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Distribution and provenance of heavy metals in sediments of the Vrbas River, Bosnia and Herzegovina

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Abstract: Heavy metals are naturally occurring elements, but they are regarded as significant environmental pollutants due to high density and high toxicity even at low concentrations. The aim of this paper is evaluation of the pollution level of heavy metals in the river and riverbank sediments as well as the estimation of their origin and spatial differences along the course of the Vrbas River through Banja Luka. The concentrations of metals have been assessed using the Inductively coupled plasma – optical emission spectrometry and Advanced mercury analyzer for mercury determination. Anthropogenic impact on heavy metal concentration in sediments was estimated by calculating pollution indices: Geoaccumulation index (I_{geo}), Contamination factor (C_f), Pollution Load Index (PLI), and Potential Ecological Risk Index (E_r). Obtained results indicate that there is no statistically significant spatial difference in metal concentration, indicating that heavy metals in sediments have a constant source. The anthropogenic impact expressed by values of pollution indices showed that sites are generally uncontaminated by Co, Cr, and V and moderately contaminated by Zn, Cu, and Ni. On the contrary, lead, mercury and cadmium pose the highest ecological risk. The anthropogenic source of Pb, Hg and Cd is industry, municipal waste and the combustion of fossil fuels. Obtained results demonstrate the high ecological risk and need for environmental monitoring, supporting an efficient strategy to reduce local pollution and contamination of the investigated system.

Keywords: pollution indices; anthropogenic impact; river sediments.

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INTRODUCTION

The Vrbas River is an important river ecosystem in Bosnia and Herzegovina with a length of 250 km and catchment areas of 5,900 km^2. Before reaching Banja Luka, it passes through a canyon and numerous gorges, which are, from 1955, protected by the Law on the Protection of Natural Values. The Vrbas River , as a right tributary of the Sava, belongs to the Black Sea basin. Along the entire course, this river flows through many towns and villages, but the main anthropogenic influence comes from Banja Luka, one of the largest cities in Bosnia and Herzegovina.

Presence of microelements, dominantly heavy metals, is undoubtedly one of the most important indicators of environmental quality and assessing their content in river sediments is an imperative for estimating the environmental risk.[1] Heavy metals are naturally occurring elements, but they are regarded as significant environmental pollutants due to high density and high toxicity even at low concentrations. The fact that they might remain permanently present in the environment due to their impossibility of degradation and biodegradation, and in that way affect metabolical processes of flora and fauna, identifies them as high category pollutants.[2] The occurrence of heavy metals in waters, sediments and biota can indicate the presence of natural sources (weathering of rocks, atmospheric precipitate, and wind erosion) or anthropogenic activities (urbanization itself, agricultural and urban activities, industrial discharge, mining, transport).[3-6] Rivers, which approximately deliver 20 billion metric

tons of transported sediment to oceans every year, play a key role in Earth surface processes, marine sedimentation and biogeochemical cycles in oceans.[7] Thus, rivers have an essential role in the acceptance and transportation of heavy metals, which can accumulate in the sediments through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the adsorbed components.[8] Hence, water sediments are a highly dynamic part of river systems, not tied to a particular area and are transported through countries in the same river basin. The quality of sediment affects the downstream areas. In particular, the presence of contaminants, such as heavy metals, threatens the good ecological and chemical status of waterways and other water bodies (affecting living organisms, water resources and water management), which are the focal point of the European Water Framework Directive[9], where the Vrbas River belongs as well.

Due to the expanding frequency of the anthropogenic activities, which results in an increase in the concentration of heavy metals in surface sediments and soil, various factors, such as Geoaccumulation index (I_{geo}) - quantitative measure of the extent of metal pollution in the studied sediments, Contamination factor (C_f) - the enrichment in metals in relation to the background concentrations of each metal in sediments, Pollution Load Index (PLI) - the level of pollution, or Potential Ecological Risk Index (E_r) - the degree of heavy metal pollution in

sediments, according to the toxicity of heavy metals and the response of the environment, were introduced to assess the origin of these elements.[5,7,8,10-12]

The aim of this paper is evaluation of the pollution level of heavy metals in the river and riverbank sediments as well as the estimation of their origin and spatial differences along the course of the Vrbas River in Banja Luka city.

EXPERIMENTAL

Study area

The Vrbas River springs at 1715 m above sea level, and flows into the Sava River as its right tributary at 90 m above sea level. The 90 % of the Vrbas basin relief is mountain-hilly, while the lower area of the basin, the remaining 10 %, represents the river plain.[13] This 10 % of river plain, parts of the middle and lower course of the Vrbas River are exposed to floods during high water levels. One of the most threatened municipalities by the Vrbas outflow is Banja Luka, along with the countryside at the confluence with the Sava River.[14] The study area encompasses the part of the Vrbas flow that passes through the Banja Luka city (Fig. 1), located in a valley at an altitude of 164 m in the northwestern part of Bosnia and Herzegovina at the crossing between the Dinaric Mountains in the South and the Pannonian Basin in the North. While the Vrbas River flows through the city center, the confluence with its tributary, Vrbanja is in the immediate urban area.

