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Short communication

SHORT COMMUNICATION

Transport and storage of heavy metals in the Sava River Basin in Serbia

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Abstract: Selected heavy metals (Cu, Zn, Pb and Cd) in the water and sediment of the Sava River in Serbia were investigated from three locations in the vicinity of industrial and urban settlements (Šabac, Obrenovac and Belgrade) during the period spring 2007 to autumn 2011. The fluxes of heavy metals from the river water to the sediment due to sedimentation and heavy metal re-suspension fluxes arising from sediment re-suspension at high flows were determined, by application of a model for the assessment of the transport the pollutants through rivers. These fluxes were attributed mainly to natural processes.

Keywords: flux of heavy metal; river sediment; sediment re-suspension.

INTRODUCTION

Toxic heavy metals have been the subject of many studies, mostly in river systems, due to their toxicity, abundance and persistence in the environment, and subsequent accumulation in aquatic habitats.[1–5] Heavy metals of anthropogenic origin are generally introduced into river systems 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 in the labile extractable fraction of a sediment.[6]

Usually, trace metal levels in the sediment display marked seasonal and regional variations, which have been attributed to anthropogenic influences and natural processes.[7,8]

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The speciation of Cd, Cu, Zn and Pb in sediments showed higher bioavailability compared to the other studied metals, and consequently they posed a greater ecological risk.[9]

The Sava River has not been exposed to anthropogenic influence due to dam construction, which decreases sediment transport through sediment retention in the reservoirs. As an integral and dynamic part of the Sava River Basin, the river sediment originates from upstream weathering of minerals and soils, and is susceptible to transport downstream by the river water. The sediment particles were mostly silt and fine-grained sand composed of calcite, quartz, feldspars, ilite and kaolinite.

In the recent past, attention was paid to the water quality of the Sava River in respect to microbiological, chemical and radiochemical parameters.[10–12] In a previous paper,[13] the results of the distribution and accumulation of heavy metals in the water and sediments of the Sava River displayed seasonal fluctuations, which were attributed mainly to natural processes. The sediment studies were performed mainly because sediments are receptors in water bodies. However, re-suspension of sediments leads to a release of soluble heavy metals in the water body.[14] Hitherto, no relevant method has been suggested to assess and quantify the transport of heavy metals between sediments and the overlying water.[15]

The objective of this study was to quantify the transport and storage of heavy metals in the Sava River Basin in Serbia by determination of the fluxes of heavy metals from the river water to the sediment and their re-suspension fluxes under favourable hydraulic conditions.

EXPERIMENTAL

Three sampling sites were chosen along a 100-km stretch of the Sava River upstream from its confluence with the Danube River. For the experiment, water and sediment samples were taken from three sampling locations along the Sava River (Fig. 1). Location No. 1 is near an industrial area of the town of Šabac. Location No. 2 is downstream of the coal-fired power plant “Nikola Tesla”, where the Kolubara River flows into the Sava River. Location No.3 is at the confluence of the Sava and the Danube, in the wider metropolitan area of Belgrade. A total of 60 water and sediment samples were collected between 2007 and 2011 at six-month intervals to cover both the dry (autumn, at low flow, $q \leq 500$ m^3 s^{-1}) and wet (spring, at high flow, $q \geq 1200$ m^3 s^{-1}) seasons. Ten litre-size water samples were collected from a depth of 50 cm. Sediment samples were collected at the depth of 10 cm from the top of sediment surface. All samples were dried at 105 °C until constant mass was attained. The caked sediment was then finely ground to grains below 1.0 mm in diameter. Samples of the sediment (2.5 g) were dissolved in 25 cm^3 of 1/1 HNO_3.

The concentrations of heavy metals were determined by flame atomic absorption spectrometry in an air/acetylene flow, using a Perkin Elmer AA200 spectrometer.[16] The cadmium concentration was determined by the graphite furnace atomic absorption spectrometry, using a Perkin Elmer AA600 with a transversely-heated graphite atomizer (THGA) using a Zeeman Effect background correction system. The analytical injection (20 µl) and the atomization were undertaken in five steps, controlled by the appropriate software and auto-sampler.

