DETECTION OF GEOCHEMICAL ANOMALIES IN STREAM SEDIMENTS OF THE UPPER SAVA RIVER DRAINAGE BASIN (SLOVENIA, CROATIA)

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ABSTRACT

Sava River is a transboundary river of supra-regional interest, draining 95,719 km^2 in Slovenia, Croatia, Bosnia and Herzegovina, and Serbia. It is a typical Alpine river, flowing from Julian Alps. On entering Croatia, it becomes a typical lowland river. The possible influence of sediments of the sub-basins of Savinja, Krka and Kupa rivers on the sediments of the main course of Sava River was studied.

Mineralogical composition was determined by X-ray diffraction (XRD), and chemical composition by inductively coupled plasma mass spectroscopy (ICP-MS). Two different procedures to identify anomalous geochemical data, the box plot method and the median absolute deviation (MAD), were used.

Results obtained by the box plot method showed that anomalous concentrations (extremes or outliers) of Zn, Pb, In, Cu, Co, Se, Zr, Cd, As, K, Na, Tl, Ba, B, Mn, and Fe are present in sediments of the Celje region, as well as of Cr, Ni, S, In, Cu, Mo, Pb in Moste dam (pollution traced down to Camping Šobec), and of Hg in Litija-Zagorje mining region. The MAD method is more sensitive, and depicts the same polluted areas, but with more anomalous values, which are above threshold values for toxicity.

The results of the selected toxic elements, with concentrations limiting the quality of freshwater sediments, are particularly discussed. Both statistical methods (box plot detection method and MAD method) show two anomalous values for Hg in Sava River near Kranj and Zagorje. The concentrations are much higher than those causing significant toxic effects >>2 ppm. Two locations of Sava River in Croatia (Strelečko and Lukavec Posavski) show a very clean environment with respect to trace elements, although Sava River passed big cities of Zagreb and Sisak. The results clearly indicate self-purification mechanisms of Sava River.

A similar future sediment study is recommended on middle and lower Sava drainage basin, of interest for Croatia, Bosnia and Herzegovina and Serbia, to detect possible pollution centers. In the case of significant pollution, remediation measures should be applied to improve sediment quality and management.

KEYWORDS:
chemical composition, geochemical anomalies, mineral composition, pollution, Sava River, self-purification, stream sediments.

INTRODUCTION

The Sava River is a transboundary river, with a length of about 1.000 km. It drains an area of 95.719 km^2 in Slovenia, Croatia, Bosnia and Herzegovina, and in Serbia.

The river flows into the Danube River at Belgrade (Serbia). The geochemical composition of the related stream sediments is not well-known, because a limited number of elements was studied so far. Štern and Förstner [1] described the heavy metal distribution in the sediments of the Sava basin in Slovenia. They found two pollution centers, one in the Sava River, near to the Moste power plant (close to Jesenice) with high concentrations of Zn, Pb, Cd, Hg. The other pollution center is in the Savinja River (tributary of the Sava River), in the Celje district with high concentrations of Cr, Zn, Cu, Pb, Cd. A preliminary report of the state of sediments in the upper Sava River (section of about 380 km downstream from Zelenci, Sava Dolinka source to Lukavec Posavski, after Kupa River inflow) has shown an almost unpolluted environment. Only a site at the Camping Šobec, situated about 10 km downstream from the pollution center of Moste power plant, gives evidence for environmental pollution [2]. According to Kotnik et al. [3], the stream sediments in Moste are polluted by Cd, Cr, Cu, Ni, Pb and Zn. Sediments of the polluted Celje district were studied in detail by Frančišković-Bilinski et al. [4, 5]. Attic dust and soil of this region, as complementary sampling media, were investigated by Žibret [6] and

Šajn [7]. Accordingly, the Celje region is still contaminated, particularly with Zn and Cd. The contamination is not dissipated in the lower flow of the Savinja River, saving the river, as concluded from box plot method [5]. Sediments of the Sava River in Croatia were studied less intensively. Halamić et al. [8] studied the heavy metal distribution in the topsoil over alluvial sediments in NW Croatia. With the exception of higher Hg contents in the city of Zagreb, the Sava River valley in NW Croatia shows no anomalous values of heavy metals. Oreščanin et al. [9] have studied the influence of the Krško nuclear power plant downstream to Zagreb in size-fractionated Sava River sediments. The concentrations of 13 investigated elements (K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Rb, Sr, Y, Zr, Pb) indicate that the examined Sava River sediments do not constitute an environmental problem. Pavlović et al. [10] studied the impact of the former Pb-Zn-Ba mining activities in Slovenia on overbank sediments of the Sava River in Croatia and concluded that the studied overbank profiles were affected by the former mining activities. Van der Meulen et al. [11] have studied the sulphate sources in the Sava and Ljubljanica rivers, and found that they contain sulphates of different sources. Using solution data, they found no evidence for the introduction of sulphate from factories into rivers.

The database available till now is insufficient to accurately delineate the geochemical anomalies within the Sava River drainage basin. The objective of this research is, therefore, to extend the data set and to study the possible influence of sub-basins of Savinja, Krka and Kupa rivers on the geochemical and mineralogical status of the main course of the Sava River from its source in Zelenci (Slovenia) down to Lukavec Posavski (Croatia), after the Kupa River inflow. Geochemical anomalies and, especially, anthropogenic pollution sites are detected by alternative methods and discussed in comparison to former works. It is expected that the obtained results will be a contribution to EU legislation on soil and sediment protection.

MATERIALS AND METHODS

Study area

The sampling locations of the study area cover the Sava River drainage basin within Slovenia (together with two large sub-basins of Krka and Savinja rivers), and also two sampling points downstream in Croatia, near Sisak (one before and one after Kupa River inflow). The details of each sampling location, name of the rivers, name of locality, geographic coordinates (X, Y), together with the anomalies at each location are presented in Table 3.

