Distribution and accumulation of heavy metals in the water and sediments of the River Sava

ŽIVORAD VUKOVIĆ[1], MIRJANA RADENKOVIĆ[1], SRBOLJUB J. STANKOVIĆ[1]*
and DUBRAVKA VUKOVIĆ[2]

[1]*Institute of Nuclear Sciences Vinča, P. O. Box 522, Belgrade 11001 and* [2]*Institute of Veterinary Medicine, Vojvode Toze 24, Belgrade 11000, Serbia*

Abstract: The distribution and accumulation of assorted heavy metals and a long-lived radionuclide (Cu, Zn, Pb, Cd, U, Th and ^{137}Cs) in the water and sediment of the River Sava (in Serbia) were investigated at three locations in the vicinity of industrial and urban settlements (Sabac, Obrenovac, Belgrade). The concentrations of heavy metals in the sediment were found to be in the ranges (mg kg^{-1}): 29.6–145.1 for Cu, 53.2–253.6 for Zn, 14.2–78.6 for Pb, 0.3––24.6 for Cd, and 4.0–12.5 Bq l^{-1} for ^{137}Cs. These values correlate to the concentrations in the river water if expressed by equilibrium distribution coefficients K_d (dm^3 g^{-1}) between the solid and liquid phases. The degrees of accumulation and enrichment of tracer metals were determined.

Keywords: accumulation; cesium; enrichment; heavy metals; K_d; sediment.

INTRODUCTION

The studies of heavy metals and other pollutants in river water and sediments have multiplied in recent years, especially for large rivers such as the Danube,[1] Po[2] and Tisza.[3]

Discharges of inorganic and organic micro-pollutants and radioactivity from various industrial, agricultural and municipal sources have resulted in permanently contaminated water, polluted sediments and the accumulation of chemicals in the aquatic food-chain.

In view of the persistence of many micro-pollutants and their potential for bioaccumulation, sediments are regarded as an important source that seriously threatens natural ecosystems[2]. Unlike organic pollutants, heavy metals are not removed by natural processes of decomposition. Heavy metals entering natural waters become part of the water sediment system and their distribution processes

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are controlled by a dynamic set of physical and chemical interactions and equilibria.[4]

Heavy metals are among the most common environmental water and biota pollutants, indicating the presence of both natural and the anthropogenic sources. Heavy metals of anthropogenic origin are generally introduced into the river system as inorganic complexes or hydrated ions, which are easily adsorbed on the surfaces of sediment particles through relatively weak physical or chemical bonds. Thus, heavy metals of anthropogenic origin are found predominantly as a labile extractable fraction in sediments.[5]

The trend of heavy metal accumulation over the last hundred years[6] shows increasing concentrations of heavy metals in surface sediments, which mainly result from anthropogenic activities. The trace metal levels in sediments usually displayed marked seasonal and regional variations, which were attributed to anthropogenic influences and natural processes.[7,8]

An analysis of the River Po sediment quality identified three major factors which explained the observed variance.[2] The first and second factors corresponded to anthropogenic inputs and geological factors, while the third one included seasonal processes of minor importance.

The Sava became an international river in 1992. It drains 95.700 km^2 of land in former Yugoslavia, before entering the Danube at Belgrade in Serbia. For the supply of potable water, both large cities and small villages in the Sava catchment area rely on ground water. Only Belgrade, the Serbian capital, uses ground water and river water conjunctively. The other uses of the river and its surroundings include agriculture, forestry, power generation, recreation *etc*. Increasing industrialization and the growth of large urban centers have been accompanied by increased pollution of the aquatic environment. Furthermore, the changes in the water environment effected by human activity have affected the ecological system of the Sava catchments. Notwithstanding the investigations performed on the upper stretches of River Sava in Slovenia and Croatia,[9,10] little attention has been paid to the quality of its water in Serbia.[11] In this study, the contents of assorted heavy metals and long-lived radionuclides were analyzed with the objective to predict the level and trends of River Sava water and sediment pollution in Serbia.

