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Study of Heavy Metal Pollution in Sediments from the Iron Gate (Danube River), Serbia and Montenegro

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Abstract

The pollution of aquatic ecosystems by heavy metals has assumed serious proportions due to their toxicity and accumulative behavior. River dams are especially at risk of contamination by different contaminants from anthropogenic sources including heavy metals since change of the sediment regime often occurs. The largest hydropower dam and reservoir system along the entire Danube, the Iron Gate, is located at the Djerdap Gorge (117 km long) in Serbia and Montenegro. In order to determine the degree of pollution of the Iron Gate by heavy metals, composite sediment samples were collected from seven reaches of the river from Smederevo (river-km 1112) upstream from the Iron Gate dam to Radujevac (river-km 851) downstream from the gorge. The concentrations of As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni and Zn were determined in the sediments. The lowest heavy metal concentrations were measured around river-km 854, downstream from the gorge. The data from this study were compared with data obtained 20 years ago in the same area. It was found that the range of mean concentrations over the entire gorge of Fe, Mn, Ni, Zn, Cu, Cr and Cd increased by 46.6% (Zn at the site Tekija) to 156.2% (Ni at the site Veliko Gradiste). Decreases in concentrations were observed for Hg and Pb. Metal levels in the sediments did not exceed Dutch intervention values, but were higher than the target values for Ni, Zn, Cu, Cr and especially for Cd, indicating contamination not sufficiently high to require remediation/intervention, but not excluding risk to the ecosystem.

Keywords: sediments, heavy metals, sediment quality assessment, Iron gate (Danube River)

Introduction

River sediments, as basic components of our environment, provide foodstuffs for living organisms. They also serve as a sink and reservoir for a variety of environmental contaminants. It has been recognized that aquatic sediments absorb persistent and toxic chemicals to levels many times higher than the water column concentration [1, 2, 3]. Namely, when released into the aquatic environment, many anthropogenic chemicals bind or adsorb onto particulate matter. Depending on the river morphology and hydrological conditions, suspended particles with associated contaminants can settle along the watercourse and become part of the bottom sediments, often for many kilometers downstream from the chemical sources [4, 5, 6].

Trace metals derived from natural inputs and anthropogenic emissions are ubiquitous in the global environment. Consequently, sediment-associated pollutants can influence the concentrations of trace metals in both the water column and biota if they are desorbed or become available

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*Corresponding aurhor: e-mail: risticm@tmf.bg.ac.yu to benthic organisms. One of the major problems that heavy metals cause with respect to their effects on aquatic organisms is their long biological half-life. Therefore, they are among the most frequently monitored micropollutants, and reliable techniques have been established for their extraction and quantification [7-11], since sediment contamination by heavy metals in rivers and estuaries has become an issue of increasing environmental concern. Such contamination is often caused by human activities, including mining, smelting, electroplating and other industrial processes that have metal residues in their wastes, and by non-point source surface runoff. In past years, tremendous efforts have been made to characterize the fate, loading and distribution of heavy metals in sediments [12-18]. These studies have improved our understanding of heavy metal contamination in river and estuary ecosystems.

The topic of heavy metal pollution in sediments of European rivers has received the attention of many scientists. Much work to date has focused on more industrial parts of Europe, such as the Rhine River of Germany and the Netherlands [19, 20] or the Elbe River of Germany [21, 22, 23]. Others have documented the storage of heavy metals in the mined drainage of Europe [24-27]. Also in recent years, an immense and increasing international effort has been put into characterizing the current ecological and chemical status of the river Danube [28, 29]. A few studies on sediment contamination in some stretches of the Danube in Serbia have also been performed [30, 31], but systematic investigations in the biggest hydropower dam and reservoir system along the entire Danube, the Iron Gate (Djerdap Gorge-117 km long) have not been conducted. The environmental impact of a dam include, among other parameters, alteration of the hydrological regime of the surface and groundwaters and change of the sediment regime (natural balance of erosion and sedimentation processes) [6, 32]. There are several indications that the Iron Gate reservoirs, the largest impoundments on the Danube River, are significant sinks for nutrients, as well as pollutants [33, 34]. Namely, it was found that the sediment flux at the upper limit of the lower section of the river Danube was estimated at approximately 30 million t/yr, which is trapped in the barage lake of Iron Gate I.

