratory, with two exceptions: one for Cd were the lower results can be explained by partial extraction procedure and the second for Pb were the results are higher than the certified concentration results caused may be, by some contamination of the sample.

Results and Discussion

For 172 samples the trace elements and metals were analyzed from Danube river sediment and its tributaries.

The evaluation of the results was made based on sediment Dutch limits [4] presented in Table 3.

Danube River - Priority list of hazardous metals

For the hazardous metals from the priority list Hg, Cd, Pb and Ni the evaluation of the results was made based on three main characteristics: concentration, ratios of T.V. and MPC and longitudinal trend of hazard metals and metals concentrations along the Danube river. The results are presented in Table 4.

Table 3 Sediment Dutch limit used for results evaluation.

Determinant	TV *	MPC**
As	29	55
Al	-	-
Cd	0.8	12
Cu	36	73
Cr	100	380
Pb	85	530
Ni	35	44
Zn	140	620
Fe	-	-
Mn	-	-
Hg	0.3	10

* target value which indicate the long term pollution
** maximum permissible concentration which indicate short term pollution

Table 4 Results obtained for hazardous metals in Danube river.

Element	Concentration		
	range (mg/kg)	The lowest recorded value location	The highest recorded value location
Hg	0.06-1.57	JDS 65 Upstream Timok (L)	JDS 31 Rackeve - Soroksar Danube Arm - start (R)
Cd	0.25-4.24	JDS 29 Upstream Budapest (R)	JDS53 Aval Pacevo (L)
Pb	1.97-8704.32	JDS77 Downstream Zimnicea / Svishtov (R)	JDS61 Donji Milanovac (L)
Ni	18.96-319.5	JDS33 Adony / Lorev (R)	JDS80 Upstream Ruse (R)

From the longitudinal trend point of view, for hazardous metals the following remarks could be mentioned:

– in case of mercury, for river km 2000 – 1500 all the data are bellow MPC, presenting some exceeding of TV.

– For cadmium all the results are lower than MPC – for the stretch uptil 125 and between 400-0 the most of recorded values are bellow TV, the excedance of TV was recorded for the stretch 1250-500.

In case of lead for the upper part of Danube up till 1075 Km all the data are lower than MPC but equally or above TV. A high excedance of MPC was recorded for the stretch 1075-750 the lower sector 500-0 Km presented some variation in the range TV – MPC with higher spreaded values in comparison with upper part.

– In the case of nickel, the most of the data are higher than TV and MPC. This excedance of the TV and MPC may be due to the natural background and as a consequence the selected TV, MPC are not relevant for this metal.

Danube River – other metals

Table 5 Results obtained for other metals in Danube river.

Element	Concentration		
	Range (mg/kg)	The lowest recorded value location	The highest recorded value location
As	6.42 – 437.94	JDS 33 Adonz / Lorev (R)	JDS 60 PF I Iro Gate reservoir (Golubac / Koronin)
Al	9342.18 – 120700.34	JDS 65 Upstream Timok	JDS 70 Upstream Iskar
Cu	33.3 – 5952.0	JDS 35 Dunafoldvar L	JDS 45 Ilok/Backa Palanka (L)
Cr	34.42 – 252.4	JDS 29 Upstream Budapesta R	JDS 85 Down stream Arges Oltenita (L)
Zn	105.76 – 785.08	JDS 33 Adony/Lorev R	JDS 38 Baja (R)
Fe	21013.22 – 63517.02	JDS 35 Dunafoldvar (L0	JDS 70 upstream iskar (Bajkal) (R)
Mn	395.74 – 1479.11	JDS 31 in Rackeve – Soroksar Danube arm (R)	JDS 75 Downstream Olt (R)

For other metals Cu, Cr, Zn, Fe and Mn the following remarks should be mentioned:

– For arsenic, all the data are higher than MPC with a decrease of the concentration in the stretch 1750-1500 Km followed by the increasing of the concentration in the stretch 1250 – 1000 Km.

– in case of copper the most of the data are above both of TV and MPC even in the upper part of Danube river. As in the case of Ni, it might be related with the natural background and than the selected TV / MPC could be considered to not be relevant for this metal.

– For chromium, all of the data are bellow MPC, fluctuation along TV line particularly 1500Km –500Km where the most of the data were higher than TV

– In case of zinc, with few exceptions (upper than 2000 Km) all of the data were situated above TV but bellow MPA, with a maximum in the stretch 1250 Km: – 750 Km. however the TV seems to be too low and should be related with the natural background for this metal.

- In case of iron, it was observed an increasing of the concentration in the lower part of the Danube form the 1250 Km up till 600 Km.
- For manganese there were not identified any problems, all the data are constant distributed.

Danube tributaries - Priority list of hazardous metals

Table 6 Results obtained for hazardous metals in Danube tributaries.

Element	Concentration		
	Range (mg/kg)	The lowest recorded value location	The highest recorded value location
Hg	0.06 – 1.44	JDS RL2 Russenski Lom	JDS 49 Tisa (km 1.0) R
Cd	0.23 – 8.44	JDS RL2 Russenski Lom	JDS 71 Iskar (km 0.3)L
Pb	22.82 – 2111.25	JDS TI 1	JDS 71 Iskar (km 0.3)L
Ni	5.08 – 182.76	JDS 25 Ipoly (km 0.7) L	JDS Prut 2

In case of Danube tributaries, as it was presented in the above table, the most higher concentration that exceeded the TV were determined in Iskar (for Cd R = 10.55; Pb R = 9.2 and Ni R = 9.2) and Tisa (Hg R = 4.80). Reporting to the MPC, the most polluted tributaries were Timok (with R = 3.08 for Cd) and Iskar (with R = 3.9 for Pb and R=7.3 for Ni).

