A new approach to the analysis of the accumulation and enrichment of heavy metals in the Danube River sediment along the Iron Gate reservoir in Serbia

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Abstract: The concentrations of heavy metals (Cu, Zn, Pb and Cd) and long--lived radionuclides (U, Th and Cs) along the Iron Gate reservoir of the River Danube in Serbia were determined. In the years 2005–2009, water and sediments were sampled at six sites along 200 km of the River Danube from Belgrade to the Djerdap (Iron Gate) hydroelectric power plant. The concentrations of heavy metals in the sediment were found to be in the ranges of 27.9–149.3 mg kg^{-1} for Cu, 55.2–228.4 mg kg^{-1} for Zn, 13.5–71.6 mg kg^{-1} for Pb, 0.3–25.2 mg kg^{-1} for Cd and 4.0–17.5 Bq L^{-1} for ^{137}Cs. These values are in correlation with the concentrations in the river water when expressed by the equilibrium coefficients (K_d) between the solid and liquid phases. The behaviors of the heavy metals were evaluated by applications models for the prediction of the behavior of pollutants in rivers. The fluxes of heavy metals from water to sediment and *vice versa* were also determined.

Key words: distribution coefficients; heavy metals; MOIRA model; sediment.

INTRODUCTION

The Danube is the second largest river in Europe, spanning between its source and mouth in the Black Sea a total length of 2,875 km and covering an overall catchments area of 817,000 km^2. Thirteen countries are connected by the Danube and are responsible for the protection of the water quality of the river and its catchments. The territory of Serbia represents approximately 10 % of the Danube river basin. Three large rivers, the Tisza, the Sava, and the Velika Morava, increase the water volume of the Danube in Serbia by more than 2.5 times. On entering Serbia at 1425.5 km from the mouth, the average flow rate of the Danube is 2400 m^3 s^{-1}, while it is 5500 m^3 s^{-1} on leaving the country at 825 km

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from the mouth. The largest in central Europe, the Iron Gate reservoir was constructed for a 1200 MW hydroelectric power plant on the Danube River, 933 km from its mouth in the Black Sea.

Due to the Iron Gate, the flow of the Danube in this section is retarded. A high level of suspended solids, consisting of fine sediments, causes the sedimentation rate to rise as the Danube water approaches the Iron Gate canyon. Therefore, the Iron Gate reservoir acts as a depository of fine sediments and pollutants.

In the Danube River catchment area, both large cities, such as Belgrade, and smaller settlements conjunctively rely on ground water and surface water. Other uses of the rivers and their surroundings include agriculture, forestry, power generation and recreation.

Heavy metals are known to cause deleterious effects on human health.[1] In view of the persistence of many micropollutants and their potential for bioaccumulation, sediments are regarded as important sources that seriously threaten natural ecosystems.[2,3] Unlike organic pollutants, natural processes of decomposition do not remove heavy metals. Upon entering natural waters, heavy metals and radionuclides, originating from anthropogenic sources in traceable concentrations, become part of the water sediment system and their distribution processes are controlled by a dynamic set of physical and chemical interactions and equilibria.[4]

Heavy metals of anthropogenic origin are generally introduced into river systems as inorganic complexes or hydrated ions, which are easily adsorbed on surfaces of sediment particles by relatively weak physical or chemical bonds. Thus, heavy metals of anthropogenic origin are found in sediments predominantly in the labile extractable fraction.[2,5]

The enrichment of heavy metals in the environment can result from both anthropogenic activities and natural processes. High concentrations of heavy metals with geogenic origins in sediments do not imply high potential toxicity to ecology.[6] Consequently, a clear differentiation of the anthropogenic from the geogenic heavy metals is important in evaluating the extent of pollution, preventing further environmental damages and planning remedial strategies. The trend of heavy metal accumulation in sediment surfaces over the last one hundred years showed increased concentrations of heavy metals, originating mainly from anthropogenic activities.

The results of the Joint Danube Survey for the concentrations of heavy metals in sediment along the entire course of the River Danube and several of its main tributaries performed in year 2001 showed the values: 28.3–197.7 mg kg^{-1} for Cu; 99–398 mg kg^{-1} for Zn; 18.2–85.0 mg kg^{-1} for Pb and < 1.1–7.6 mg kg^{-1} for Cd. Downstream from the Iron Gate reservoir, the concentrations of heavy metals remained stable or decreased slightly down to the Danube delta.[7] Heavy

metals are among the most common environmental pollutants. In water and biota, they indicate the presence of natural and anthropogenic sources.