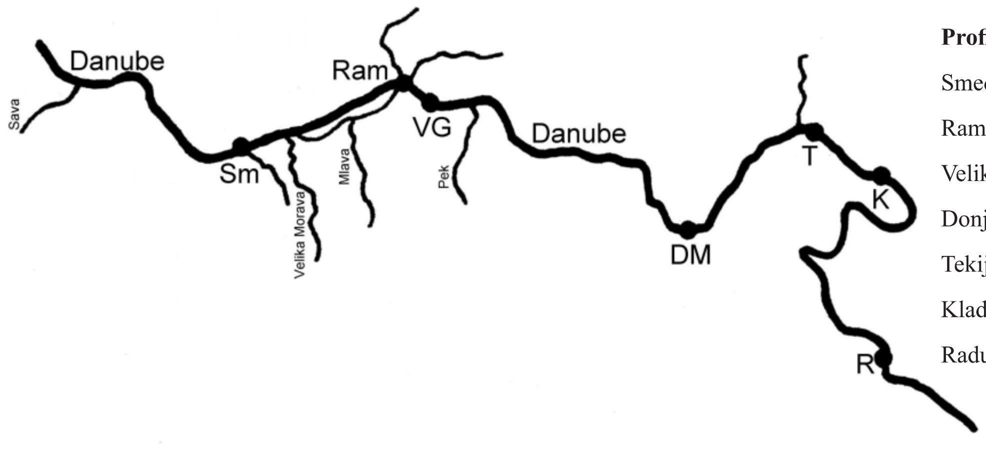
The total length of the Danube river is approximately 2,800 kilometres and its length in the territory of Serbia is 588 km, or approximately 20% of its total length. The Danube River basin covers 87% of the country's territory. It also represents the most developed and densely populated part of Serbia and comprises the Tisza River sub-basin, the Sava River sub-basin, and the Velika Morava sub-basin. The average width of the Danube in Serbia is 1 km, thus forming a total water surface of 520 km^2. Nowadays, the flood area of the Danube is approximately 1000 km^2, while the accumulation lake of the hydroelectric power plant Iron Gate I has a surface area of about 10.50 km^2 and that of Iron Gate II about 8 km^2. The Serbian section of the Danube mainly covers the region of the mid and, partly, the lower Danube, with a relatively low overall river slope value.

The objectives of this paper were to illustrate the distribution and levels of sediment contamination by heavy metals in the Iron Gate, and to compare recent data with those collected during the early 1980's. The metals As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni and Zn were chosen because of their abundance and toxic effects in the environment of highly industrialized and urbanized areas.

Experimental

The sediments were sampled during June, 2002 at the Serbian, right riverbank, in the section of the river flow slowing down. The river mean flow in this period was ca. 5000 m^3/s. Superficial sediment samples were taken at seven positions along the river from Smederevo (River-km 1112) down to Radujevac (River-km 851). Four of them (Ram, Veliko Gradiste, Donji Milanovac and Tekija) are in the acumulation of Iron Gate I, Kladovo is in Iron Gate II, and one profile (Radujevac) is downstream from Iron Gate II (Fig. 1.).

At each site samples were taken with an Ekman grab sampler. Composite sediment samples were transported to the laboratory and stored at 4°C.



Profiles	River-km
Smederevo (Sm)	1112
Ram (Ram)	1072
Veliko Gradiste (VG)	1059
Donji Milanovac (DM)	991
Tekija (T)	956
Kladovo (K)	934
Radujevac®	851

Fig. 1. Schematic map showing the locations of the sampling stations within the investigated area.

Sediment samples were analyzed using the “total” digestion method [7, 10, 31]. The determination of total content of heavy metals in sediments is particularly useful to collect information on the genesis of the soil and on the level of contamination. Also, the comparison of sediments to effects-range guidelines involves the use of metal concentrations from total or strong acid digests (because the guidelines themselves are derived from such data). The sediment was dried for moisture determination in petri-dishes at 105°C for 48 h and then ground into a powder. The sediment (1 g) was weighed into a 100 ml beaker and digested using a nitric/perchloric acid digestion [11, 35, 36]. Concentrated HNO_3 (5 ml) was added and the mixture was boiled gently until the volume of liquid was approximately 15 ml. The beaker was cooled and a new portion of 5 ml of HNO_3 was added. The sample again was allowed to cool before the addition of 5 ml of trace metal grade $HClO_4$. The samples were heated and the temperature raised gradually to 160°C. The digestion was complete when the white smoke stopped evolving. The concentration of metals in the extracted solution was determined by air/acetylene flame absorption spectrometry (Ni, Cr, Fe, Mn, Zn and Cu) and electrothermal atomic absorption spectrometry (Pb, Cd and As) on a Perkin-Elmer 560 HGA 400 atomic absorption spectrophotometer. Hg concentrations were determined by Cold Vapour Atomic Absorption Spectrometry (CV-AAS). Quantification was conducted with six matrix-matched external calibration standards. All the chemicals used were of analytical reagent grade. A preparation/reagent blank sample was prepared for every 20 samples and all concentrations were below the method detection limits. Each sample was analyzed in triplicate with a relative standard deviation <5% for all the trace metals analyzed. Recovery after digestion was checked using a certified reference material CRM 277 (trace metals in estuarine sediment). Percentage recoveries were always over 95% and no evidence of contamination was found, whereas only Cd concentration seemed to be slightly overestimated (109.5%).