The geology of Slovenia is of high diversity [12]. Therefore, geologic setting of the studied area is presented in a simplified geological map showing locations of sampling points (Fig. 1). It is based on Geological Map of SFR Yugoslavia 1:500000, sheet Zagreb. To take the geochemical signature of the river sediments into account, 6 lithotypes (unconsolidated Miocene-Pliocene sediments, magmatic rocks, Eocene flysch sediments, Paleozoic metasediments, Mesozoic carbonate rocks and Quaternary sediments) are considered. The details about geological setting of Slovenia and Croatia can be found in [13] and [14].

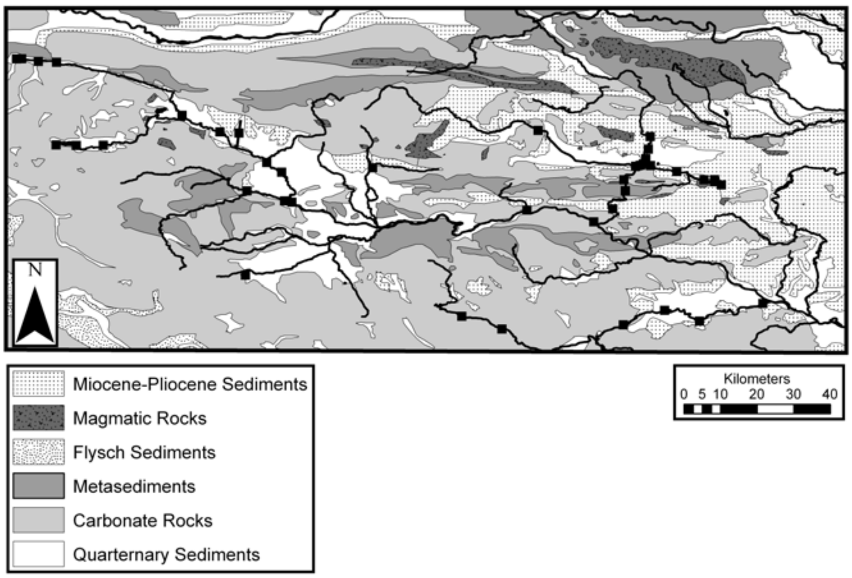

FIGURE 1 - Simplified geological map of the studied area. The main right tributaries of Sava River are Sora, Ljubljanica, Krka and Kupa. The main left tributary of Sava River is Savinja with its tributaries Voglajna and Hudinja. Coordinates and detailed description of sampling localities are presented in Table 3.

The Sava River springs in Zelenci, where the geology is dominated by Mesozoic carbonate rocks. In the middle part, the Sava River drains Quaternary sediments, whereas its lower parts are dominated by Mesozoic to Cenozoic carbonates and meta-sediments. Within Croatia, downstream to Sisak, the Sava River flows mostly through Quaternary beds.

The Ljubljanica River (a tributary of the Sava River in Slovenia) drains a semi-dried marsh pan of alluvial sediments, lenses and delta-type clastic sediments like gravel, sand and clay [15]. The catchment of the Ljubljanica River drains Mesozoic carbonates and Upper Paleozoic sedimentary rocks. Most of the water at its springs is derived from the surrounding karst area.

The geology of the Voglajna region was described in detail by Nosan [16], Hamrla [17], and Buser [18]. The studied area represents a young tectonic basin, filled by Quaternary deposits. In the northern part of Voglajna region, there are Pleistocene clays, quartz gravel and sand. In the SE part, Miocene sand, sandstone, marly limestone and lithothamnian limestone are exposed as part of the Celje Syncline. Magmatic rocks crop out in the southern part of the studied young tectonic basin.

The Krka River flows in its upper and middle part through Mesozoic carbonate rocks, and in its lower part through Quaternary deposits.

The Kupa River has a very large and geologically diverse drainage basin. The hydrogeological characteristics of the Kupa River drainage basin were described by Ivković et al. [19]. The Kupa River springs in the Risnjak National Park (Croatia) at the contact of Jurassic limestones with hornfels, dolomites and limestones from Tertiary and Permian clastic rocks. At Ozalj, at its middle flow, the Kupa River flows through unconsolidated lower Pliocene clastites and limestones. In the downstream direction, it flows into Holocene sediments, until the confluence with Sava River at Sisak.

In addition to previously collected sediments from Savinja drainage basin, additional stream sediment samples were collected, mostly during times of low water flow, in the summertime of the years 2001, 2002 and 2003. Sampling was performed further away from the riverbank to avoid contamination from soil. The sediments were wet-sieved and dried at 80 ºC. Mineralogical and chemical analyses were performed in the sediment fraction of silt and clay (<63 μm).

The mineral composition of the samples was determined by X-ray powder diffraction method using a Philips X-Pert MPD diffractometer (Cu tube, graphite monochromator, generator settings: 40 kV, 40 mA, range scanned 4-63º 2Θ). Crystalline phases were identified by comparison with Powder Diffraction File [20] using computer program X'Pert High score.

Chemical analysis of 56 elements was performed by the ACTLABS laboratory (Ontario, Canada), using the Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) program "Ultratrace 2". In this procedure, 0.5 g of sample was dissolved in aqua regia at 90 ºC in a microwave digestion unit. The solution was diluted and analyzed by a Perkin Elmer SCIEX ELAN 6100 ICP-MS instrument, using the USGS GXR-1, GXR-2, GXR-4 and GXR-6 reference materials. This digestion is not total. However, the international standard methods for determining action limits are also based on an aqua regia leach [21] and justify, therefore, the applied procedure.

Two different statistical procedures (box plot and MAD methods) were used to identify anomalous geochemical data. At first, dependent on the empirical cumulative distribution plots, normal or lognormal box plots were constructed, and box length was the interquartile range. Outliers were values between 1.5-3 box lengths from the upper or lower edge of the box. Far outliers (extremes) were values more than 3 box lengths from the edge of the box [22, 23].