In the Saricay Stream Basin of southwestern Turkey,[8] the traceable metal levels in the sediments displayed marked seasonal and regional variations, which were attributed to anthropogenic influences and natural processes.

An analysis of the sediment quality of the River Po[9] identified three major factors which explained the observed variance. The first and the second factors corresponded to anthropogenic inputs and geological factors, while the third included seasonal processes of minor importance.

The investigation of heavy metal contamination of the River Yamuna in India showed significant enrichment of the sediment with Cd and Ni.[10] Many authors use enrichment factors when assessing the pollution level of rivers. The heavy metal enrichment factor (*EF*) suggested concentrations above the background level in the study area.

The enrichment of trace elements in river-basin water indicates their impact as potentially hazardous to the environment and human health.

The present study was conducted to determine the heavy metals distribution and accumulation in the Danube Iron Gate reservoir and to estimate the traceable metal fluxes from river water to sediment and *vice versa*. This is of fundamental importance in the environmental study of river systems, especially of the Danube Iron Gate reservoir.

MATERIALS AND METHODS

From the autumn of 2005 to the spring of 2009, samples of both the sediment and water of the River Danube were collected at the six sites marked in Fig. 1: Belgrade (1), Smederevo (2), Veliko Gradište (3), Donji Milanovac (4), Tekija (5) and Kladovo (6). The specimens were taken for analysis in appropriate containers, according to the standard procedure.[11] The sediment samples were collected using grab sampler from the top 10 cm of the sediment surface.
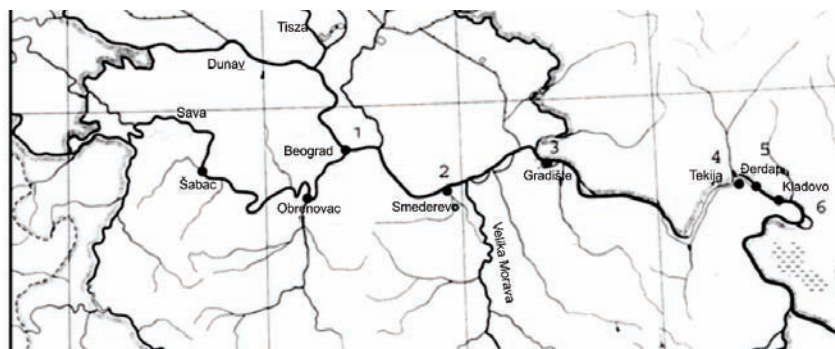

Fig. 1. Locations and distances from mouth of the sampling stations on the Danube River: 1) Belgrade, 1162 km; 2) Smederevo, 1116 km; 3) Veliko Gradište, 1059 km; 4) Donji Milanovac, 990 km; 5) Tekija, 955 km and 6) Kladovo, 944 km.

The sediment samples were dried in an oven at 105 °C to constant weight. The caked sediment material was then finely ground and 2.5 g samples were dissolved in 25 cm^3 1/1 HNO$_3$. For the investigation of the quality parameters of the river water, standard analytical methods were used, as well as atomic absorption spectrometry.[12,13] The concentrations of heavy metals were determined by flame atomic absorption spectrometry in an air/acetylene flow, using a Perkin Elmer AA 200 spectrometer. The cadmium concentration was determined by the graphite furnace technique using a Perkin Elmer AA 600 with a transversely heated graphite atomizer (THGA) with the Zeeman background correction. The THGA provides a uniform temperature distribution over the entire tube length, rapid heating and an integrated L'vov platform, resulting in an improved signal/interference ratio and high analytical sensitivity.[14] Analytical injection (20 μL) and atomization were realized in five steps, controlled by appropriate software and an auto-sampler.

For both techniques, adequate hollow cathode lamps (HCL) were used for irradiation and mixed reference standard solutions were prepared for analysis, using Merck certified atomic absorption stock standards (1000 μg mL^{-1}) and Mili-Q purified water. No modifiers were added. The standard reference material used to verify the accuracy of the methods for the determination of heavy metals in water. The precision of these methods was better than 10 %.