The climate of Banja Luka is typically temperate continental, with moderately cold winters and warm summers. Climatological and hydrological datasets of temperature values, precipitation, and flows collected at Banja Luka's meteorological station and hydrological station "Delibašino Selo" were analyzed on a seasonal and annual basis (Figs. 2 and 3).

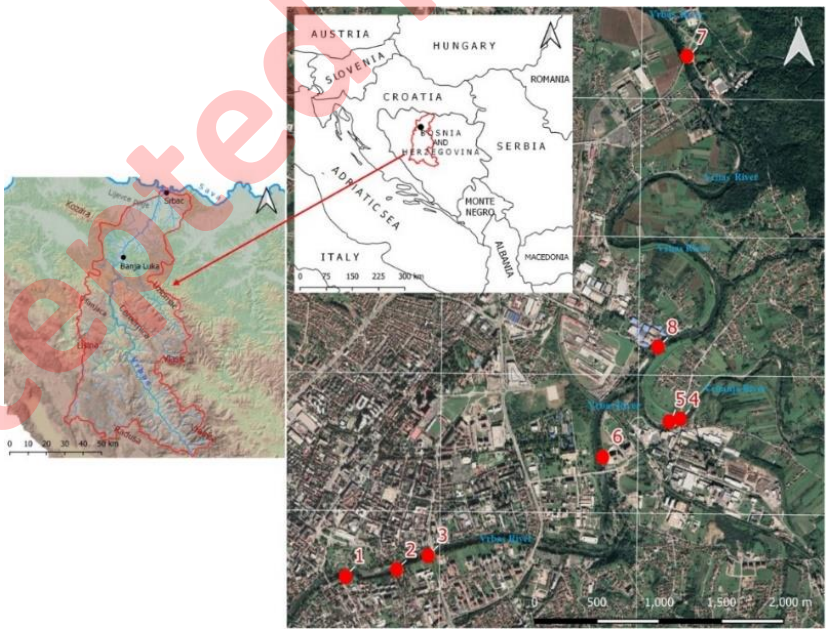

Fig. 1. Map of the Vrbas watershed on the left; map of Banja Luka city with labeled sampling locations along the Vrbas River on the right (Inset: position of Bosnia and Herzegovina in Europe)

During the period 1961-2020, the average annual temperature was 11.2 °C, and there was a positive linear trend in the average annual temperature with a noticeable increase of 0.46 °C per decade in the last 30 years. The consequences of climate change are reflected in the distribution of precipitation during the year, and they are more pronounced by seasons than on an annual basis. As a consequence of these changes, the pluviometric regime was also disturbed (Fig. 3).

With the increased precipitation and its greater seasonal variability, as well as the increased contribution of heavy rains to the total precipitation, the risk of floods in the north-eastern part of Bosnia and Herzegovina increased. The most catastrophic floods in recorded history were in May 2014. During this period, the maximum water level was recorded at the Delibašino Selo hydrological station at 816 cm (Fig. 3), while the extraordinary level of flood protection at that measuring point was 370 cm. In the last 20 years, floods were recorded in 2001 (water level maximum 677 cm) and 2019 (water level maximum 630 cm), in addition to the one mentioned in 2014.[14]

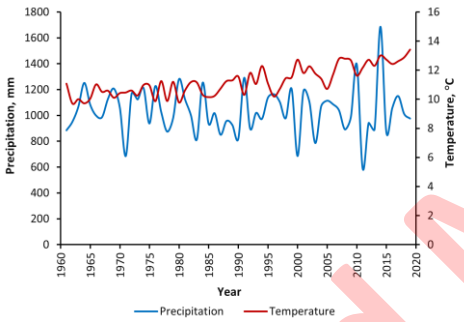

Fig. 2. Average precipitation and temperature values at the Vrbas River (1961-2020) – Banja Luka meteorological station.