<div align="center">EXPERIMENTAL</div>

From the autumn of 2005 to the spring of 2009, samples of both river sediment and water were collected at three locations: Sabac (marked with 1), Obrenovac (2) and Belgrade (3). A map of the final stretch of the Sava River with sample collection locations marked is shown in Fig. 1.

The specimens were taken for analysis in proper dishes, according to the standard procedure.[12] The sediment samples were collected with a grab sampler.
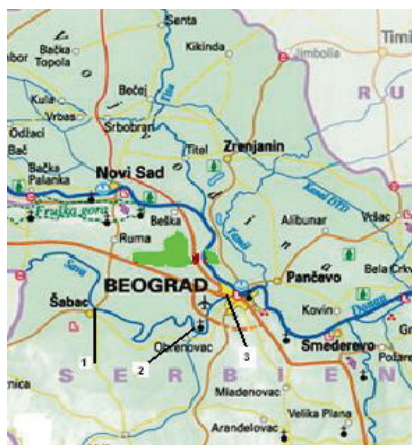
Fig. 1. Location of sampling stations on the Sava River: Šabac – location No. 1, Obrenovac – location No. 2 and Belgrade – location No. 3.

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 of 1/1 HNO$_3$. For investigation of the river water quality parameters, standard analytical methods[13] were used, as well as atomic absorption spectrometry.[14] 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 Perkin Elmer AA 600 with a transversely-heated graphite atomizer (THGA) and a Zeeman Effect background correction system. THGA provides a uniform temperature distribution over the entire length of the tube length, rapid heating and an integrated L'vov platform, resulting in an improved signal/interference ratio and high analytical sensitivity. The analytical injection (20 µl) and the 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 activity of the gamma-ray emitter was analyzed by a multichannel analyzer using a reverse electrode HPGe detector of 23 % relative efficiency. The radioactivity of sediment samples was measured on the fraction of particles that passed through a 1.0 mm sieve, after establishment of the radioactive equilibrium between ^{220}Rn and its daughter products.

RESULTS AND DISCUSSION

The concentrations of heavy metals in the river sediment at the three studied locations, marked Fig. 1, are presented in Table I. There were no large fluctuations in the concentrations of heavy metals in the sediments. Differences in the concentrations existed between the spring and autumn seasons, which were more then 20 % higher in the autumn in the case of Pb and Cd, but negligibly higher for Cu and Zn. The mean values of the concentrations for all the samples amounted to: 56.0 mg kg^{-1} for Zn; 39.0 mg kg^{-1} for Cu; 27.0 for Pb and 4.6 mg kg^{-1} for Cd. In the upper stretch of the Sava River, about 450 km from its confluence, these values were: 136.0 mg kg^{-1} for Zn; 29.0 mg kg^{-1} for Cu, and 22.5

mg kg^{-1} for Pb.[9] Thus, a large discrepancy was obtained only for Zn. In the Sava River sediment in Slovenia, the concentrations of Cd were below 0.8 mg kg^{-1}.[10]

TABLE I. Concentrations of heavy metals in sediment (mg kg^{-1}) from autumn 2005 to spring 2009, min. – minimum, max. – maximum, mean – mean value

Heavy metal	Location No. 1 concentration, mg kg^{-1}			Location No. 2 concentration, mg kg^{-1}			Location No. 3 Concentration, mg kg^{-1}		
	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.
Zn (autumn)	52.0	66.2	83.3	56.5	68.1	78.1	51.5	72.3	86.5
Zn (spring)	28.2	38.9	45.8	48.9	57.5	71.4	49.2	61.8	72.3
Cu (autumn)	28.2	34.3	43.3	45.8	51.4	59.3	39.3	48.2	58.6
Cu (spring)	25.2	31.5	39.1	33.6	47.6	57.3	35.5	46.1	56.0
Pb (autumn)	14.7	20.3	29.1	38.3	42.6	52.0	36.7	43.5	58.2
Pb (spring)	13.9	17.1	19.6	15.4	17.4	19.5	15.3	20.2	22.4
Cd (autumn)	3.9	5.7	8.5	3.8	5.8	7.3	5.8	7.7	8.6
Cd (spring)	2.8	3.8	5.6	3.6	4.9	6.6	3.7	5.1	6.9