Activity of the gamma-ray emitters was analyzed by a multichannel analyzer using a reverse electrode HPGe detector with 23 % relative efficiency. Sediment samples were dried in a drying oven at 105 °C temperature. The radioactivity of sediment samples was measured for the fraction of particles that passed through a 1.0 mm sieve, after establishing the radioactive equilibrium between ^{220}Rn and its daughter products.

The methods of correlation analysis were applied in the treatment of the experimental data. Relative standard deviation was generally less than 15 %.

RESULTS AND DISCUSSION

Distribution of heavy metals in the Iron Gate Danube River reservoir

The quantities of heavy metals found in the sediments of the River Danube in the slowdown section from Belgrade to the Djerdap hydroelectric power station are presented in Table I. The concentrations of heavy metals in sediment were found to be in the ranges: 27.9–149.3 mg kg^{-1} for Cu, 55.2–228.4 mg kg^{-1} for Zn, 13.5–71.6 mg kg^{-1} for Pb and 0.3–25.2 mg kg^{-1} for Cd.

TABLE I. Concentrations of heavy metals in the sediments (mg kg^{-1}) at different sampling sites. Locations and distances from the mouth of the sampling stations on the Danube River: 1) Belgrade, 1162 km; 2) Smederevo, 1116 km; 3) Veliko Gradište, 1059 km; 4) Donji Milanovac, 990 km; 5) Tekija, 955 km and 6) Kladovo, 944 km

Location	Cu (min)	Cu (max)	Zn (min)	Zn (max)	Pb (min)	Pb (max)	Cd (min)	Cd (max)
1	31.70	118.20	56.60	173.20	13.50	50.10	0.40	4.20
2	35.80	107.60	55.20	199.00	15.60	59.30	0.30	4.80
3	27.90	102.30	62.50	201.30	23.20	60.70	0.50	7.80
4	35.30	125.50	69.10	205.60	21.40	67.20	0.80	12.60
5	39.70	149.30	77.20	228.40	19.60	70.30	2.30	25.20
6	33.40	111.30	70.50	223.60	19.70	71.60	1.80	20.40

The heavy metal levels in sediment displayed seasonal variation. The level of heavy metals in the sediment in autumn, when the water level was lower than in spring, was higher by up to 20 % in comparison to the spring levels. The heavy metals concentrations slightly increased down to Iron Gate reservoir (location 5, just before the dam). Compared to the values at locations 1 to 4, higher Cd concentrations were observed in the proximity of the dam. The concentrations of heavy metals in river water are presented in Table II. The heavy metals levels in the River Danube water and sediment displayed seasonal fluctuations. Many factors influence the seasonal variations in concentrations of heavy metals in river sediment. The seasonal behavior of heavy metals can be explained by the impact of wastewaters that cause high levels of metals during the dry season, and by the flushing of agricultural land, which enriches river water with compounds containing trace metals.

TABLE II. Concentrations of heavy metals in the water (μg dm^{-3}) at different sampling sites. Locations and distances from the mouth of the sampling stations on the Danube River: 1) Belgrade, 1162 km; 2) Smederevo, 1116 km; 3) Veliko Gradište, 1059 km; 4) Donji Milanovac, 990 km; 5) Tekija, 955 km and 6) Kladovo, 944 km

Location	Cu (min)	Cu (max)	Zn (min)	Zn (max)	Pb (min)	Pb (max)	Cd (min)	Cd (max)
1	25.20	106.50	63.20	147.10	4.90	15.60	0.40	1.70
2	22.30	99.80	68.50	145.70	5.10	18.30	0.80	3.10
3	18.40	103.20	67.50	154.80	3.80	16.70	0.50	2.80
4	16.70	88.50	62.10	106.80	2.80	14.60	0.50	3.10
5	18.20	132.50	79.60	104.20	2.70	11.30	0.30	2.40
6	15.30	88.20	61.60	96.60	2.20	14.40	0.20	2.50

Enrichment factors (*EF*s) have traditionally been used to evaluate possible anthropogenic inputs to the observed sediment metals. In this study, the *EF*s were calculated as follows:[15]

$$EF = (\text{Me/Al})_{\text{sample}}/(\text{Me/Al})_{\text{crust}} \qquad (1)$$

The *EF* is the ratio between the mass fractions of the examined metal and aluminum (Al) in the sample and their mass fractions in uncontaminated crust minerals. The baseline values for Me_{crust} were taken from published data.[16] Baseline values for Me_{crust} were as follows: 127.0 mg kg^{-1} for Zn, 32.0 mg kg^{-1} for Cu, 16.0 mg kg^{-1} for Pb, 0.2 mg kg^{-1} for Cd, and 6.9 % for Al.