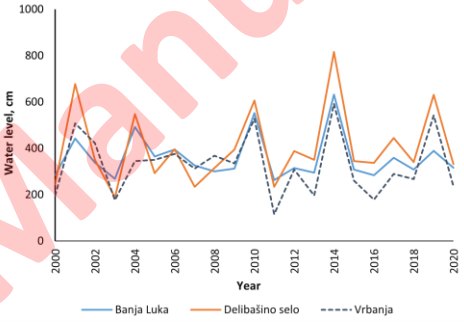

Fig. 3. Maximum water levels at the Vrbas River (2000-2020) – Hydrological stations "Banja Luka", "Delibašino selo" and "Vrbanja"

Twenty-eight municipalities with approximately 464,000 inhabitants, which is about 15 % of the population of Bosnia and Herzegovina, with the Banja Luka as the most densely populated part, are located in the Vrbas drainage basin.[15,16] The results of the 2013 census of population and housing units showed Banja Luka as the second biggest city in Bosnia and Herzegovina with a population of 180,053.[16]

The anthropogenic impact of the urbanized part of the Vrbas drainage basin is assumed to cause permanent pollution, which originates mainly from industrial activities, discharge of community sewage, illegal waste disposal, and agriculture. A large number of different economic activities are related to Banja Luka, which is the main factor in the emergence of greater anthropogenic pressure on the water quality of the Vrbas River and its tributaries in the lower part of the basin.[14] The anthropogenic impact on the Vrbanja River , one of the largest tributaries, is undeniable, primarily by municipal wastewater, as well as industrial wastewater, and the examination of its impact is also significant.

Sampling

Total of 32 sediment samples were collected at eight sites along the course of the Vrbas River in the city of Banja Luka during summer 2020. Four samples, two river and two

riverbank sediments, were collected at locations which were selected based on the vicinity of potential sources of anthropogenic pollution (Fig. 1). Locations 1 and 3 represent sites near bridges with frequent traffic and high number of sewage outlets. Sampling site 2 is on the promenade, where the possible pollution source is the nearby sewage outlet. Sites marked with numbers 4 and 5 represent the samples collected in the largest tributary of the Vrbas River , Vrbanja, and they are in the vicinity of Incel Bridge and former Incel, nowadays Celex Company, which is producing cellulose and paper. Sampling point 6 is in the vicinity of the thermal power plant, and therefore also close to the sewage outlet. Close of the sampling site 7 is the Banja Luka Brewery and the bridge - the main road. The "Vitaminka" is a food industry in the vicinity of sampling point 8. The collected samples were placed in a clean polyethylene bag, transported to the laboratory and conserved at 4 °C in the dark until analysis.

Content of heavy metals

Concentrations of heavy metals were determined on sediment fraction size <63 μm, which was obtained by the wet-sieving method. The following heavy metals were determined in 16 river sediments and 16 riverbank sediments: Cd, Co, Cr, Cu, Ni, Pb, V, Zn, and Hg. All the chemicals used for analysis were of analytical reagent grade and deionized water with resistivity 18.2 MΩ cm^{-1} obtained from a Milli-Q system (Elga Purelab Ultra). The sediment samples were prepared by weighing 0.5 g of sample into PFA vessels and adding 9 ml HNO_3 (65 %), 3 ml HF (48 %) and 2 ml HCl (37 %) and digested according to standard procedure for closed-vessel acid digestion of siliceous and organically based matrices (EPA Method 3052). After digestion, the solutions were cooled, then filtered and diluted with deionized water to the total volume of 50 mL in volumetric flasks.

The blank sample contained all reagents in the same amounts as used in sample processing and was run through the complete procedure. Each sample was analyzed in duplicate. Certified reference material Sewage Sludge 2 (CRM 029-50G, Fluka Analytical) was used to validate the method. The quality of data was also checked through recovery experiments by spiking several samples with a known concentration of standards. The results showed an acceptable agreement with the certified values. The recovery values were in the acceptable range (80–110 %) for each element.

The calibration of each element was performed by preparing 5 standard solutions in the range of 0.01 to 1.0 mg L^{-1}. A stock solution was the multi-element plasma emission calibration standard (Accu standard). The values of linear correlation coefficients were $R > 0.99$ for each element. The detection limit (LOD) was determined as a triple value of the standard deviation obtained from ten measurements of the low concentration standard.

For heavy metal determination, an Inductively coupled plasma-optical emission spectrometer Varian 730-ES (ICP-OES) with CCD detector was used, which provides true simultaneous measurement and full wavelength coverage from 167 to 785 nm. The operational parameters used in this paper were: power 1.15 kW; plasma flow 15 L min^{-1}; nebulizer pressure 200 kPa; replicate read time 5 s; stabilization delay 15 s; sample delay time 30 s; pump rate 30 rpm; rinse time 10 s; fast pump on. The selected elemental wavelengths for determination were as follows: Zn: 206.200, Cu: 327.393, Ni: 231.604, Pb: 220.353, Cr: 267.716, Cd: 214.480, V: 292.401 and Co: 228.616 nm.

For mercury determination, LECO AMA254 Advanced Mercury Analyzer – Atomic Absorption Spectrometer, specifically designed to determine total mercury content in various solids and liquids – without sample pre-treatment or sample pre-concentration, was used. The sample measured weights ranged from 0.025 to 0.080 g. The operational parameters used in

this study were: drying time 60 s, decomposition time 200 s, cuvette clear time 45 s, dosing delay time 0 s, auto select cell selection, metric for calculations peak area.