The second complementary statistical method was the median absolute deviation (MAD). It is defined as the median of the absolute deviations from the median of all data [22], see also Hanesch et al. [24]. The median value ±2 MAD defines a fence, which separates outliers and extremes from a population.

RESULTS

The mineralogical composition of the investigated samples was determined (fraction <63 μm). Quartz was the major mineral in most of the stream sediment samples within the Sava River drainage basin. Only in samples from the Lake of Bohinj (samples 43 and 44), quartz was not present. In samples 72 (Pišnica River) and 74 (source of Sava Dolinka, Zelenci), quartz occurred only in traces, and in sample 71 (Sava Dolinka at Gozd Martuljek), it was the second abundant mineral. The second most abundant minerals were dolomite and calcite. In some samples, mostly from the Savnja and Voglajna sub-basin, dolomite and calcite were present as minor or trace minerals. Muscovite/Illite was detected as minor and major mineral. Feldspar was present in most samples, as minor or trace mineral. In some samples, chlorite could be found as a minor mineral.

The geochemical composition of the part of sediments from the Sava River drainage basin is presented in Table 1. Previous results of Savinja River drainage basin were published earlier [5]. The complete dataset serves as a database for present statistical analyses, and is used for detection of anomalies. Table 2 presents some basic statistical parameters for 56 elements in the sediments of the Sava River basin. For each element, the values are given as arithmetic mean, geometric mean, median, minimal and maximal concentration, variance, standard deviation, skewness and kurtosis ones.

TABLE 1 - Total dataset of elements in sediments (fraction <63 µm) from Sava River drainage basin. obtained by ICP-MS method.