Heavy metals concentrations higher than twice the background value implies anthropogenic pollution, while *EF* values higher than 2 indicate contamination.[7,17]

In the study of heavy metal contamination of the River Yamuna, enrichment factors for each of the heavy metals in the sediments was calculated based on the background value of the metal, taken as the world average of the metal in soil.[5]

This approach is not entirely satisfactory for the evaluation of a possible anthropogenic impact.

The river sediment is an integral and dynamic part of a river basin. It originates from the upstream weathering of minerals and soils, and is susceptible to transport downstream by the river water. Sediments are usually considered as sinks for trace metals.

Sediments show high capacity to accumulate and, in time, integrate low concentrations of trace elements in water. During their transport, heavy metals are distributed between the aqueous phase and the suspended sediment. Partitioning of heavy metals between the suspended matter and water is described in terms of the distribution coefficient K_d (m^3 g^{-1}), expressed as the concentration ratio under equilibrium conditions.[18,10]

The minimum and maximum values of the distribution coefficients of the four examined metals for high (spring) and low (autumn) water level at the six locations are presented in Figs. 2–5, respectively. The K_d coefficients decreased in the order Cd>Pb>Cu≈Zn. The distribution coefficients of all the investigated heavy metals demonstrate the capability of the sediment to accumulate each of the metals.
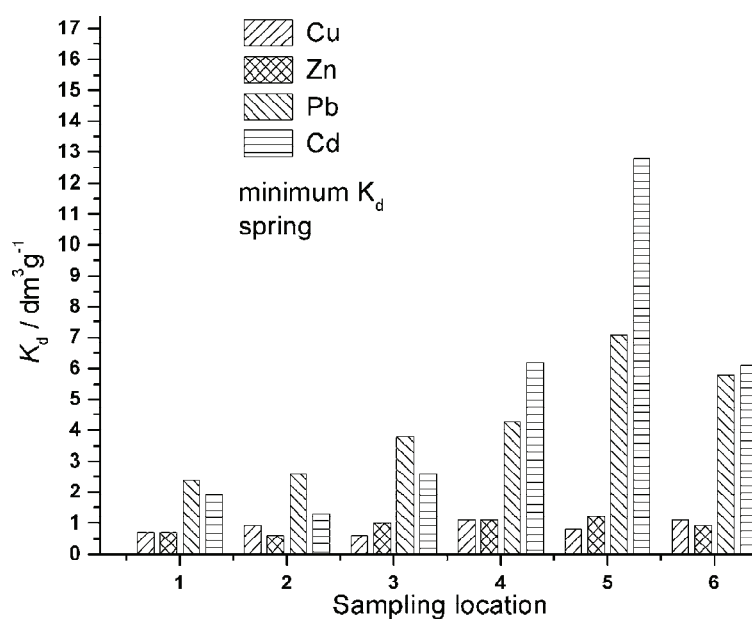