Regarding the longitudinal variation of the concentration of hazardous metals, the same situation as it was presented for the Danube river. The higher concentration from the Timok and Iskar tributaries could generate the increasing of the concentration in the lower part of the Danube river. Based on this, Timok and Iskar could be considered as specific contamination sources for this priority metals.

Danube tributaries - Other metals

Based on the above tables the most polluted tributaries with metals such as Cr, Cu, Zn, are Timok and Iskar, where the ratio between the concentration of the metal and the TV and MPC were between 3.46 (TV ratio for Cr) and 317.54 (TV ratio for Cu).

In Fig. 1 are presented the results (%) for each determined element which exceed the target value and maximum permissible concentration.

Table 7 Results obtained for other metals in Danube tributaries.

Element	Concentration		
	Range (mg/kg)	The lowest recorded value location	The highest recorded value location
As	26.57 – 608.3	JDS JA 2	JDS Ti2
Al	17355.32 – 73845.25	JDS 78 Jantra (L)	JDS 71 – Iskar (L)
Cr	46.53 – 345.7	JDS 24 Hron (R)	JDS 71 Iskar (L)
Cu	43.93 – 11431.52	JDS 25 Ipoly (L)	JDS 66 Timok (R)
Zn	106.83-923.78	JDS 90 Siret (L)	JDS 66 Timok (R)
Fe	26521.23 – 82498.43	JDS 21 Vah (L)	JDS 66 Timok (R)
Mn	728.83 – 1638.99	JDS 15 Morava (R)	JDS Velika Morava

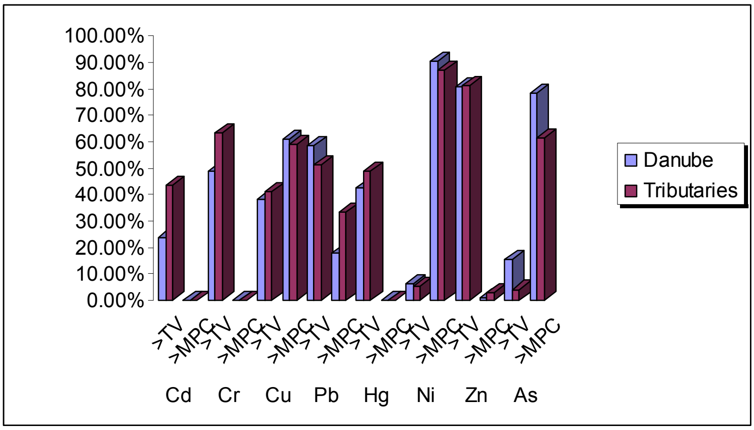

Fig. 1 *Results (%) which exceed the target value and maximum permissible concentration*

As an overall, for Cd, Cr and Hg all the results obtained were higher than TV which correspond to the long term pollution. For Cu, Ni and As the results were higher than MPC which indicate a short term pollution and for Pb and Zn the majority of the results were higher than TV.

For the analysed elements the highest concentrations were found in some tributaries, indicating the main pollution sources of the Danube.

Comparison with JDS 1 data

In 2001 it was organized the first Joint Danube Survey Expedition – JDS 1 with the same objectives.

For better evaluation of the distribution of hazardous metals and metals along the Danube River, in the table 8 it was made an comparison of the results obtained in 2001 and 2007.

Table 8 The highest element concentration recorded in JDS 2 sediment samples in comparison with JDS 1.

Element	JDS2 - Position	Concentration (mg/kg)	JDS1 - Position	Concentration (mg/kg)	JDS 1* (mg/kg)
Al	JDS 70 – Upstream Timok	120700.34			18700-50200
Fe	JDS 66 Timok	82498.43			17600-56700
Mn	JDS Veliko Morava	1638.99			442-1379
As	JDS 60Tisa	608.3	JDS 69 Timok	388	6-19-68.90
Cd	JDS 71 Iskar	8.44	JDS 74 Iskar	32.9	0,00-25,90
Cr	JDS 71 Iskar	345.7	JDS 84 Russ. Lom	556	23.1-139
Cu	JDS 66 Timok	11431.52	JDS 69 Timok	8088	26.8-662.9
Hg			JDS 26 Vah.	2.56	0.1-7.25
Ni	JDS 71 Iskar	324.46	JDS 61 Vel. Morava	173	23.9-389.1
Pb	JDS 61 Donji Milanovac	8704.32	JDS 74 Iskar	542	14.7-107.6
Zn	JDS 66 Timok	923.79	JDS 74 Iskar	2010	83-622

* these values are calculated after the elimination of the highest concentrations obtained in JDS 1 for each element

As it is presented in the above table, the highest concentrations were found in Iskar for Cd, Cr and Ni and Timok tributaries for Cu and Zn. In both expedition JDS1 and JDS 2 the highest concentration were found nearly at the same location which indicate that the tributaries Timok and Iskar could be considered the major contamination sources for Danube River. Because in JDS 1 and also in JDS 2 Timok and Iskar were detected as the major polluted tributaries for Cd and Cu, they could be considered as “hot spots” .

Conclusions

In case of sediment priority metals and metals analysis, the variation in the concentrations of elements along the entire course of Danube river reveals a contamination of sediments especially from the Km 1200 – 834 in case of Cd, Km 1481-295 in case of Cr, Km 1500-130 in case of Pb and Km 1700 – 579 in case of Hg; for Ni the majority of the results exceed the MPC and for Cu all the results exceed TV or MPC.

The concentration increase in the lower part section of the Danube river.

This increasing was recorded also for the Danube river tributaries, and this may be the explanation for the Danube contamination.

According with the Dutch TV and MPC, all the results indicate a long term pollution for majority of the studied elements with exception of Ni, were the results indicate a short term pollution.

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