Evaluation of anthropogenic impact on heavy metal concentration in sediments

Estimation of the anthropogenic impact of the toxic metal enrichment implies a comparison of the obtained metal concentration in the sample with its concentration in the background sample. The background sample represents the sample that was not exposed to the anthropogenic impact. In this study the following average metal concentrations in the Earth's continental crust (Taylor)[17] were used as background values: c_{Cd} = 0.2, c_{Co} = 25, c_{Cr} = 100, c_{Cu} = 55, c_{Ni} = 75, c_{Pb} = 12.5, c_{V} = 135, c_{Zn} = 70 and c_{Hg} = 0.08 mg kg^{-1}.

Geoaccumulation index was calculated according to Müller[18] as follows:

$$I_{geo} = \log_2\left(\frac{M_s}{1.5B_M}\right) \quad (1)$$

M_S presents the concentration of the obtained metal in the sample and B_M geochemical background concentration of the same metal.[18] According to the calculated values of the geoaccumulation index, the anthropogenic impact on the metal content in the observed sample can be classified into seven categories, from zero value to seven, according to the increasing metal contamination.[19]

For the formulation of the potential ecological risk index and the pollution load index, it is required to define the contamination factor (C_f) as the ratio of the concentration of each metal individually and its background concentration, as follows:

$$C_f = \frac{M_s}{M_B} \quad (2)$$

where M_S presents the concentration of the metal in the sample and M_B metal concentration in the background sample.[20] The nth root of the multiplicated contamination factors of all present metals in the obtained sample represents the formulation of the pollution load index.[20-22] For the first time, PLI was defined by Tomlinson,[23] as follows:

$$\mathrm{PLI} = \sqrt{C_{f1}\, C_{f2} \ldots C_{fn}} \quad (3)$$

where index numbers in contamination factors represent different toxic metals in samples. For a PLI value less than 1, it is assumed that no heavy metal contamination has occurred, respectively for values greater than 1 for the observed sample, it is considered that exposure to toxic metals pollution by anthropogenic influence was present.[23]

In 1980's one more descriptive approach of the anthropogenic impact on metal concentration was revealed by Hakanson,[24] called an index of potential ecological risk (E_r). In mathematical formulation, it is a multiplication of contamination factor (C_f) and toxic response factor (T_f), as follows:

$$E_r^i = C_f^i\, T_r^i \quad (4)$$

A toxic response factor is a constant number, its value depends on the nature of the metal, and it's known in the literature. A total potential ecological risk index (R) presents the sum of all potential ecological risk indexes for each toxic metal present in the sample individually, mathematically formulated as follows:

$$R = \Sigma E_r^i \quad (5)$$

Evaluation of anthropogenic impact on the toxic metal concentration in the observed sample is made by following ranges: for the E_r values lower than 40 (R values lower than 94 respectively), the ecological risk for the analyzed sample is considered as low; for E_r in the range of 40 to 80 (R values in the range from 94 to 188 respectively), the risk is rated as a medium; if the E_r value is in the range from 80 to 160 (R values in the range from 188 to 376), the potential ecological risk is significant, and at the end, for the E_r values larger than 160 (R values larger than 376), the potential ecological risk is very high.[24,25]

Statistical analyses

Results were quantitatively described using the descriptive statistics. An Independent t-test which determines whether there are differences between groups, in this study was used for comparison between heavy metal composition of river and riverbank sediments. Coefficient of variation is used to determine the variation within groups, and in this case was used for seeking a difference between concentrations of a certain element at different locations. The coefficient of variation shows the extent of variability of data in a sample in relation to the mean of the population. Data with coefficient of variation higher than 1 are considered to be high variance whereas those with a CV lower than 1 are considered to be low-variance. Factor analysis (Rotation method: Varimax with Kaiser Normalization) used to reduce a large number of variables into fewer numbers of factors was employed to determine which heavy metals might have the same source.

Statistical analysis was performed by IBM SPSS Statistics 20.

RESULTS AND DISCUSSION

Concentrations of heavy metals, determined in 16 river sediments (RS) and 16 riverbank sediments (BS) sampled at eight locations during the summer of 2020 along the Vrbas River in Banja Luka, are given in Table I. Riverbank sediments were deposited during the last flood (May 2014), and river sediments are constantly deposited and transported by the Vrbas River .

The average concentration of studied metals in water followed a decreasing order of Hg < Cd < Co < Pb < Ni < Cu < V < Cr < Zn. The range of concentration are: c_{Cd} = <0.05-2.13; c_{Co} = 13.13-36.73; c_{Cr} = 61.01-197.40; c_{Cu} = 47.68-426.00; c_{Ni} = 50.31-256.23; c_{Pb} = 21.85-272.00; c_{V} = 55.60-153.12; c_{Zn} = 112.47-489.00, c_{Hg} = 0.13-1.43 mg kg^{-1}.