sample	Li	Be	B	Na	Mg	Al	P	S	K	Ca	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Se	Rb	Sr
74	2.37	0.16	3.48	0.02	10.94	0.24	0.01	0.06	0.04	21.04	4.59	5.71	50.34	0.23	0.83	7.96	3.28	14.09	0.53	4.92	0.51	3.09	65.60
73	34.02	1.24	6.26	0.03	2.31	1.74	0.06	0.17	0.19	3.73	27.67	28.61	414.70	3.01	13.20	32.61	31.00	119.62	5.25	10.31	1.22	19.45	35.29
72	4.86	0.24	4.28	0.02	7.53	0.36	0.01	0.07	0.09	23.33	9.38	7.48	113.82	0.51	2.30	11.67	5.45	21.70	1.03	6.09	0.58	6.53	97.18
71	35.03	0.71	3.33	0.02	5.42	1.06	0.03	0.05	0.06	14.71	28.31	26.90	459.86	2.43	10.65	29.78	31.71	81.90	3.55	11.67	1.14	4.42	70.59
70	24.90	0.60	7.00	0.03	2.35	0.91	0.04	0.43	0.13	10.88	28.24	150.68	1590.00	3.20	20.50	172.55	104.02	470.17	3.66	10.65	1.08	12.89	134.58
43	1.43	0.70	0.70	0.02	11.50	0.16	0.06	0.13	0.02	29.14	6.25	5.28	66.35	0.42	1.73	14.86	3.19	11.92	0.29	7.38	0.53	1.48	54.25
44	2.54	0.22	1.38	0.02	3.49	0.30	0.07	0.14	0.05	29.50	8.70	11.50	140.64	0.66	2.98	19.00	10.81	33.55	0.71	8.28	0.54	3.76	89.57
42	11.03	0.52	12.47	0.05	2.83	0.92	0.10	0.12	0.17	16.95	26.90	41.78	899.75	2.20	14.97	73.48	43.72	70.68	2.42	13.54	1.83	10.57	129.23
41	17.63	0.79	3.88	0.05	4.55	1.27	0.08	0.11	0.15	14.05	27.29	69.48	1060.00	2.93	15.41	76.21	55.78	143.39	3.52	14.61	0.69	14.73	105.34
69	14.46	0.95	2.12	0.02	2.33	0.64	0.03	0.09	0.09	6.83	14.37	15.45	581.62	3.27	12.89	31.15	28.42	100.69	1.89	15.53	1.04	6.65	83.37
68	24.30	0.79	5.47	0.03	2.77	1.02	0.04	0.20	0.12	9.50	24.79	51.52	596.49	2.91	11.77	58.72	40.03	156.82	3.15	12.40	1.30	11.66	106.88
66	27.74	0.82	5.96	0.03	2.49	1.30	0.04	0.14	0.15	8.85	23.46	48.36	595.30	2.79	11.93	58.83	40.65	143.04	4.15	9.10	1.80	14.84	103.00
65	55.52	1.19	1.81	0.02	1.25	1.50	0.06	0.06	0.10	2.11	21.64	26.01	949.80	3.97	17.69	44.82	43.65	120.24	4.36	14.79	1.43	10.51	31.29
64	40.04	0.81	4.64	0.03	1.74	1.13	0.05	0.14	0.13	4.12	17.18	26.10	1500.00	3.82	17.08	51.63	40.55	125.04	3.28	9.24	3.94	10.70	52.15
40	39.19	0.79	4.32	0.05	1.64	1.41	0.06	0.13	0.14	6.28	17.45	38.72	1140.00	3.34	14.12	53.89	40.92	111.37	3.68	11.86	0.89	9.89	76.20
67	17.79	0.65	4.77	0.02	3.80	0.97	0.04	0.13	0.11	12.12	18.26	25.60	504.46	2.13	9.92	33.71	34.90	123.24	2.80	8.53	1.56	11.51	68.60
17	20.15	1.65	0.70	0.02	2.00	1.68	0.11	0.10	0.11	4.66	54.91	40.39	1650.00	3.56	18.01	49.65	25.23	110.22	4.99	12.33	0.96	13.79	39.44
52	29.70	0.72	6.08	0.03	2.18	1.31	0.09	0.10	0.14	7.75	22.21	52.32	637.08	3.04	12.90	46.88	58.50	218.01	3.79	13.24	1.85	13.25	73.81
51	29.54	0.85	6.07	0.03	1.94	1.25	0.08	0.12	0.15	7.19	18.72	45.74	957.94	3.60	16.20	47.87	64.60	209.29	3.58	15.25	1.45	13.55	80.78
1	20.50	1.07	0.70	0.01	0.62	1.39	0.03	0.02	0.13	0.57	41.29	39.24	707.96	3.89	19.48	56.93	22.89	67.76	5.91	10.94	0.34	17.72	23.57
2	18.33	1.19	0.70	0.02	0.56	1.34	0.09	0.09	0.15	1.30	43.79	35.54	13700.00	5.53	24.72	61.24	24.19	111.23	4.94	28.61	1.14	17.17	55.23
3	14.10	1.06	0.70	0.03	0.59	1.06	0.17	0.12	0.12	3.14	35.55	43.88	1140.00	5.19	20.40	55.41	30.50	135.90	3.79	16.60	1.23	13.46	101.49
4	15.21	1.11	2.20	0.04	0.90	1.21	0.18	0.32	0.15	4.90	34.20	71.84	1490.00	5.65	19.45	68.18	138.73	488.70	3.97	18.13	1.36	14.91	119.88
5	18.72	0.70	25.60	0.04	1.27	1.17	0.11	0.29	0.12	8.48	23.98	42.16	1030.00	2.95	17.93	46.49	52.50	2760.00	3.33	13.08	1.61	12.47	133.63
6	18.92	0.68	0.70	0.02	2.08	1.15	0.04	0.15	0.09	9.40	25.90	19.37	643.32	2.84	11.64	36.34	19.77	66.05	3.38	10.94	0.88	10.06	125.79
47	42.01	1.25	10.43	0.03	1.28	2.35	0.06	0.17	0.35	3.05	47.19	58.99	2590.00	4.95	20.58	84.58	33.26	112.31	7.86	16.32	1.08	30.49	95.31
48	12.57	1.40	5.14	0.02	0.36	1.19	0.10	0.06	0.16	0.64	78.27	66.05	2460.00	6.98	29.39	71.08	36.73	171.33	5.17	26.38	1.69	17.21	40.61
49	31.78	1.11	331.38	0.08	1.46	1.66	0.11	0.19	0.25	5.17	37.82	53.90	1270.00	4.08	51.80	91.21	147.93	2360.00	4.95	46.01	3.12	22.72	111.79
50	29.94	0.80	21.96	0.04	1.45	1.70	0.07	0.23	0.19	6.89	26.33	41.77	1240.00	3.17	15.81	52.95	43.88	198.56	5.18	10.87	1.28	20.33	124.10
79	30.37	1.07	154.51	0.05	1.60	2.02	0.08	0.14	0.25	5.47	41.69	45.01	860.55	3.74	34.26	82.85	114.72	1040.00	3.64	30.46	2.72	28.05	88.80
80	22.71	0.93	13.31	0.02	1.71	1.68	0.07	0.12	0.23	5.50	34.47	35.65	774.66	3.37	17.41	43.01	72.66	469.84	3.81	30.30	1.19	23.32	83.04
81	23.38	0.85	5.41	0.02	1.82	1.62	0.07	0.11	0.24	5.67	33.35	36.21	606.97	3.28	13.64	43.33	37.10	144.79	4.71	16.34	1.07	25.31	75.60
82	24.89	0.82	5.13	0.02	1.68	1.71	0.06	0.10	0.27	4.68	36.73	40.15	625.43	3.33	14.95	45.36	38.04	128.28	5.04	16.97	1.03	27.62	69.78
83	23.57	0.87	30.52	0.04	1.51	1.53	0.07	0.17	0.16	5.58	26.81	41.77	1160.00	2.88	17.43	49.23	47.04	500.32	3.52	14.37	1.31	17.39	102.90
84	23.15	0.80	16.85	0.03	1.83	1.48	0.08	0.23	0.15	6.67	27.93	42.12	1160.00	3.20	18.75	53.33	50.89	469.09	3.05	14.69	1.40	17.12	119.86
61	20.06	1.03	3.59	0.02	2.53	1.24	0.06	0.08	0.09	13.42	30.49	30.12	993.77	2.25	12.21	39.92	25.26	121.42	3.61	9.55	1.31	11.70	124.07
62	21.96	1.80	2.69	0.02	1.35	1.98	0.10	0.07	0.12	8.57	54.12	52.64	1080.21	4.04	23.31	46.80	31.40	184.75	6.19	14.40	1.33	18.63	69.60
63	17.39	1.35	3.18	0.02	1.53	1.60	0.10	0.09	0.10	12.38	44.35	37.14	753.05	3.14	14.84	35.49	26.70	213.13	4.83	10.05	2.11	14.99	80.03
75	21.77	2.12	1.40	0.03	3.37	2.91	0.05	0.07	0.15	9.39	84.14	53.29	641.23	3.47	13.58	33.98	25.19	111.48	8.09	17.10	1.07	29.40	48.74
76	7.14	0.75	1.75	0.02	1.87	0.83	0.07	0.22	0.06	20.57	23.31	26.08	473.34	1.63	5.93	18.06	18.35	69.36	2.44	8.80	1.07	10.02	61.27
77	17.76	1.00	3.56	0.03	0.84	1.69	0.08	0.10	0.11	16.43	40.77	41.50	1000.00	2.10	16.95	31.22	22.50	378.76	4.63	9.03	1.14	20.39	78.58
S42	8.06	0.84	4.30	0.08	3.34	0.65	0.33	0.18	0.01	9.80	27.48	27.19	1370.00	2.92	6.50	23.41	23.09	115.83	1.26	1.89	1.21	7.68	75.73
S43	16.99	0.59	0.70	0.01	2.43	1.31	0.11	0.18	0.12	8.05	22.52	52.00	493.57	2.08	9.29	37.69	54.47	228.81	3.55	6.10	0.75	11.56	94.16