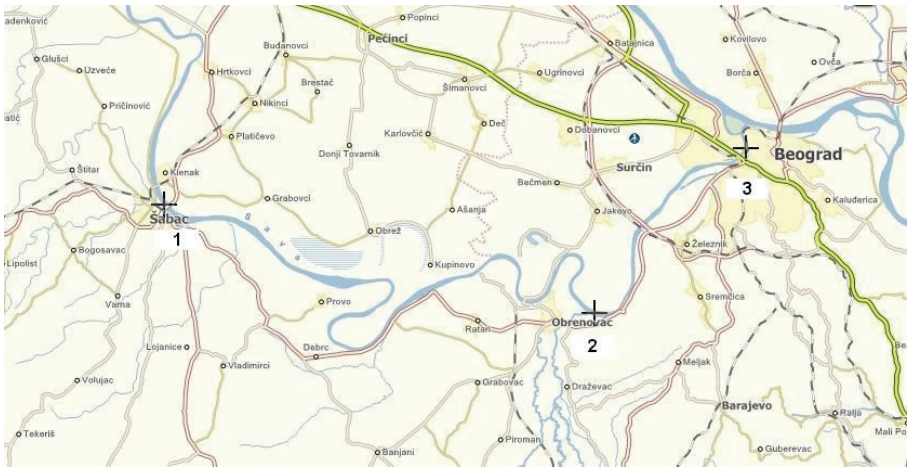


Fig. 1. Location of sampling stations on the Sava River: Šabac – location No. 1, Obrenovac – location No. 2 and Belgrade – location No. 3.

For both techniques, adequate hollow cathode lamps (HCL) were used for irradiation. Mixed reference standard solutions were prepared for the analysis using Merck certified atomic absorption stock standards (1000 μg ml^{-1}) and Milli-Q purified water. No modifiers were added. The quality control (QC) program included reagent blanks, duplicate samples and certified reference materials. The detection limits (DL) for Cu and Zn were 1, for Pb 0.11 and for Cd 0.09 μg dm^{-3}. Measurement errors were less than 5 %.

RESULTS AND DISCUSSION

The minimum, maximum and mean, with standard deviation, concentrations of the heavy metals in the sediments and river water of the studied sites at three locations are presented in Table I for the autumn and spring seasons, respectably. The level of heavy metals in the autumn was higher in comparison to the level in spring. The heavy metal concentrations in the water samples were lower than the maximum permitted concentrations for the protection of aquatic life.[17]

TABLE I. The minimum, maximum and mean concentration of heavy metal in the sediments of the studied sites, for 5 years, from spring 2007 to autumn 2011; total number of sediment samples: 60

Heavy metal (season)	Sediment concentration, mg kg^{-1}		
	Min.	Mean±*SD*	Max.
Zn (spring)	34.5	51.9±18.6	64.8
Zn (autumn)	47.2	62.5±19.7	88.6
Cu (spring)	25.1	41.3±16.2	56.0
Cu (autumn)	28.2	47.5±16.2	72.3
Pb (spring)	13.9	18.1±3.8	22.6
Pb (autumn)	14.7	27.6±12.8	48.2
Cd (spring)	2.8	4.1±2.3	6.9
Cd (autumn)	3.9	4.9±2.7	8.6

A common approach to characterize the partition of an element between the particulate and the dissolved phase is the use of an empirical equilibrium – such as an expression connects dissolved and particulate concentrations *via* the partition coefficient (K_d). Although K_d is not a true thermodynamic mass action constant, it represents a straightforward and easy approach to describe partitioning between dissolved and particulate phases.[19]

The distribution of heavy metals between different phases gives the opportunity to estimate the fluxes of heavy metals from water to sediment due to sedimentation and heavy metals fluxes from the sediment to water due to sediment re-suspension and direct exchange of heavy metals from the sediment to water. The flux of heavy metal migrating to sediment due to sedimentation is given by:[18]