The independent t-test results revealed no statistically significant difference between river and riverbank samples (Table S-I of the Supplementary material), indicating that sediments are exposed to the same source of heavy metals. Furthermore, the low coefficient of variation indicates that concentrations of heavy metals are similar among locations (CV<1; Table II). Although the sampling size is small, this result confirms the constant source of heavy metals.

Factor analysis helped to reduce the dimensionality of the metal contamination from 9 original variables to 3 factors (Table II). These new variables accounted for 84.4 % of the total variance. Factor analysis showed that there are three groups that have similar mechanisms of transport and accumulation within the sediments: Factor 1 accounted for Co, Cr, Ni, and Hg, Factor 2 Cu, Pb, and Zn, and Factor 3 Cd, and V.

TABLE I. The concentrations of heavy metals in riverbank and river sediments

Sample site		Concentrations, mg kg^{-1}									
		Cd		Co		Cr		Cu		Ni	
		a	b	a	b	a	b	a	b	a	b
BS	1	1.35	2.12	13.74	16.68	84.20	101.72	82.70	73.81	80.37	77.99
RS		1.55	<1	16.85	13.13	86.87	61.01	188.00	69.05	77.80	50.31
BS	2	1.80	1.90	18.45	18.36	101.74	98.46	78.60	71.33	91.98	74.88
RS		1.56	1.40	17.55	14.48	107.34	75.51	122.60	82.96	93.85	63.83
BS	3	1.93	1.44	15.48	17.91	110.64	104.26	95.70	77.11	90.80	76.62
RS		1.36	1.24	14.79	18.50	91.60	79.49	88.24	119.11	79.44	73.43
BS	4	1.59	1.29	20.92	23.74	134.02	117.03	64.40	55.85	157.00	138.48
RS		1.22	1.64	22.65	27.79	121.09	158.27	71.23	90.00	150.00	207.00
BS	5	1.78	1.18	25.52	22.09	180.74	107.43	59.70	52.88	235.00	128.23
RS		1.80	1.35	31.51	36.68	176.37	183.35	59.72	94.55	260.00	256.23
BS	6	1.64	1.73	15.80	20.03	89.20	84.77	141.00	74.96	76.70	84.21
RS		1.22	1.29	17.59	14.44	101.00	65.78	47.68	426.00	89.20	59.96
BS	7	1.81	1.24	22.50	28.05	133.71	129.76	83.53	56.42	150.00	141.13
RS		1.21	1.67	16.98	36.73	104.57	197.40	91.68	66.90	109.00	180.71
BS	8	1.47	1.21	15.48	17.86	90.50	78.70	96.53	93.26	80.13	69.67
RS		1.57	1.56	30.56	29.62	170.56	134.44	57.50	79.36	195.00	155.82

Sample site		Pb		V		Zn		Hg	
		a	b	a	b	a	b	a	b
BS	1	33.52	35.13	95.25	117.69	192.06	141.74	0.35	0.28
RS		43.40	22.21	90.67	66.63	355.12	168.99	0.96	0.28
BS	2	36.34	33.29	116.91	114.01	171.04	163.37	0.34	0.28
RS		40.50	30.67	116.00	80.32	233.28	226.96	0.69	1.43
BS	3	32.02	40.92	116.89	120.83	174.82	176.88	0.34	0.32
RS		32.22	47.84	103.00	84.64	272.41	258.29	0.77	0.46
BS	4	21.85	23.04	96.85	88.76	134.50	112.47	0.14	0.52
RS		23.10	29.30	92.40	114.00	126.38	172.00	0.59	0.58
BS	5	24.71	23.10	124.00	82.90	167.89	113.41	0.17	0.13
RS		24.80	77.85	114.00	112.77	217.89	249.29	0.23	0.18
BS	6	29.83	40.57	80.30	86.36	261.24	201.31	0.46	0.16
RS		26.40	272.00	90.60	55.60	120.10	489.00	0.43	0.54
BS	7	27.52	33.44	110.00	110.16	176.92	140.00	0.36	0.25
RS		25.10	30.13	88.20	153.12	197.51	143.27	0.38	0.36
BS	8	31.10	49.20	75.30	81.19	254.31	233.07	0.51	0.61
RS		23.80	54.34	141.00	111.71	133.09	171.95	0.17	0.18

BS – riverbank sediment; RS – river sediment; a, and b – sample duplicates.

The I_{geo} values for Co, Cr, and V below 0 classify investigated sediments as uncontaminated (Fig. 4; Table S-II). The only positive value is 0.13 for Cr at location 5 (close to the Incel Bridge). Most sites are uncontaminated or unconta-minated to moderately contaminated with Cu and Ni, with a slightly higher value for Cu (I_{geo} = 1.02) at the site near the thermal power plant. The majority of

samples are uncontaminated to moderately contaminated or moderately contaminated with Zn and Pb, except for a higher I_{geo} value for lead (I_{geo} = 2.23), again at site 6, near the power plant. The vast majority of samples are moderately contaminated with Hg (I_{geo} = 1 – 2), with the exception of I_{geo} = 2.51 at site 2 (promenade) in which is moderate to strongly contaminated.