sample	Y	Zr	Nb	Mo	Ag	Cd	In	Sn	Sb	Te	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Au	Tl	Pb	Bi	Th	U	Hg
74	2.07	0.58	0.07	0.15	0.02	0.49	0.01	0.21	0.19	0.01	0.42	12.73	1.82	4.13	1.76	0.39	0.07	0.07	0.14	0.07	0.13	0.36	11.81	0.17	0.26	0.42	29.00
73	10.58	0.64	0.62	0.55	0.08	0.51	0.04	0.66	0.32	0.05	2.27	68.87	9.61	21.44	11.22	3.12	0.66	0.48	0.79	0.11	2.90	0.74	42.89	0.50	2.44	0.91	189.00
72	3.14	1.01	0.19	0.40	0.02	0.54	0.01	0.36	0.25	0.01	0.65	15.21	2.97	6.42	3.08	0.71	0.14	0.07	0.21	0.07	0.13	0.25	12.05	0.15	0.60	0.87	38.00
71	6.25	0.58	0.24	0.57	0.18	0.49	0.02	0.63	0.23	0.04	0.88	59.21	6.24	13.04	7.27	1.71	0.39	0.24	0.46	0.07	0.83	0.21	26.70	0.25	0.72	0.80	1255.00
70	8.48	0.93	0.30	5.24	2.49	0.70	0.11	2.23	0.28	0.09	0.91	53.95	9.37	20.14	10.35	2.43	0.53	0.32	0.67	0.07	0.13	0.20	153.60	0.65	2.38	0.88	3204.00
43	2.24	1.08	0.07	0.16	0.02	0.41	0.01	0.25	0.10	0.06	0.20	13.90	1.60	3.08	1.36	0.29	0.07	0.07	0.13	0.07	0.13	0.05	8.19	0.06	0.16	0.30	381.00
44	4.29	1.95	0.14	0.29	0.02	0.52	0.01	1.94	0.24	0.07	0.41	21.75	4.89	8.72	4.27	0.93	0.16	0.13	0.25	0.07	4.04	0.06	50.17	0.11	0.21	0.30	488.00
42	10.77	1.52	0.23	0.86	0.02	0.70	0.03	3.98	0.35	0.17	0.74	51.64	9.86	15.57	10.40	2.40	0.53	0.33	0.67	0.07	2.67	0.15	40.23	0.23	0.55	0.76	1006.00
41	10.83	1.73	0.27	2.39	1.15	0.75	0.04	1.72	0.74	0.12	0.90	74.08	10.63	22.53	10.90	2.62	0.54	0.38	0.74	0.11	0.13	0.26	78.28	0.46	1.26	0.97	919.00
69	6.87	0.50	0.23	1.01	0.13	0.28	0.04	0.58	0.11	0.01	1.05	80.18	3.87	8.91	4.96	1.59	0.35	0.29	0.52	0.07	0.13	0.17	33.41	0.35	1.99	0.86	1459.00
68	8.91	0.65	0.39	1.64	0.84	0.42	0.05	0.95	0.15	0.06	1.03	63.51	9.97	20.71	10.43	2.65	0.50	0.37	0.69	0.07	0.13	0.17	46.35	0.40	1.94	0.90	1210.00
66	11.33	0.81	0.43	1.38	1.06	0.45	0.06	1.02	0.11	0.02	1.18	66.73	11.79	23.93	12.25	2.88	0.56	0.38	0.78	0.10	0.92	0.20	40.71	0.35	2.28	0.92	5433.00
65	10.27	1.07	0.44	0.84	0.15	0.39	0.04	0.80	0.13	0.01	2.15	109.27	8.76	19.56	10.92	3.33	0.72	0.47	0.82	0.12	0.13	0.19	44.27	0.48	3.34	1.79	1791.00
64	8.55	0.93	0.35	0.78	0.16	0.39	0.04	0.86	0.26	0.07	1.76	125.64	8.19	18.34	9.48	2.85	0.54	0.40	0.72	0.10	0.13	0.14	98.26	0.38	3.97	1.00	1011.00
40	9.85	0.52	0.28	1.54	0.80	0.29	0.04	3.76	0.75	0.09	1.72	109.45	8.83	18.14	9.45	2.84	0.58	0.40	0.82	0.11	31.85	0.16	54.11	0.43	1.46	0.90	2179.00
67	9.32	0.58	0.45	1.35	0.10	0.64	0.03	0.76	0.18	0.03	0.74	56.13	11.68	23.39	10.73	2.43	0.42	0.32	0.62	0.07	0.13	0.19	43.50	0.26	1.57	0.68	1469.00
17	22.06	2.11	0.58	1.89	0.25	1.10	0.05	1.22	0.80	0.13	0.49	89.96	22.21	42.85	21.43	4.68	0.96	0.66	1.44	0.21	0.90	0.39	46.60	1.59	1.61	0.94	346.00
52	8.79	1.15	0.42	1.08	2.42	0.54	0.04	2.01	0.45	0.03	1.96	129.80	13.49	25.21	11.84	2.93	0.56	0.36	0.66	0.07	45.65	0.15	84.09	0.47	1.75	0.97	6918.00
51	8.78	0.89	0.35	1.21	1.66	0.54	0.03	3.13	0.69	0.06	2.07	149.26	13.56	26.27	12.27	2.96	0.59	0.37	0.65	0.07	5.44	0.17	98.88	0.49	2.42	1.19	3131.00
1	14.46	1.22	0.51	0.78	0.02	0.16	0.04	0.47	0.57	0.05	1.53	67.06	23.90	46.68	22.06	4.66	0.99	0.58	1.14	0.16	0.13	0.20	17.44	0.34	4.00	0.97	177.66
2	14.34	1.71	0.38	1.49	0.09	0.78	0.05	0.82	0.78	0.11	0.87	238.01	19.14	40.28	18.08	4.00	0.84	0.54	1.09	0.15	3.20	0.23	33.85	0.40	3.66	0.76	304.39
3	15.53	1.14	0.41	1.75	0.46	0.67	0.04	8.49	0.83	0.07	0.86	124.69	19.42	40.28	18.78	4.22	0.86	0.61	1.14	0.16	16.26	0.19	43.87	0.35	3.09	0.87	606.24

TABLE 1 – continued.