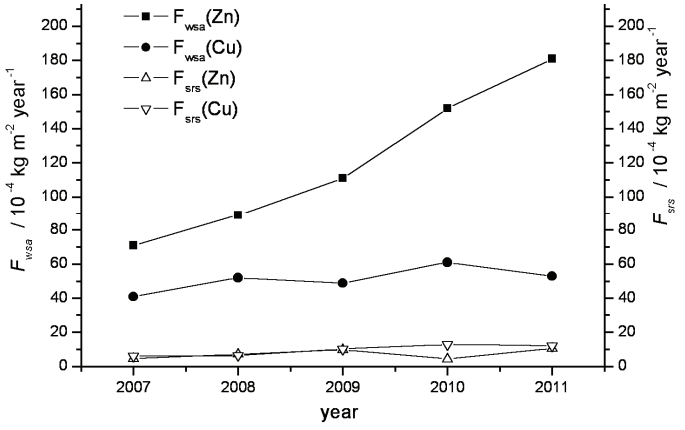
$$F_{ws} = S_f K_d c_w \quad (1)$$

where: F_{ws} is the flux of a heavy metal migrating to the sediment due to sedimentation, S_r is the net sedimentation rate (kg m^{-2} s^{-1}), $K_d = c_s c_w^{-1}$; and c_s (mg kg^{-1}) and c_w (mg m^{-3}) are the concentrations of heavy metals in the sediment and river water, respectively. The flux from water to sediment was calculated according to Eq. (1) using 1.0×10^{-6} m s^{-1} as the value for the sedimentation velocity, taken from modelling studies.[19,20]

The fluxes of heavy metals on a yearly level comprised two fluxes: the flux from water to sediment (F_{wsa} (kg m^{-2} y^{-1}) and the re-suspension fluxes from the deposited sediment to the sediment water interface F_{srs} (kg m^{-2} y^{-1}). The yearly fluxes of the heavy metals from water to the sediment, as well as the fluxes due to sediment re-suspension from the bottom sediment, calculated as the difference of the fluxes F_{ws} at the low flow regime (below 3 m s^{-1}) and the same fluxes at the high flow regime, are presented in Figs. 2a and b (for site 1), 3a and b (for site 2) and 4a and b for site 3. The F_{srs} fluxes were much lower than the F_{wsa} fluxes, because the high flow regime lasted, yearly, between 1.5 and 3.0 months. Re-suspension of the sediment at a high flow, which resulted in the movement of heavy metals between the sediment and overlying water, apparently does not deteriorate the water quality (Table II) but increase the transport of heavy metals by the suspended sediment to the Danube River. The fluxes of heavy metals to the Sava River sediments (Figs. 2–4) were lower than the reported fluxes in the reservoir and lake sediments derived from industrial sites within the watershed.[21,22]

The heavy metal levels in the sediments were greatly reduced due to the transfer of suspended and re-suspended load. Suspension load of sediments in water varies broadly depending on characteristics of the river considered. For the Sava River, with an average flow rate of 1100 m^3 s^{-1}, the suspension load at its confluence is 1.0 10^{-1} kg m^{-3} or 3.5 10^6 t y^{-1}.[23] The distribution coefficients at

high flow were lower in the wet season than in the dry season, due to the re-suspension of the bottom sediment. A high flow rate did not prevent the storage of heavy metals in the sediments, but reduced their accumulation quantity, depending on the duration of the high water regime ($0 \leq F_{srs} \leq 10$ %, Figs. 2–4). The F_{srs} fluxes showed that the sediments would become a source of heavy metals to overlying water if hydraulic changes occurred in the Sava River.



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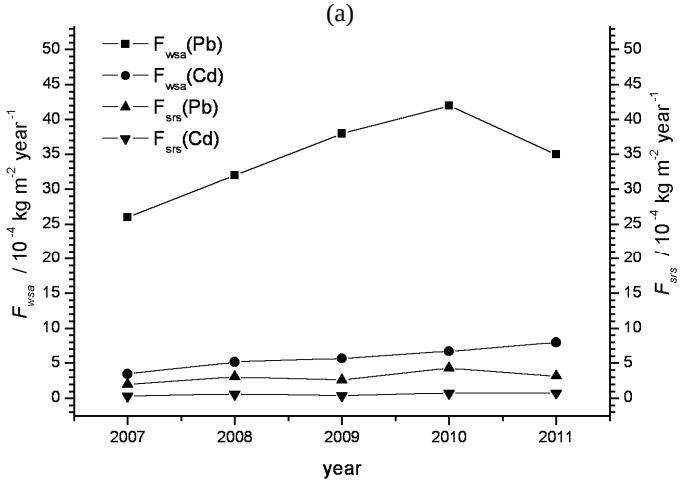


(b)

Fig. 2. The fluxes F_{wsa} / kg m^{-2} y^{-1} and F_{srs} / kg m^{-2} y^{-1} of a) Zn and Cu and b) Pb and Cd for location No. 1 in the five-year period.