Results and Discussion

The trace metal levels in the examined sediments are outlined in Table 1 and Figs. 2-4.

It was found that the environmentally mobile elements were arranged in the order Fe> Mn> Zn> Cr> Ni> Cu> Pb> As> Hg in samples collected in the examined

Table 1. Heavy metal concentrations in the examined sediment.

Sites	Heavy metal concentrations (mg/kg)							
	Hg	As	Ni	Zn	Cu	Cr	Pb	Cd
Smederevo	0.18	5.08	46.8	219.1	23.9	51.8	19.4	4.03
Ram	0.30	14.73	116.4	328.4	36.8	112.5	40.9	2.84
Veliko Gradiste	0.27	12.68	99.9	389.5	41.0	105.9	40.9	3.2
Donji Milanovac	0.19	3.15	69.9	285.7	45.3	68.0	25.8	3.79
Tekija	0.23	9.24	74.5	307.8	57.6	93.3	43.6	2.98
Kladovo	0.19	3.16	59.2	197.5	31.6	71.1	28.0	2.12
Radujevac	<0.06	0.99	23.7	49.4	17.8	30.6	2.85	2.91

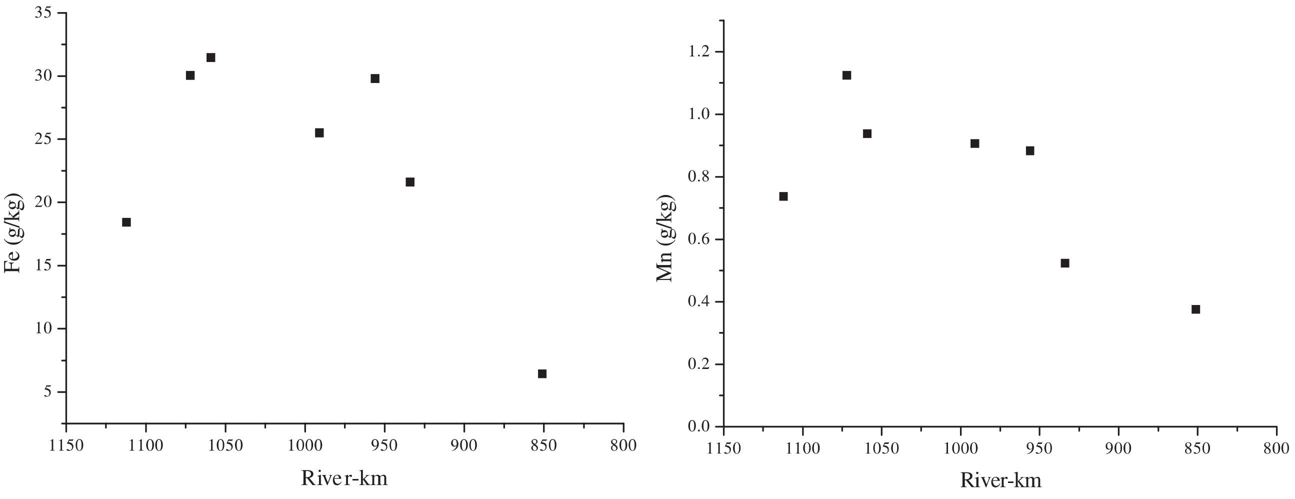


Fig. 2. Variations of the concentrations of Fe and Mn by location.