Fig. 2. The minimum K_d values at high water levels for 6 locations (spring, period 2005–2009). Locations and distances from the mouth of the sampling stations on the Danube River: 1) Belgrade, 1162 km; 2) Smederevo, 1116 km; 3) Veliko Gradište, 1059 km; 4) Donji Milanovac, 990 km; 5) Tekija, 955 km and 6) Kladovo, 944 km.
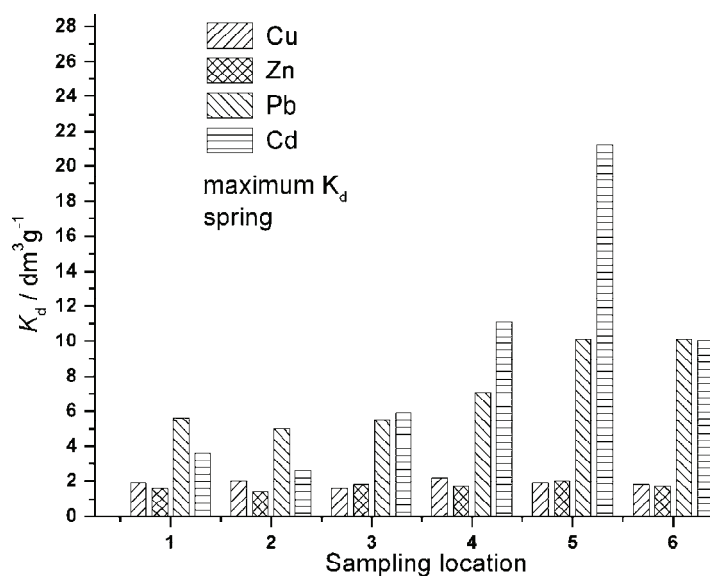
Fig. 3. The maximum K_d values at high water levels for 6 locations (spring, period 2005–2009). Locations and distances from the mouth of the sampling stations on the Danube River: 1) Belgrade, 1162 km; 2) Smederevo, 1116 km; 3) Veliko Gradište, 1059 km; 4) Donji Milanovac, 990 km; 5) Tekija, 955 km and 6) Kladovo, 944 km.
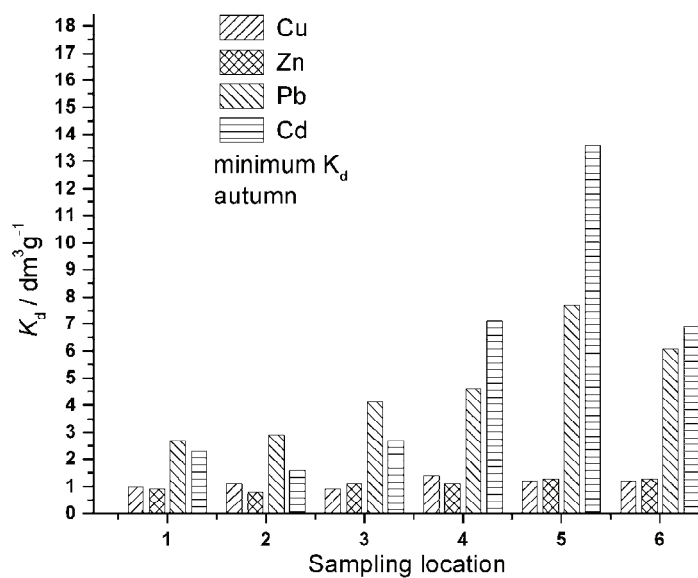

Fig. 4. The minimum Kd values at low water levels for 6 locations (autumn, period 2005–2009). Locations and distances from the mouth of the sampling stations on the Danube River:1) Belgrade, 1162 km; 2) Smederevo, 1116 km; 3) Veliko Gradište, 1059 km; 4) Donji Milanovac, 990 km; 5) Tekija, 955 km and 6) Kladovo, 944 km.
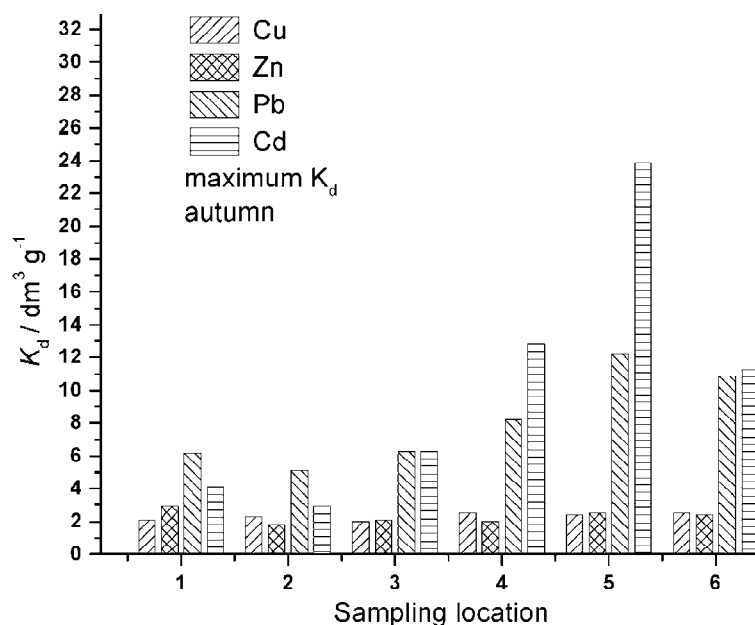
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Fig. 5. The maximum K_d values at low water levels for 6 locations (autumn, period 2005–2009). Locations and distances from the mouth of the sampling stations on the Danube River: 1) Belgrade, 1162 km; 2) Smederevo, 1116 km; 3) Veliko Gradište, 1059 km; 4) Donji Milanovac, 990 km; 5) Tekija, 955 km and 6) Kladovo, 944 km.