4	17.06	1.40	0.43	6.28	0.55	2.66	0.08	5.40	6.71	0.10	0.99	166.39	23.01	47.78	20.75	4.69	0.87	0.65	1.23	0.16	27.05	0.26	133.39	0.79	2.54	0.92	914.04
5	9.84	1.12	0.48	1.14	3.32	3.83	0.06	1.71	1.07	0.10	1.25	274.28	11.61	24.31	10.89	2.51	0.52	0.37	0.67	0.07	106.38	0.28	66.69	0.47	0.52	0.61	568.88
6	8.93	1.04	0.43	0.71	0.11	0.31	0.03	0.81	0.75	0.09	1.00	64.90	8.36	18.43	9.13	2.32	0.49	0.34	0.61	0.07	1.60	0.16	23.90	0.28	1.12	0.59	332.82
47	13.91	2.42	0.35	0.39	0.07	0.35	0.06	1.79	0.07	0.03	1.81	92.20	25.18	50.03	24.54	5.15	0.98	0.57	1.02	0.15	0.13	0.16	32.52	0.42	7.88	1.07	1260.02
48	19.43	1.82	0.32	2.09	0.02	0.83	0.07	5.77	0.18	0.01	1.38	127.18	22.93	47.93	23.02	5.21	1.13	0.75	1.60	0.22	0.13	0.24	62.61	0.29	6.16	0.92	1112.81
49	13.36	5.19	0.90	2.00	1.72	12.44	0.17	6.29	0.86	0.06	1.40	189.27	20.79	41.19	19.73	4.11	0.74	0.49	1.06	0.14	8.82	0.96	229.02	0.55	3.99	1.06	2411.06
50	11.25	1.13	0.70	0.87	0.88	0.70	0.04	1.39	0.19	0.03	1.53	161.57	15.42	31.17	14.72	3.33	0.63	0.40	0.80	0.11	27.61	0.21	52.25	0.37	2.43	0.78	1086.60
79	12.44	1.13	0.88	1.36	3.02	7.35	0.09	1.99	1.39	0.08	1.83	988.47	18.58	41.53	18.97	4.08	0.86	0.51	1.04	0.14	38.36	0.46	86.91	0.57	3.07	1.22	345.08
80	10.88	0.57	0.78	1.11	1.31	1.44	0.07	1.52	0.75	0.07	1.62	1010.00	15.56	35.86	16.30	3.58	0.75	0.46	0.93	0.13	14.05	0.33	63.91	0.38	3.38	1.08	292.33
81	10.78	0.43	0.82	0.97	1.24	0.50	0.04	0.69	0.45	0.05	1.50	107.54	15.49	34.60	16.32	3.57	0.75	0.44	0.94	0.13	35.01	0.22	38.53	0.33	3.34	1.04	211.32
82	10.15	0.46	0.90	1.18	0.14	0.42	0.04	1.06	0.59	0.04	1.80	113.39	15.83	35.15	16.24	3.44	0.74	0.44	0.93	0.13	22.72	0.21	35.62	0.33	4.05	1.04	121.51
83	10.91	0.89	0.60	1.07	0.62	1.91	0.07	1.78	0.73	0.08	1.53	569.36	14.07	32.06	14.19	3.16	0.65	0.45	0.84	0.12	22.50	0.24	63.82	0.41	3.47	0.93	275.98
84	11.31	0.65	0.52	1.15	0.60	2.00	0.06	1.37	0.77	0.07	1.51	673.56	13.25	31.20	13.76	3.21	0.67	0.46	0.92	0.11	12.23	0.25	69.02	0.48	3.52	0.94	311.97
61	13.25	1.30	1.03	0.69	0.18	0.87	0.03	0.83	0.15	0.07	0.83	87.27	13.71	25.46	12.78	2.69	0.54	0.37	0.98	0.14	0.13	0.23	26.02	0.25	0.95	0.93	899.28
62	23.29	2.16	1.30	0.98	0.21	1.21	0.04	3.14	0.10	0.07	1.00	94.37	25.07	55.26	23.85	4.99	1.00	0.68	1.57	0.24	0.13	0.28	46.04	0.32	2.67	0.70	2150.46
63	19.05	1.47	1.01	0.80	0.39	1.28	0.04	2.67	0.16	0.05	0.99	79.44	20.76	38.64	19.25	4.03	0.78	0.52	1.27	0.18	0.13	0.24	36.13	0.32	1.18	0.69	2858.17
75	64.87	3.52	1.93	1.15	0.07	1.49	0.05	1.14	0.34	0.08	2.43	102.19	53.04	60.99	40.24	8.07	1.76	1.20	3.58	0.50	2.90	0.43	49.69	0.49	4.76	1.05	278.41
76	18.17	1.00	0.61	1.17	0.64	1.39	0.02	2.82	0.33	0.04	0.81	72.46	16.96	33.11	16.63	3.47	0.74	0.48	1.19	0.16	4.01	0.15	32.63	0.38	1.15	0.61	128.60
77	19.48	1.19	0.77	0.87	0.39	1.93	0.03	1.82	0.44	0.06	1.94	86.47	20.48	37.76	18.96	3.83	0.80	0.51	1.32	0.19	6.47	0.32	35.80	0.36	1.48	0.70	201.91
S42	5.10	2.54	0.44	0.62	0.02	0.68	0.04	1.38	0.35	0.06	1.21	169.22	9.46	30.33	10.09	1.96	0.64	0.42	0.82	0.11	2.79	0.21	22.00	0.86	3.40	0.91	16.76
S43	8.46	0.57	0.45	0.77	0.87	0.75	0.03	1.03	0.42	0.03	1.29	140.04	10.56	21.37	10.13	2.40	0.46	0.31	0.69	0.10	48.80	0.17	65.10	0.52	1.37	1.06	697.06