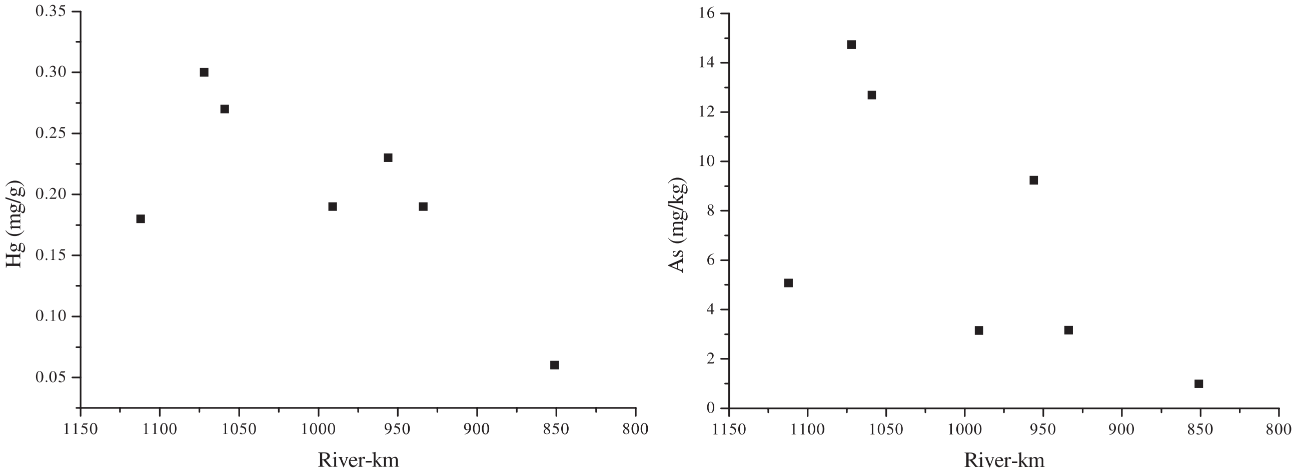


Fig. 3. Longitudinal distribution of Hg and As concentrations in the sediment samples.

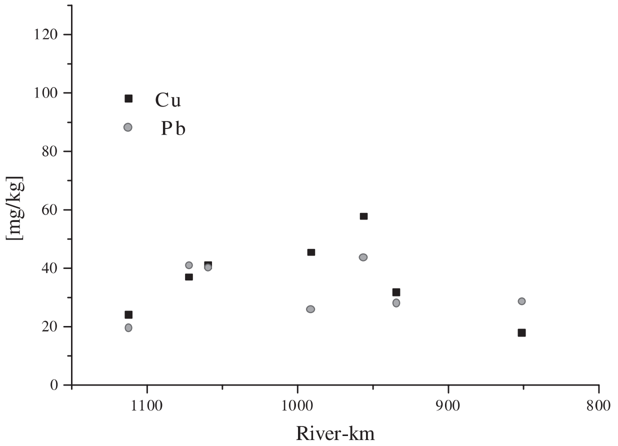


Fig. 4. Downstream changes in sediment Cu and Pb concentrations.

area. The concentration profiles of As, Cr, Ni, Hg and Zn along the course of the Danube River in the Djerdap Gorge correspond to those of Fe and Mn, which represent the main constituents of sediments not subjected to anthropogenic changes. Ram (River-km 1072) and Veliko Gradiste (River-km 1059) showed the highest concentrations of heavy metals with the exceptions of Cu, Pb and Cd. Tekija (River-km 956) was enriched with Cu and Pb, and also the second maximum for the other elements with the exception of Cd was observed.

The concentrations of all the metals, with the exception of Cd, at the site Radujevac (River-km 851) were 3 to 18 times lower than the maximum found at other sites in the deposition area.

Some 20 years ago Vasiljevic and Tomasevic [37] conducted a survey of heavy metal concentrations in the Danube sediments in Serbia. They selected six sites, two of which corresponded to those sampled in this study (Veliko Gradiste and Tekija), thus allowing for direct comparison between the sites over the intervening time period. Their results also showed higher concentrations at those sites (Table 2), where higher sedimentation occurs due to slowing down of the river.

Of great interest, however, is the increase in heavy metal concentrations in the sediments of the Iron Gate since the measurements of Vasiljevic and Tomasevic. The percent change in the concentration of metals between the studies of Vasiljevic and Tomasevic and the present study at the corresponding sites are shown in Table 3. The metals measured, namely Fe, Mn, Ni, Zn, Cu, Cr and Cd have increased in recent years at the examined sites. The range of mean concentrations of these metals over the entire gorge increased by 46.6% (Zn at site Tekija) to 156.2% (Ni at the site Veliko Gradiste). Decreases in the concentrations were observed for Hg and Pb. Table 3 shows that these metals decreased throughout the Iron Gate over the past 20 years ranging in percentage decreases from 8.2% for Pb to about 269% for Hg. This suggests that in the early 1990s, and probably today, continuous but lower level waste discharges from industry and urban areas constitute these metals to the Danube river system upstream from the Iron Gate.