The concentrations of heavy metals in the river water at the same three sites are presented in Table II. These concentrations in both the solid and the liquid phases are relatively low. The concentrations of Cd in the river water surmounted the limiting value of 5 µg dm^{-3} for class A surface waters only in a few cases. Pb as well was above its limiting value of 50 µg dm^{-3} in a few cases.[11]

TABLE II. Concentrations of heavy metals in water (µg dm^{-3}) from autumn 2005 to spring 2009, min. – minimum, max. – maximum, mean – mean value

Heavy metal	Location No. 1 concentration, mg kg^{-1}			Location No. 2 concentration, mg kg^{-1}			Location No. 3 Concentration, mg kg^{-1}		
	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.
Zn (autumn)	14.3	41.2	72.1	17.5	46.5	64.2	22.6	56.1	78.4
Zn (spring)	14.5	29.3	45.2	19.5	36.0	44.9	32.3	48.4	64.8
Cu (autumn)	13.2	20.9	32.6	9.2	15.8	24.5	11.7	15.3	17.2
Cu (spring)	16.7	21.2	29.1	7.3	13.6	17.5	5.5	12.8	16.1
Pb (autumn)	2.9	4.1	5.6	3.8	4.7	6.2	4.3	6.5	7.2
Pb (spring)	2.8	3.8	4.9	2.2	3.9	6.1	3.2	5.8	6.3
Cd (autumn)	0.5	2.1	4.1	0.4	0.7	1.0	0.4	0.8	1.3
Cd (spring)	0.3	0.5	0.7	0.3	0.5	0.9	0.3	0.6	0.8

Heavy metals are among the most common environmental pollutants in water and biota, which indicate the presence of natural and anthropogenic sources. The reason for the small fluctuations of the concentrations is the absence of heavy metals in the Sava water originating from point sources at the tested locations. Diffuse pollution originates from many small sources. Most diffuse pollutants stem from the use of land for agriculture, forestry, industry, and urban settlements.[15]

The anthropogenic impact can be quantified by calculating the enrichment factor. Enrichment factors (*EF*) were used to evaluate possible anthropogenic intakes of the observed sediment metals and were calculated according to the formula:

$$EF = (M_{sample} / A_{sample}) / (M_{crust} / A_{crust}) \qquad (1)$$

where M_{sample} and M_{crust} are the levels of the targeted metals in the sediment samples and local uncontaminated crust minerals, respectively, and A_{sample} and A_{crust} are the corresponding values for a normalizing element presumed not enriched due to local contamination. The baseline values for M_{crust} were taken from published data.[1,14]

The values of heavy metals sediment concentrations correlate to their concentrations in the river water. The heavy metal enrichment factor (*EF*) usually suggests concentrations above the background level in the study area. An element concentration higher than twice the background content implies anthropogenic pollution; *EF*s higher than 2 indicate contaminated sites.[1] A similar approach was used in many studies.[3,6,14,16] The present approach to the interpretation of the experimental results was different. In this paper, the partitioning of heavy metals between suspended matter and water is described in terms of the equilibrium distribution coefficient K_d (dm^3 g^{-1}), expressed as the concentration ratio under equilibrium conditions. The processes of heavy metals and radionuclides sorption and desorption by suspended particles and bottom sediments are instantaneous, reversible, and described by a constant distribution coefficient K_d.[17,18] The values of distribution coefficients of the examined four metals are presented in Figs. 2–4 for locations 1–3, respectively. The values of the K_d coefficients fall in the direction Cd > Pb > Cu ≈ Zn. The distribution coefficient for each heavy metal demonstrates the capability of the sediment to accumulate it. In the absence of anthropogenic influences, distribution coefficients reflect the background levels of trace elements in a river sediment, according to the distribution law.