TABLE II. Results of Factor analysis (FA) after Varimax rotation and Coefficient of variation (CV) for concentration of heavy metals in the Vrbas River sediments

Element	Factor analysis			Coefficient of variation
	1	**2**	**3**	
Cd			0.951	0.09
Co	0.940			0.24
Cr	0.916			0.25
Cu		0.955		0.34
Ni	0.934			0.43
Pb		0.936		0.47
V			0.643	0.12
Zn		0.902		0.15
Hg	-0.502			0.30

The most severe is the anthropogenic impact of cadmium on the Vrbas River sediments collected in the City of Banja Luka. In each sample, the calculated values of I_{geo} for Cd (2.08 – 2.29) show a moderately to strongly contaminated environment. Cd is closely related to industrial activities in the upstream areas.[31]

According to values of contamination factor,[24] analyzed sediment samples mostly have a low degree of contamination with V and Co, or they are moderately contaminated with Cr, Ni, Cu, and Zn. However, in some samples, they have a considerable degree of contamination, *e.g.*, in the case of Cu and Zn near the thermal power plant, or Zn at sampling points 1 and 3, which are impacted by frequent traffic and number of sewage outlets (Fig. 4; Table S-III). The C_f values for lead represent a moderate to considerable contamination for all sampling sites, except thermal power plant (C_f = 7.03) where the level of contamination is very high. All sampling sites are considerably contaminated with mercury, except samples from site 2 near the promenade, with a very high degree of contamination. The contamination factor values for Cd (C_f > 6) imply a very high degree of contamination at all locations (Fig. 4; Table S-III).

The calculated pollution load index (PLI) values of metals in sediment are in the range 1.79-2.27 (Table S-III), confirming that the deposition of the urban stretch of the Vrbas River is polluted (PLI > 1) which might be due to urban activities.

The most significant value of the C_f that contributes to the PLI values are values of contamination factors for Cd, Pb, and Hg.

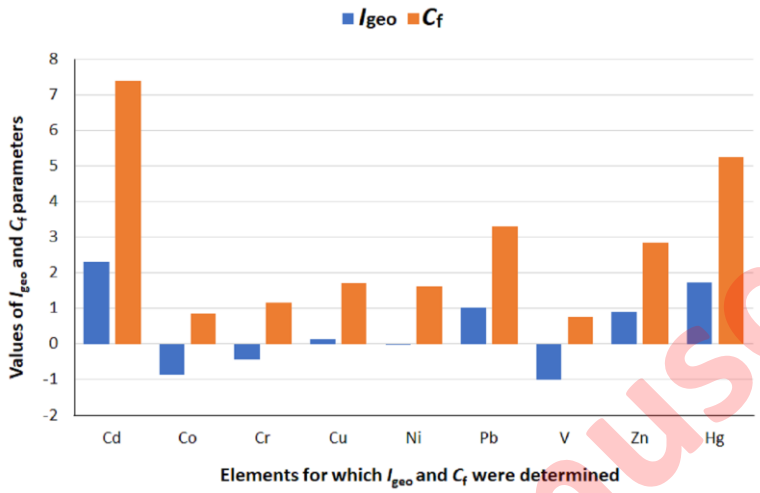

Fig. 4. Geoaccumulation index (I_{geo}) and contamination factor (C_f) for average heavy metal concentrations measured in the Vrbas River sediments (Classes of contamination related to I_{geo} values: <0 Uncontaminated, 0-1 Uncontaminated to moderately contaminated, 1-2 Moderately contaminated, 2-3 Moderately do strongly contaminated, 3-4 Strongly contaminated, 4-5 Strongly to extremely strongly, >5 Extremely contaminated; C_f values: <1 Low degree, 1-3 Moderate degree, 3-6 Considerable degree, >6 Very high degree).

Potential ecological risk (E_r) regarding the content of the Cd and Pb in observed sediments is estimated as very high. These values are a few times to a few ten's times greater than the value defined as a minimum value for very high ecological risk (Table III).

Although the statistical difference between heavy metal concentrations at different locations does not exist (CV<1), certain trends can be observed (Table II). The correlations obtained by the factor analyses (Table II) have proved that the elevation of certain elements coincides with some specific locations. For example, Cd and Hg have the highest concentrations at location 2, Pb, Cu, Zn at location 6 and Co, Cr and Ni at locations 5, 7 and 4. This further implies the same source of correlated elements.