Unlike metal concentrations in surface water, where there are clear and unambiguous EC guidelines, there are no agreed European standards of metal levels in river or floodplain sediments. Within the policy of water protection, the European Union replaced the "user" approach by the "ecosystem" approach in 1992. The EU Framework Directive in the field of water policy (Water Framework Directive – WFD) acquired a "combined" approach within the integrated water management of river basins. For the first time the importance of sediment quality for the entire aquatic system was emphasized, but for the time being the EU has not regulated the quality criteria. However, the Netherlands and Canada have a long legislative tradition in this area. They have developed criteria and regulations on sediment quality and many authors are using their criteria in sediment quality assessment. In Serbia and Montenegro continual monitoring of sediment quality is not performed and there are no regulations concerning quality standards. In this paper sediment quality surveys are evaluated according to Dutch guidelines [38] due to the lack of national legislation. Since there are also no legal regulations in Poland concerning bottom sediment quality test and assessment, Polish researchers considered it appropriate to use Dutch regulation values [39, 40].

We have chosen to use the latest (2000) Dutch Ministry of Housing, Spatial Planning and Environment target and intervention values for soil remediation (Table 4) on the basis that it is a long-established (first introduced in the early 1980's), tried and tested scheme, where the intervention values are based on extensive studies of both the human and eco-toxicological effects of soil contaminants.

The Dutch intervention values for soil/sediment remediation are considered to be numeric manifestations of the concentrations above which it may be said that there is a case of serious contamination. These values indicate the concentration levels of metals, above which the functionality of the soil for human, plant and/or animal life may be seriously compromised or impaired. Target values indicate the level at which there is a sustainable soil quality and gives an indication of the benchmark for environmental quality in the longterm on the assumption of negligible risk to the ecosystem.

It may be concluded that the sediments from Iron Gate can be regarded as unpolluted with As and Pb. A serious contamination of the gorge may be discussed for Zn, while contamination with Cd was observed in the whole examined area, upstream and downstream from the gorge.

Downstream from Tekija (River-km 956) there is an overall decline in the concentration of all metals. Around river-km 851, downstream from the Djerdap gorge, they fall below the target values, except for Cd.

Metal levels in sediments did not exceed intervention values, but were higher than the target values for Ni, Zn, Cu, Cr and especially for Cd, indicating contamination not sufficiently high to require remediation/intervention, but not excluding risk to the ecosystem.

Conclusions

The obtained results indicate the continuous accumulation of heavy metals in the bottom sediment system, which is associated with the sedimentation of suspended solids carried by Danube water.

The increase in heavy metal contamination of the Iron Gate is cause for concern as these metals have the ability

Table 2. Heavy metal concentrations in the sediment of the River Danube (mg/kg) at the sampling sites of Vasiljevic and Tomasevic [37].

Sites	Heavy metal concentrations (mg/kg)						
	Hg	Ni	Zn	Cu	Cr	Pb	Cd
Slankamen	0.30	16.0	150	17	40	27	0.5
Grocka	1.10	32.0	200	21	47	42	1.1
Veliko Gradiste	0.80	39.0	230	25	54	53	1.7
Tekija	0.85	34.0	210	35	50	53	1.4
Milutinovac	0.12	27.0	70	11	28	21.5	0.2
Brza Palanka	0.59	38.0	140	21	42	54	0.6

Table 3. Percent change in heavy metal concentrations in the sediment of the Iron Gate (boldly marked numbers indicate a decrease) between the studies of Vasiljevic and Tomasevic [37] and the present study at corresponding sites.

Percent change									
Sites	Hg	Ni	Zn	Cu	Cr	Pb	Cd	Fe	Mn
Veliko Gradiste	**96**	156.2	69.3	64	96.1	**8.2**	88.2	74.8	70.5
Tekija	**269**	119	46.6	64.6	86.6	**21.6**	112.9	75.3	92

Table 4. Target values and soil remediation intervention values for selected metals in soils from the Dutch Ministry of Housing, Spatial Planning and Environment [38].

	Hg	As	Ni	Zn	Cu	Cr	Pb	Cd
Target value (mg/kg)	0.3	29	35	140	36	100	85	0.8
Intervention value (mg/kg)	10	55	210	720	190	380	530	12

to bioaccumulate in the tissues of various biota, and may also affect the distribution and density of benthic organisms, as well as the composition and diversity of infaunal communities. The gorge sediments serve as reservoirs for heavy metals and their concentrations are controlled by a variety of physical and chemical factors. It is important to determine the source of these heavy metals and to manage their input into the Iron Gate so that their concentrations in the sediment do not reach toxic values.

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