The expanding industrial activity over the post-WW2 years regularly introduced heavy and toxic metals into the river ecosystems. Studies demonstrate that surface water quality has deteriorated noticeably in many countries over past decades, due to poor land use practices.[19]

However, the industrial activity in Serbia slowed down during the past two decades, which is the reason for the weakly noticeable anthropogenic input of heavy metals in the Sava River system from the nearby environment. In spite of this, the high values of K_d for the four examined heavy metals indicate their accumulation in the sediment.

In our opinion, the enrichment factor (*EF*) is more correctly evaluated by comparing the minimal and maximal values of K_d, because a K_d value expresses the real state of a river system, based on the distribution law.
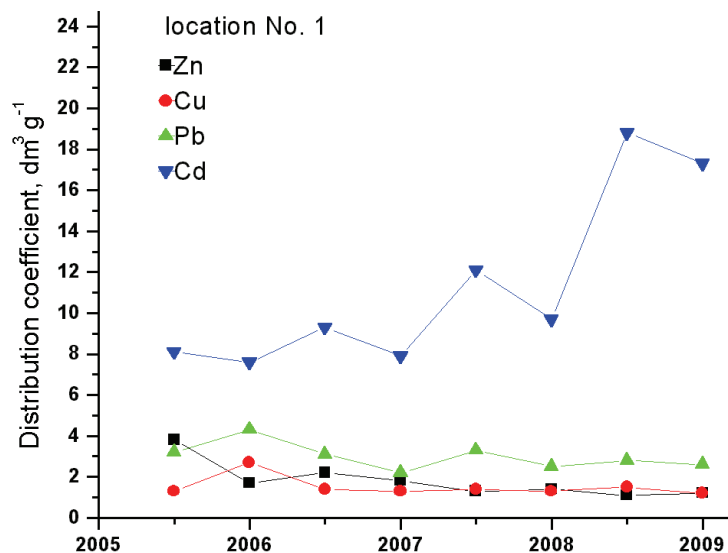
Fig. 2. Distribution coefficient K_d (dm^3 g^{-1}) for location No. 1 in the four-year period.
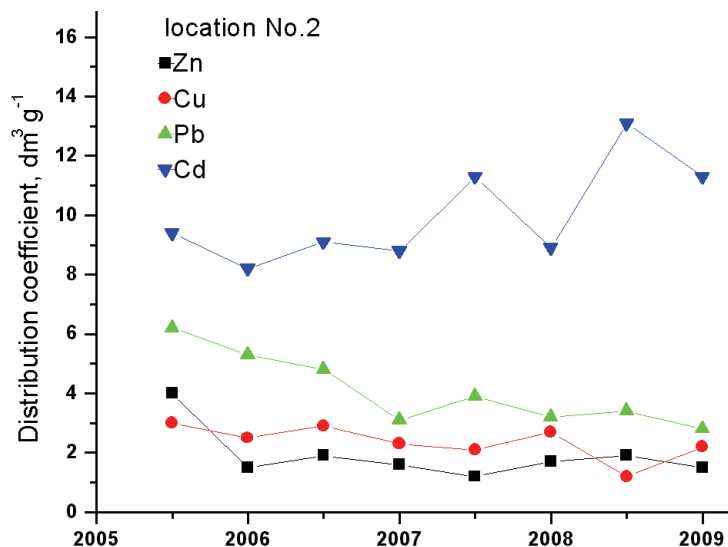

Fig. 3. Distribution coefficient K_d (dm^3 g^{-1}) for location No. 2 in the four-year period.

Experimental results of many studies showed high sorption of heavy metals in sediments, but there were clear differences among the sediments and soil samples.

Hydraulic processes are mainly responsible for the transport and diffusion of toxic substances through water, whereas geochemical processes influence the interaction of dissolved tracer metals with suspended matter and bottom sedi-