The highest Pb, Cu and Zn concentrations, and consequently highest pollution indices at location 6, can be due to the effect from point and non-point sources, such as leaded gasoline, municipal runoffs and atmospheric deposition.[28,29] Elevated concentrations of Pb and Cu might also be originating from urban and industrial wastes.[30] Also, traffic pollution and road dust could be responsible for the high heavy metal concentrations, including Cu and Pb.[31]

Pollution of Cd is due to anthropogenic sources such as fertilizers and pesticides used in agricultural and industrial activities.[31,32] Mercury can be a significant sediment contaminant in environmental systems not always obviously

originating from a local point source which can also be related to atmospheric deposition[33] but most often originates from anthropogenic emission sources of mercury, mostly from solid wastes (municipal and medical) incineration.[34]

TABLE III. Potential ecological risk index (E_r) and total potential ecological risk index (R) ranges for heavy metals measured in river and riverbank sediments

Element	1	2	3	4	5	6	7	8
				E_r				
Cd	38.09	50.00	44.90	46.40	46.69	39.98	44.53	43.64
Co	75.50	86.05	83.35	114.24	146.81	87.40	130.33	116.90
Cr	166.90	191.53	193.00	249.08	328.75	181.71	282.72	237.10
Cu	516.95	444.36	475.20	375.74	337.28	834.45	373.16	408.31
Ni	358.09	405.68	400.36	747.76	1112.14	442.61	726.05	625.78
Pb	167.83	176.00	191.25	143.53	188.00	439.16	145.24	198.05
Zn	214.43	198.58	220.54	158.33	186.94	245.85	164.32	198.01
Hg	18.70	27.40	18.90	10.70	14.60	16.00	13.50	14.70
				R				
	2019.29	2113.64	2159.20	2332.77	2910.61	2673.91	2456.69	2353.98

Classes of contamination related to the values of the potential ecological risk indexes and literature values of toxic response factors used for E_r calculations[24,27]

	T_r	E_r	R	
Cd	30[23]	< 40	< 94	Low ecological risk
Co	5[26]	40 – 80	94 – 188	Medium ecological risk
Cr	2[23]	80 – 160	188 – 376	Significant ecological risk
Cu	5[23]	> 160	> 376	Very high ecological risk
Ni	5[26]			
Pb	5[23]			
Zn	1[23]			
Hg	40[24]			

PLI is decreasing in the following order of locations: 5>6>8>7>2>3>4>1. Since PLI can provide understanding about the quality of the environment and also provides valuable information to the decision-makers on the pollution status of the area[29] these results indicated that sediments in the lower and middle stretch of the urban part of the Vrbas sediments are under higher risk (R) of pollution than the upper stretch. The total potential ecological risk index also indicated that the middle and lower stretch is under the highest potential ecological risk (5>6>7>4>8>3>2>1).

CONCLUSION

Concentrations of heavy metals determined in 16 river sediments and 16 riverbank sediments sampled at eight locations along the Vrbas River in Banja Luka city during the summer of 2020 indicate that there is neither a statistically significant difference in metal concentration between river and riverbank samples

nor the statistically significant difference between heavy metal concentrations between selected locations. Although there are no statistically significant differences between heavy metal concentrations among locations, some trends are observed. Cadmium and Hg have the highest concentrations at location 2, Pb, Cu, Zn at location 6 and Co, Cr and Ni at locations 5, 7 and 4. This further implies the same source of correlated elements. The anthropogenic impact expressed by values of pollution indices showed that sites are generally uncontaminated by Co, Cr, and V and moderately contaminated by Zn, Cu, and Ni. On the contrary, lead, mercury and cadmium pose the highest ecological risk. The anthropogenic source of Pb, Hg and Cd is industry, municipal waste and the combustion of fossil fuels. Obtained results demonstrate the high ecological risk and need for environmental monitoring, supporting the development of an efficient strategy to reduce local pollution and contamination of the investigated system.

SUPPLEMENTARY MATERIAL

Supplementary Material, is available electronically from Journal Web site https://www.shd-pub.org.rs/index.php/JSCS/article/view/10834.

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ИЗВОД

ПРИМЕНА ИНДЕКСА ЗАГАЂЕЊА У ОДРЕЂИВАЊУ ПРОСТОРНИХ И ВРЕМЕНСКИХ РАЗЛИКА У КОНЦЕНТРАЦИЈИ ТЕШКИХ МЕТАЛА У СЕДИМЕНТИМА РЕКЕ ВРБАС, (БАЊА ЛУКА, БОСНА И ХЕРЦЕГОВИНА)