TABLE 2 - Basic statistical parameters for 56 elements in sediments of 43 sampling locations in Sava River drainage basin.

Element	Arithmetic mean	Geometric mean	Median	Minimum	Maximum	Variance	Std. Dev.	Skewness	Kurtosis
Li (ppm)	21.709	17.7994	20.5000	1.4250	55.52	126	11.209	0.52661	0.95197
Be (ppm)	0.845		0.8210	-1.6000	2.12	0	0.559	-1.75271	8.33343
B (ppm)	16.253		4.2840	-16.0000	331.38	2997	54.746	5.14733	28.05507
Na (%)	0.029	0.0267	0.0250	0.0120	0.08	0	0.015	2.14259	5.12566
Mg (%)	2.582	1.9799	1.8720	0.3640	11.50	5	2.344	2.68356	7.69440
Al (%)	1.293	1.1434	1.3000	0.1640	2.91	0	0.539	0.21686	1.28103
P (%)	0.078	0.0655	0.0690	0.0090	0.33	0	0.053	2.95627	12.74798
S (%)	0.139	0.1208	0.1240	0.0226	0.43	0	0.078	1.69390	4.22328
K (%)	0.133		0.1290	-0.1600	0.35	0	0.079	-0.55250	4.40072
Ca (%)	9.499	7.0976	7.7460	0.5690	29.50	48	6.960	1.34801	1.61305
Ti (%)	-0.003		-0.0100	-0.0100	0.03	0	0.013	1.39943	0.35584
V (ppm)	29.750		27.2940	-16.0000	84.14	313	17.705	0.75343	2.61411
Cr (ppm)	40.726	34.5105	40.3900	5.2770	150.68	547	23.385	2.38207	10.95358
Mn (ppm)	1213.307	773.8486	899.7500	50.3350	13700.00	4089255	2022.191	5.86355	36.73089
Fe (%)	3.131	2.6972	3.1700	0.2318	6.98	2	1.342	0.19217	1.36153
Co (ppm)	15.704	12.8674	14.9720	0.8260	51.80	77	8.778	1.64503	6.16409
Ni (ppm)	49.380	42.9511	46.7980	7.9600	172.55	746	27.305	2.20198	8.95600
Cu (ppm)	42.888	33.2030	36.7268	3.1930	147.93	993	31.508	1.90281	3.95086
Zn (ppm)	303.085	152.9813	128.2780	11.9180	2760.00	290810	539.268	3.77310	14.53914
Ga (ppm)	3.801	3.2676	3.6570	0.2920	8.09	3	1.667	0.14135	0.90988
Ge (ppm)	-0.135		-0.1000	-1.6000	-0.10	0	0.229	-6.55744	43.00000
As (ppm)	14.131	12.3740	12.3990	1.8940	46.01	63	7.945	2.02901	5.63935
Se (ppm)	1.254		1.1940	-1.6000	3.94	1	0.807	0.20713	5.70934
Rb (ppm)	14.720	12.7188	13.5500	1.4800	30.49	50	7.044	0.43858	-0.08739
Sr (ppm)	83.737	77.8107	80.7840	23.5740	134.58	869	29.486	-0.07575	-0.73740
Y (ppm)	12.549	10.4986	10.7770	2.0710	64.87	91	9.531	4.08269	21.96335
Zr (ppm)	1.285	1.0853	1.0790	0.4260	5.19	1	0.891	2.50255	8.40292
Nb (ppm)	0.480		0.4340	-1.6000	1.93	0	0.485	-1.16222	8.72639
Mo (ppm)	1.272	0.9906	1.0700	0.1480	6.28	1	1.126	3.20277	11.87470
Ag (ppm)	0.650		0.2480	-0.0500	3.32	1	0.853	1.70143	2.42684
Cd (ppm)	1.251		0.6710	-1.6000	12.44	5	2.164	3.97327	18.29431
In (ppm)	0.035		0.0390	-0.3200	0.17	0	0.064	-3.89359	22.57443
Sn (ppm)	1.886		1.3660	-0.8000	8.49	3	1.813	1.85736	3.88596
Sb (ppm)	0.573		0.3440	-0.3200	6.71	1	1.014	5.52412	33.83538
Te (ppm)	0.048		0.0580	-0.3200	0.17	0	0.070	-3.46246	17.94288
Cs (ppm)	1.200		1.1820	-1.6000	2.43	0	0.694	-1.36367	5.07463
Ba (ppm)	166.292	102.0652	94.3720	12.7280	1010.00	50010	223.628	2.95516	8.41640
La (ppm)	14.462	11.9548	13.4850	1.6020	53.04	77	8.786	1.97060	7.70768
Ce (ppm)	28.925	24.6043	26.2740	3.0780	60.99	194	13.935	0.16565	-0.45640
Nd (ppm)	14.041	11.9221	12.2680	1.3580	40.24	51	7.172	1.00631	2.96448

TABLE 2 - continued.