The behaviors of heavy metals depend on hydraulic and geo-chemical processes. For an evaluation of toxicity, it is important to determine the fluxes of the heavy metals from the river water to the sediment and *vice versa*, and from the sediment to the deep sediment. The fraction in the sediment is not expected to present a direct danger provided that the metal ions are immobilized due to encapsulation. Thus, distribution coefficients between the sediment and the river water indicate to the exchangeable and mobile fractions of the heavy metals responsible for the eco-toxicological potential of heavy metals.

The interaction of dissolved heavy metals in river water with suspended solids and bottom sediment is based on the hypotheses of a reversible and rapid equilibrium between dissolved (c_w, mg m^{-3}) and the adsorbed (c_s, mg kg^{-1}) phases of the heavy metals, where:

$$K_d = c_s/c_w \tag{2}$$

The partitions of the heavy metals between the different phases presented the opportunity to apply models for predicting their behavior in the Iron Gate reservoir. In this study, models for predicting the migration of radionuclides through rivers[18] were applied in order to evaluate the contamination level of the River Danube ecosystem and its anthropogenic intake of heavy metals.

The Moira model calculated the radionuclide flux from water to sediment (F_{ws}) by multiplying the concentration of dissolved radionuclide by the migration velocity (v) and the sedimentation velocity (v_s). The Moira model was applied to calculate the heavy metal flux from water to sediment (F_{ws}):

$$F_{ws} = (v + v_s)c_w \qquad (3)$$

The flux of heavy metal migrating to the sediment due to sedimentation is given by:

$$F = S_r K_D c_w \qquad (4)$$

where S_r is the net sedimentation rate (kg m^{-2} s^{-1}).

The heavy metal flux from sediment to water (often called re-suspension) can be calculated using the formula:

$$F_{sw} = K_{sw} D_{ep} \qquad (5)$$

where K_{sw} is the rate of migration (s^{-1}) and D_{ep} is the heavy metal deposit (kg m^{-2}).

The non-reversible process of tracer interaction with bottom sediment is modeled by the equation:

$$F_{ds} = K_{ds} D_{ep} \qquad (6)$$

The fluxes from water to sediment (F_{ws}) according to Eq. 3 (in 10^8 kg m^{-2} s^{-1}) were 1.5–2.6 for Cu; 2.4–3.2 for Zn; 2.3–3.8 for Pb and 3.8–7.8 for Cd. The fluxes were calculated using a value for the velocity ($v+v_s$) of 3.5×10^{-7} m s^{-1}. This value for velocity was taken from a published modeling study,[19] while taking into account that the published data were determined for ^{90}Sr. The analogy with heavy metals comes from the similar mobility in the aquatic environment. The rate of migration, K_{sw}, according to the Moira model (Eq. (5)), was 5.6×10^{-9} s^{-1}, which implies values of heavy metal flux from sediment to water of the order of magnitude 10^{-12}–10^{-10} kg m^{-2} s^{-1}.

The migration rate to the deep sediment K_{ds} (Eq. (5)) accounts for non-reversible processes that prevent the re-suspension of heavy metals to water. These processes are significant for ^{137}Cs, while negligible for ^{90}Sr.[18] The present results lead to a similar conclusion for the investigated heavy metals. Irreversible processes of heavy metals migration to the deep sediment were not significant, and neither were processes of re-suspension. The implicit enrichment of heavy metals in the sediment can be recognized from the differences in the K_d values, which originate from the intake of heavy metals from anthropogenic sources. The high total concentrations of heavy metals in sediment may not necessarily indicate anthropogenic contamination because of the different background levels in the parent materials and sediment properties.[20] In addition, heavy metals in fluvial systems can be transported along hydraulic gradients for hundreds of kilometers in a relatively short time.[21]