The New Serbian Official Regulation on limiting values for pollutants in surface and ground waters and sediments[24] for the first time regulated the limiting values of heavy metals in sediments. By definition, sediment is an essential, dynamic and solid component of aquatic ecosystems, which, due to the strong

tendency to bind pollutants, becomes a reservoir of toxic and persistent compounds of anthropogenic origin.

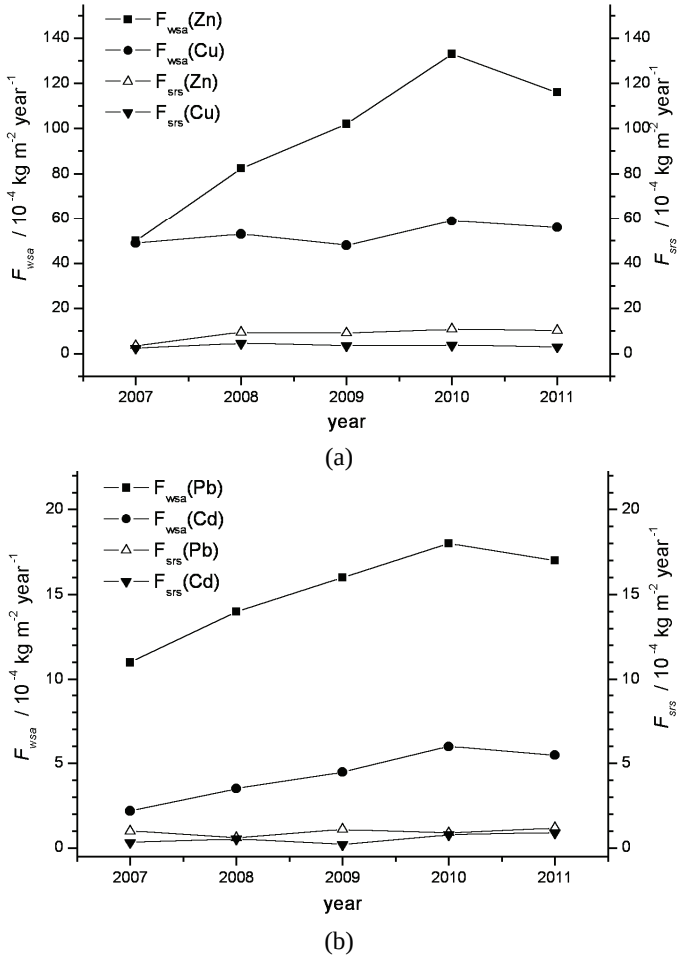
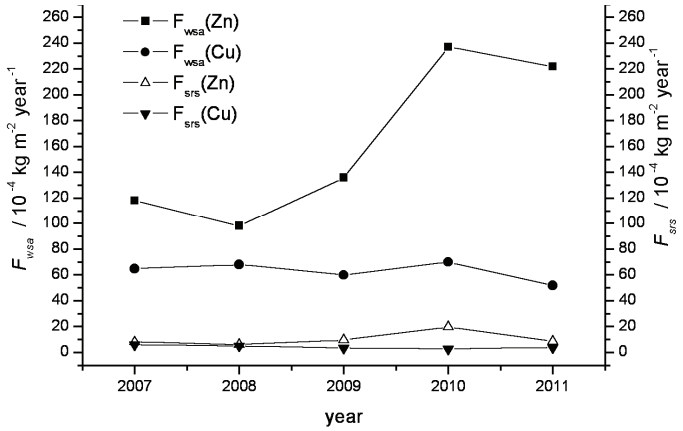
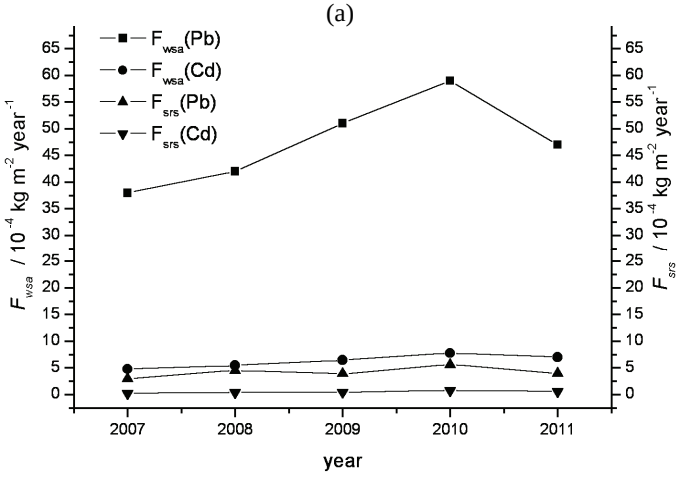