ment.[18] River sediment is an integral and dynamic part of a river basin. It originates from the weathering of minerals and soil upstream and is susceptible to transport downstream by the river water.
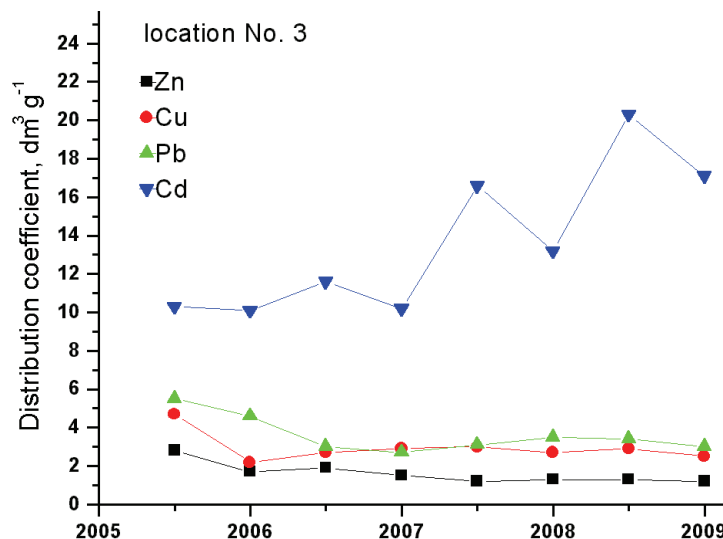

Fig. 4. Distribution coefficient K_d (dm^3 g^{-1}) for location No. 3 in the four-year period.

The reason for the weakly noticeable accumulation of heavy metals in the Sava River sediment lies in the fact that the suspension load of sediment varies broadly depending on the traits of the river streams. The International Atomic Energy Agency default value for rivers[20] is 5.0×10^{-2} kg m^{-3}. The high value of the suspension load, resulting in higher mass loading, arises because the flow of the River Sava is greater down-stream. In this way, large amounts of tracer heavy metals are transported by the Sava River stream to the River Danube and the Black Sea.

The long lived natural radionuclides behaved similar to the investigated heavy metals.[17,18] The results of long-lived radionuclide accumulation in the ecosystem of the Sava River were the subject of a previous study.[21] It was proven that the natural radioactivity of the Sava sediment reflects the natural background (the activity is 26–33 Bq kg^{-1} for ^{238}U and 28–49 Bq kg^{-1} for ^{232}Th). In contrast to the heavy metals, the natural radionuclides do not show seasonal variations because there are no identified point or diffuse sources of natural radionuclides. In addition to the natural radioactivity, there is also anthropogenic radioactivity present in the Sava River ecosystem, as a result of nuclear weapons tests and the Chernobyl nuclear accident. As a consequence of the Chernobyl fallout, ^{137}Cs concentrations of between 4 and 13 Bq kg^{-1} were also detected in the Sava sediment. In earlier findings, the ^{137}Cs radioactivity was below 0.01 Bq l^{-1} in the

river water, and between 12 and 41 Bq kg^{-1} [21] in the sediment. The present results show an absence of radionuclide accumulation in the Sava River sediment. In this case, the flux of Cs radionuclide from sediment to water, due to sediment re-suspension and direct exchange of radionuclide from the bottom sediment, prevails over the radionuclide flux from the water to the sediment.[22]

CONCLUSIONS

The levels of heavy metals in the Sava River water and sediment displayed seasonal fluctuations, which were attributed mainly to natural processes, with a barely noticeable accumulation. The influences of anthropogenic sources are not pronounced. The concentrations of heavy metals in the bottom sediment are in correlation with their concentration in the river water. The degree of accumulation was calculated by comparing the minimal and maximal values of the distribution coefficients for each heavy metal.

The low level of radioactivity from anthropogenic radionuclides (^{137}Cs) originates from the Chernobyl accident and gradually decreases without evidence of any new contamination.

И З В О Д

РАСПОДЕЛА И АКУМУЛАЦИЈА ТЕШКИХ МЕТАЛА У ВОДИ
И СЕДИМЕНТУ РЕКЕ САВЕ

ЖИВОРАД ВУКОВИЋ[1], МИРЈАНА РАДЕНКОВИЋ[1], СРБОЉУБ Ј. СТАНКОВИЋ[1] и ДУБРАВКА ВУКОВИЋ[2]

[1]Инсійшійуій за нуклеарне науке "Винча", ій .йр. 522, 11001 Беоїрад и [2]Инсійшійуій вейіеринарске медицине, Војводе Тозе 24, 11000 Беоїрад