The distribution coefficient K_d is often used to characterize the mobility of heavy metals in aquatic environments.[22] Low K_d values indicate that most of the metals present in the system remain in the water phase and are available for transport, chemical processes, and plant uptake; on the other hand, large K_d values reflect a large affinity of sediment for heavy metals. The relatively high K_d values in the Iron Gate reservoir of the Danube imply that the sorption capacity of its sediment is far from saturated, despite the adsorption mechanism. Heavy metals occupied an initial region on vacant sites, nearly linear for the K_d values. Enriched sediment concentrations of heavy metals originating from anthropogenic sources under such conditions do not indicate the level of contamination. In the case of contamination, the K_d values will be lower and the concentrations heavy metals in the river water higher. The enrichment of pollutants in river sediment usually reflects upstream source(s) of heavy metals resulting from anthropogenic contamination. Comparisons of the minimum and maximum K_d values (Figs. 2–5) imply a negligible anthropogenic impact of Cu and Zn, but for sites 4 to 6, it imply anthropogenic influence and enrichment of Pb and Cd in the sediment at distances of about 50 km before the dam.

This means that instead of the total metal concentration, the changes in K_d could be used as a criterion to assess potential effects of sediment concentrations of heavy metals. The use of total metal concentration as a criterion to assess the potential effect of sediment concentrations implies that all forms of a given metal have an equal impact on the environment; such an assumption is untenable.[20]

Distribution of long-lived radionuclides

The accumulation of long-lived radionuclides in the River Danube ecosystem was the subject of a previous study.[23] It was proven that the natural radioactivity of the Danube sediment reflects an equilibrium distribution. The concentrations of long-lived natural radionuclides in the sediment practically did not change in years 2005–2009. The activities measured were ^{238}U: 23–34 Bq kg^{-1} and ^{232}Th: 26–45 Bq kg^{-1}. Unlike the examined heavy metals, the input of the heavy metals uranium and thorium originated mainly from diffuse sources of geogenic origin, ascertained from the small fluctuation in concentrations and absence of point sources. Compared to results of 20 years ago, there were no oscillations in the thorium content.[23]

In addition to the natural radioactivity, there is also anthropogenic radioactivity present in the Danube river ecosystem, because of nuclear weapons tests and the Chernobyl nuclear accident. In the Danube sediment, measurable concentrations of ^{137}Cs were also detected because of the Chernobyl fallout. The concentrations of ^{137}Cs found in the sediment were between 4.0 and 11.0 Bq kg^{-1}. In earlier findings, the radioactivity from ^{137}Cs in the river water was below 0.01 Bq L^{-1} and in the sediment between 12 and 33 Bq kg^{-1}. The present results show an absence of further accumulation of radionuclides in the River Danube sedi-

ment. The equilibrium distribution of ^{137}Cs implies the rate of decline in the concentrations ^{137}Cs activity in river water, corresponding to an effective ecological half life (T_{eff}) in the 11–22-year range.[24]

The measurements of radionuclides accumulation in the sediment show that the concentration of Cs is lower near the River Danube mouth than in its estuary itself. The Cs is transported *via* sea currents, rather than by river waters. In addition, river slime sediment contains lower Cs concentration than sea slime sediment.[25]

CONCLUSIONS

This study was based on the application of the distribution law in determining the coefficients of distribution of heavy metals between solid and liquid phases, and models for predicting the migration of traceable metals (heavy metals and radionuclides) through rivers. The fluxes of heavy metals from water to sediment and *vice versa* show their accumulation in sediment, which is a mayor concern in the assessment of the effects of anthropogenic influences. This approach enables the determination of the degree of accumulation of heavy metals and their impact as potentially hazardous to the environmental and human health.

The levels of heavy metals in the Danube water and sediment along the Iron Gate reservoir displayed seasonal fluctuations, with an accumulation before the dam. Anthropogenic origin was indicated only for Cd and Pb.

Effective ecological half-life (T_{eff}) of ^{137}Cs in the river water ranged from 11 to 22 years.