Fig. 3. The fluxes F_{wsa} / kg m^{-2} y^{-1} and F_{srs} / kg m^{-2} y^{-1} of a) Zn and Cu and b) Pb and Cd for location No. 2 in the five-year period.

The obtained results showed that anthropogenic input of heavy metals in the environment of the Sava River Basin in Serbia was not in known amounts. No high variability in analytical data obtained is indicative of modest external sources of heavy metals in the sediment and surface water, mainly due to poor regional industrial activity. An increase of F_{wsa} would be an indicator of the anthropogenic origin of heavy metals in Sava River Basin, because as mass accumulation fluxes they could quantify the contribution of human activities. The fluxes F_{wsa} and F_{srs} were not previously determined.



(a)



(b)

Fig. 4. The fluxes F_{wsa} / kg m^{-2} y^{-1} and F_{srs} / kg m^{-2} y^{-1} of a) Zn and Cu and b) Pb and Cd for location No. 3 in the five-year period.

TABLE II. The minimum, maximum and mean concentration of heavy metal in the river water of the studied sites, for 5 years, from spring 2007 to autumn 2011; total number of sediment samples: 60

Heavy metal (season)	River water concentration, mg m^{-3}		
	Min.	Mean±*SD*	Max.
Zn (spring)	19.3	49.3±16.8	61.4
Zn (autumn)	24.3	45.3±26.5	78.4
Cu (spring)	7.1	17.3±9.9	29.2
Cu (autumn)	9.2	20.1±11.2	33.6
Pb (spring)	2.2	4.6±2.2	6.3
Pb (autumn)	2.9	4.8±2.1	6.7
Cd (spring)	0.3	0.7±0.3	0.9
Cd (autumn)	0.4	1.3±1.1	4.1

CONCLUSIONS

The performed analyses of heavy metals in the Sava River water and sediment at three selected sites in Serbia showed that their accumulation in the sediments was predominantly influenced by natural factors. The fluxes of heavy metals from the river water to the sediments and heavy metal re-suspension fluxes due sediment re-suspension under favourable hydraulic conditions were determined. The study indicated that the Sava River sediment is a sink for heavy metals, but also the source of heavy metal transfer to the water column under favourable hydraulic condition. At high flow, fluvial erosion occurs and removes part of the previously deposited heavy metals from the sediments.

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И З В О Д

ТРАНСПОРТ И СКЛАДИШТЕЊЕ ТЕШКИХ МЕТАЛА У БАЗЕНУ РЕКЕ САВЕ

ДУБРАВКА ВУКОВИЋ[1],СРБОЉУБ СТАНКОВИЋ[2], ЖИВОРАД ВУКОВИЋ[2] и КСЕНИЈА ЈАНКОВИЋ[3]

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Испитивани су изабрани тешки метали (Cu, Zn, Pb и Cd) у речном систему Саве на три локације у близини индустријских и урбаних насеља (Шабац,Обреновац и Београд) у периоду пролеће 2007.–јесен 2011.године. Одређени су флуксеви тешких метала из воде у седимент, као и повратни флуксеви из седимента због ресуспензије седимента у воду при високом протоку, применом модела за процену транспорта полутаната у реци. Ови флуксеви потичу првенстено од природних извора.

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