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Тешки метали су елементи природног порекла, али се сматрају значајним полутантима животне средине због велике густине и токсичности чак и при малим концентрацијама. Циљ овог рада је процена нивоа загађености речних и приобалних седимената тешким металима, као и процена њиховог порекла и просторне расподеле дуж тока реке Врбас кроз Бањалуку. Концентрације тешких метала одређиване су помоћу индуктивно спрегнуте плазме – оптичке емисионе спектрометрије и наменског живиног анализатора. Антропогени утицај на концентрацију тешких метала у седиментима процењен је израчунавањем различитих индекса загађења: индекса геоакумулације (I_{geo}), фактора контаминације (C_f), индекса оптерећења загађењем (PLI) и индекса потенцијалног еколошког ризика (E_r). Добијени резултати указују да не постоје статистички значајне просторне разлике у концентрацији метала, што указује на то да тешки метали у испитиваним седиментима имају константан извор. Антропогени утицај изражен у вредностима индекса загађења показао је да су локације генерално незагађене кобалтом, хромом и ванадијумом, а умерено загађене цинком, бакром и

никлом. С друге стране, кадмијум, жива и олово представљају највећи еколошки ризик. Антропогени извори ових метала су индустрија, комунални отпад и сагоревање фосилних горива. Добијени резултати показују висок еколошки ризик и потребу за мониторингом животне средине, подржавајући развој ефикасне стратегије за смањење локалног загађења и загађења испитиваног подручја.

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SUPPLEMENTARY MATERIAL TO

Distribution and provenance of heavy metals in sediments of the Vrbas River , Bosnia and Herzegovina

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TABLE S-I. independent t-test for heavy metal concentrations measured in river and riverbank sediment samples (n=32)

Element	*t*-value	*p*-value
Cd	2.183	0.047
Co	-0.997	0.336
Cr	-0.643	0.531
Cu	-1.524	0.15
Ni	-0.758	0.461
Pb	-1.235	0.237
V	0.02	0.984
Zn	-1.788	0.095
Hg	-1.856	0.085

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TABLE S-II. Geoaccumulation index (I_{geo}) ranges for heavy metal concentrations measured in river and riverbank sediments

Element	I_{geo}								
	1	2	3	4	5	6	7	8	Average value
Cd	2.08	2.47	2.32	2.37	2.38	2.15	2.31	2.28	2.29
Co	-1.31	-1.12	-1.17	-0.71	-0.35	-1.10	-0.52	-0.68	-0.87
Cr	-0.85	-0.65	-0.64	-0.27	0.13	-0.72	-0.09	-0.34	-0.43
Cu	0.33	0.11	0.20	-0.13	-0.29	1.02	-0.14	-0.01	0.13
Ni	-0.65	-0.47	-0.49	0.41	0.98	-0.35	0.37	0.15	-0.01
Pb	0.84	0.91	1.03	0.61	1.00	2.23	0.63	1.08	1.04
V	-1.13	-0.92	-0.93	-1.06	-0.88	-1.39	-0.81	-0.99	-1.01
Zn	1.03	0.92	1.07	0.59	0.83	1.23	0.65	0.92	0.90
Hg	1.96	2.51	1.98	1.16	1.60	1.74	1.49	1.61	1.76

Classes of contamination related to the values of the geoaccumulation indexes.[26]

Class	I_{geo}	
0	< 0	Uncontaminated
1	0 – 1	Uncontaminated to moderately contaminated
2	1 – 2	Moderately contaminated
3	2 – 3	Moderately to strongly contaminated
4	3 – 4	Strongly contaminated
5	4 – 5	Strongly to extremely strongly contaminated
6	> 5	Extremely contaminated

TABLE S-III. Contamination factor (C_f) and Pollution Load Index (PLI) ranges for heavy metal concentrations measured in river and riverbank sediments

Element	1	2	3	4	5	6	7	8	Average value
					C_f				
Cd	6.35	8.33	7.48	7.73	7.78	6.66	7.42	7.27	7.38
Co	0.60	0.69	0.67	0.91	1.17	0.70	1.04	0.94	0.84
Cr	0.83	0.96	0.96	1.25	1.64	0.91	1.41	1.19	1.14
Cu	1.88	1.62	1.73	1.37	1.23	3.03	1.36	1.48	1.71
Ni	0.95	1.08	1.07	1.99	2.97	1.18	1.94	1.67	1.61
Pb	2.69	2.82	3.06	2.30	3.01	7.03	2.32	3.17	3.30
V	0.69	0.79	0.79	0.72	0.81	0.57	0.85	0.76	0.75
Zn	3.06	2.84	3.15	2.26	2.67	3.51	2.35	2.83	2.83
Hg	5.84	8.56	5.91	3.34	4.56	5.00	4.22	4.59	5.25
					PLI				
	1.79	2.00	1.95	1.88	2.27	2.17	2.02	2.04	1.79

Classes of contamination related to the values of the contamination factors[23]

C_f		PLI value[23]
< 1	Low degree of contamination	<1 Unpolluted condition
1 – 3	Moderate degree of contamination	>1 Polluted condition
3 – 6	Considerable degree of contamination	
> 6	Very high degree of contamination	