Тешки метали (Cu, Zn, Pb и Cd) и дугоживећи радионуклиди (U, Th и ^{137}Cs) испитивани су у води и седименту реке Саве у току кроз Србију на три локације у близини индустријских и урбаних насеља (Шабац, Обреновац и Београд). Концентрације тешких метала у седименту варирале су у опсегу (mg kg^{-1}): 28,1–145,1 за бакар, 53,2–253,6 за цинк, 14,2––78,6 за олово и 3,0–24,6 за кадмијум. Ове вредности су у корелацији са концентрацијама тешких метала у речној води изражене преко коефицијента дистрибуције K_d (dm^3 g^{-1}) између чврсте и течне фазе. Одређивани су степени акумулације и концентрисања трасерских количина тешких метала.

REFERENCES

1. P. Woitke, J. Wellmitz, D. Helm, M. Kube, P. Lepom, P. Litheraty, *Chemosphere* **51** (2003) 633
2. M. Camusso, S. Galassi, D. Vignati, *Water Res.* **36** (2002) 2491
3. S. M. Sakan, D. S. Djordevic, D. D. Manojlovic, P. S. Polic, *J. Environ. Manage.* **90** (2009) 3382
4. C. K. Jain, *Water Res.* **38**(2004) 569
5. K. P. Singh, A. Malik, N. Basant, V. K. Sing, A. Basant, *Chemom. Intell. Lab. Syst.* **87** (2007) 185

6. B. Xu, X. Yang, Z. Gu, Y. Zhang, Y. Chen, Y. Lv, *Chemosphere* **75** (2009) 442
7. A. L. Tuna, F. Yilmaz, A. Demirak, N. Ozdemir, *Environ. Monit. Assess.* **125** (2007) 47
8. A. Sood, K. D. Singh, P. Pandey, S. Sharma, *Ecol. Indic.* **8** (2008) 709
9. V. Orescanin, L. Mikelic, S. Lulic, G. Pavlovic, N. Coumbassa, *Nucl. Instrum. Meth. B* **263** (2007) 85
10. S. Murko, R. Milačić, M. Veber, J. Ščančar, *J. Serb. Chem. Soc.* **75** (2010) 113
11. J. Krizan, M. Vojinovic-Miloradov, *Water Res.* **31** (1997) 2914
12. N. D. Drndarski, S. Maric, *J. Radioanal. Nucl. Chem.* **130** (1989) 287
13. R. N. Reeve, *Environmental Analysis*, Wiley, Chichester, UK, 1994, p. 200
14. S. Olivares Rieumont, D. Rosa, L. Lima, D. W. Graham, K. D. Alessandro, J. Borroto, F. Martinez, J. Sanchez, *Water Res.* **39** (2007) 3945
15. R. C. Ferrier, B. J. D. Arci, J. MacDonald, M. Altken, *Water Environ. J.* **19** (2005) 361
16. A. Kaushik, A. Kansal, S. Meena, S. Kumari, C. P. Kaushik, *J. Hazard. Mater.* **164** (2009) 265
17. I. Kryshev, P. Boyer, L. Monte, J. E. Brittain, N. N. Dzyuba, A. L. Krylov, A. I. Kryshev, A. V. Nosov, K. D. Sanina, M. I. Zheleznyak, *Sci. Total Environ.* **407** (2009) 2349
18. L. Monte, P. Boyer, J. E. Brittain, L. Hakanson, S. Lepicard, J. T. Smith, *J. Environ. Radioactiv.* **79** (2005) 273
19. S. Li., S. Gu, X. Tan, Q. Zhang, *J. Hazard. Mater.* **165** (2009) 317
20. A. Aguero, *Sci. Total Environ.* **348** (2005) 32
21. Ž. Vukovic, V. Sipka, D. Todorovic, S. J. Stankovic, *J. Radioanal. Nucl. Chem.* **268** (2006) 129
22. J. T. Smith, R. T. Clarke, M. Saxén, *J. Environ. Radioactiv.* **49** (2000) 65.