И З В О Д

НОВИ ПРИСТУП У АНАЛИЗИ АКУМУЛИРАЊА И КОНЦЕНТРОВАЊА ТЕШКИХ МЕТАЛА У ЂЕРДАПСКОЈ АКУМУЛАЦИЈИ

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Одређиване су концентрације тешких метала (Cu, Zn, Pb и Cd) и дугоживећих радионуклида (U, Th и Cs) у води и седименту Дунава и Ђердапске акумулације на шест локација дужине тока 200 km. Концентрације тешких метала у седименту биле су у опсегу од 27,9––149,31 mg kg^{-1} за бакар, 55,2–228,4 mg kg^{-1} за цинк, 13,5–71,6 mg kg^{-1} за олово, 0,3–25,2 mg kg^{-1} за кадмијум и 4,0–17,5 Bq kg^{-1} za ^{137}Cs. Ове вредности су у корелацији са њиховим вредностима у речној води ако се изразе помоћу коефицијента расподеле (K_d) између чврсте и течне фазе. Понашање тешких метала оцењено је на основу примене модела за прогнозирање понашања полутаната у рекама. Одређени су флуксеви тешких метала из воде у седимент и обрнуто.

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REFERENCES

1. B. Song, M. Lei, T. Chen, Y. Zheng, Y. Xie, X. Li, D. Gao, *J. Environ. Sci.* **21** (2009) 1702
2. K. P. Singh, A. Malik, N. Basant, V. K. Sing, A. Basant, *Chemom. Intell. Lab. Syst.* **87** (2007) 185
3. S. Audry, J. Schafer, G. Blanc, J. M. Jouananneau, *Environ. Pollut.* **132** (2004) 413
4. C. K. Jain, *Water Res.* **38** (2004) 569
5. W. Zhang, H. Feng, J. Chang, J. Qu, H. Xie, L. Yu, *Environ. Pollut.* **157** (2009) 4318
6. B. Xu, X. Yang, Z. Gu, Y. Zhang, Y. Chen, Y. Lv, *Chemosphere* **75** (2009) 442
7. P. Woitke, J. Wellmitz, D. Helm, M. Kube, P. Lepom, P. Litheraty, *Chemosphere* **51** (2003) 633
8. A. L Tuna, F. Yilmaz, A. Demirak, N. Ozdemir, *Environ. Monit. Assess.* **125** (2007) 47
9. M. Camusso, S. Galassi, D. Vignati, *Water Res.* **36** (2002) 2491
10. A. Kaushik, A. Kansal, S. Meena, S. Kumari, C. P. Kaushik, *J. Hazard. Mater.* **164** (2009) 265
11. Z. Vuković, M. Radenković, S. Marković, D. Vuković, *J. Serb. Chem. Soc.* **76** (2011) 795
12. R. Reeve, *Environmental Analysis*, Wiley, New York, 1994
13. S. Murko, R. Milacić, M. Veber, J. Scantar, *J. Serb. Chem. Soc.* **75** (2010) 113
14. A. E. Greenberg, Ed., *Standard methods for the Examination of Water and Wastewater*, 19th ed., American Public Health Association, Washington (DC), 1995
15. W. Salomons, U. Forsters, *Metals in Hydrosphere*, Springer, Berlin, 1984
16. S. Olivares Rieumont, D. Rosa, L. Lima, D. W. Graham, K. D. Alessandro, J. Borroto, F. Martinez, J. Sanchez, *Water Res.* **39** (2007) 3945
17. S. M. Sakan, D. S. Djordević, D. D. Manojlović, P. S. Polić, *J. Environ. Manag.* **90** (2009) 3382
18. L. Monte, P. Boyer, J. E. Brittain, L. Hakanson, S. Lepicard, J. T. Smith, *J. Environ. Radioac.* **79** (2005) 273
19. L. Monte, *Environ. Modell. Software* **669** (2001) 13
20. K. P. Singh, D. Mohan, V. K. Singh, A. Malik, *J. Hydrol.* **312** (2005) 14
21. W. X. Liu, X. D. Li, Z. G. Shen, D. C. Wang, O. W. H. Wai, Y. S. Li, *Environ. Pollut.* **121** (2003) 377
22. M. T. Morera, J. C. Echeverria, C. Mazkiaran, J. J. Garrido, *Environ. Pollut.* **113** (2001) 135
23. Ž. Vuković, V. Sipka, D. Vuković, D. Todorović, *J. Radioanal. Nucl. Chem.* **268** (2006) 247
24. J. T. Smith, R. T. Clarke, M. Saxén, *J. Environ. Radioac.* **49** (2000) 65
25. A. Strezov, M. Milanov, P. Mishev, T. Stoilova, *Appl. Radiat. Isotopes* **49** (1998) 721.