Sm (ppm)	3.171	2.7465	3.1180	0.2850	8.07	2	1.425	0.60633	2.39766
Eu (ppm)	0.592		0.6280	-1.6000	1.76	0	0.466	-2.29215	11.74336
Tb (ppm)	0.374		0.3990	-1.6000	1.20	0	0.379	-3.33219	17.79622
Yb (ppm)	0.854		0.8160	-1.6000	3.58	0	0.661	0.46362	10.16974
Lu (ppm)	0.031		0.1080	-1.6000	0.50	0	0.288	-4.40062	25.18130
Hf (ppm)	-0.135		-0.1000	-1.6000	-0.10	0	0.229	-6.55744	43.00000
Ta (ppm)	-0.067		-0.0500	-0.8000	-0.05	0	0.114	-6.55744	43.00000
W (ppm)	0.127		-0.2000	-1.6000	2.79	0	0.663	1.75617	7.08653
Re (ppm)	0.001		0.0010	-0.0160	0.01	0	0.003	-3.55436	19.02673
Au (ppb)	11.320		2.6740	-3.2000	106.38	413	20.320	2.88585	10.72537
Tl (ppm)	0.240		0.2120	-0.3200	0.96	0	0.181	1.38033	7.89052
Pb (ppm)	55.369	45.0725	44.2660	8.1870	229.02	1631	40.391	2.41244	7.79382
Bi (ppm)	0.418	0.3667	0.3770	0.0580	1.59	0	0.240	2.91686	13.08267
Th (ppm)	2.420	1.8226	2.3770	0.1550	7.88	3	1.612	1.07073	1.98292
U (ppm)	0.821		0.9120	-1.6000	1.79	0	0.453	-3.61589	19.96916
Hg (ppb)	1163.241	588.9811	697.0619	16.7593	6918.00	2004856	1415.929	2.43760	6.95728

TABLE 3 - Sampling locations and anomalies determined from the completed dataset (Table 1) in stream sediments of Sava River drainage basin by box plot and MAD methods.

Sample No.	River	Locality	Coordinates		Positive anomaly (box plot)		Postive anomaly (MAD)
			X	Y	extreme	outlier	
74	Sava Dolinka	Zelenci	13.74240	46.49270	-	Mg	Mg, Ca, Tl
73	Sava Dolinka	Podkoren	13.75530	46.49300	-	Tl	Be, Cs, Tl
72	Pišnica	Kranjska Gora	13.79610	46.48630	-	Mg, Ca	Mg, Ca
71	Sava Dolinka	Gozd Martuljek	13.84090	46.48430	-	-	Li, Mg, Ca
70	Sava Dolinka	Kamp Šobec	14.14960	46.35350	Cr, Ni, S	In, Cu, Mo, Pb	S, Cr, Ni, Cu, Zn, Sr, Mo, In, Pb, Bi
43	Boh. jezero	Kamp Zlatorog	13.84000	46.28040	-	Mg, Ca	Mg, Ca
44	Boh. jezero	Ribičev Laz	13.88940	46.27950	-	Ca	Mg, Ca
42	Sava Bohinjka	Boh. Bistrica	13.95600	46.27960	-	Te	Na, Ca, Ni, Se, Sr, Sn, Te
41	Sava	Posavec	14.24250	46.31290	-	-	Na, Mg, Ca, Cr, Ni, Mo, Te
69	Tržaška Bistrica	Kamp Trnova	14.28920	46.31010	-	-	-
68	Sava	Kranj	14.35760	46.23740	-	-	-
66	Sava	Kranj	14.39430	46.21340	Hg	-	Hg
65	Sora	Škofja Loka	14.30890	46.16720	U	Li	Li, Cs, U
64	Sora	Goričani	14.40150	46.14280	-	Se	Li, Se, Pb
40	Sora	Medvode	14.41940	46.13940	-	Na	Li, Na
67	Kam. Bistrica	Kamnik	14.61790	46.22410	-	-	Mg
17	Ljubljanica	Vrhnika	14.30520	45.95930	Bi	-	Be, P, V, Y, Zr, Te, Sm, Tb, Yb, Tl, Bi
52	Sava	Zagorje	14.99730	46.12000	Hg	-	Se, Cs, Pb, Hg
51	Sava	Zidani Most	15.16140	46.09090	-	-	Pb, U
1	Slivniško jez.	Zg. Rakitovec	15.45960	46.18950	-	-	Ga, La, Ce, Nd, Sm, Eu
2	Voglajna	Gorica	15.43270	46.19450	Mn	Fe	V, Mn, Fe, Co, As, Ba
3	Voglajna	Vrbno	15.36570	46.21480	-	P	P, Fe, Sn
4	Voglajna	Teharje	15.30090	46.22960	Cu	Fe, Bi, Mo, P, Pb, S, Sb	Al, S, P, Cr, Fe, Cu, Zn, Mo, Cd, In, Sn, Sb, La, Ce, Sm, Tb, Pb, Bi
5	Savinja	Tremerje	15.23520	46.19480	Zn	-	B, P, S, Zn, Sr, Ag, Cd, Ba
6	Savinja	Letuš	15.02470	46.31620	-	-	Sr
47	Dobrinjski potok	Hrastje	15.47510	46.18200	K	Ga, Rb, Th	Li, Be, Al, K, V, Mn, Fe, Ni, Ga, Rb, Zr, La, Ce, Nd, Sm, Th
48	Ločnica	Lipovec	15.45840	46.19500	Fe	Co, Tb, V	B, W, Cr, Mn, Fe, Co, Ni, As, Se, Y, Mo, Sn, Ce, Nd, Sm, Eu, Tb, Yb, Th
49	Voglajna	Celje	15.27560	46.23050	Zn, Pb, In, Cu, Co, Se, Zr	Cd, As, K, Na, Tl	B, Na, P, K, Co, Ni, Cu, Zn, As, Se, Rb, Zr, Nb, Cd, In, Sn, Tl, Pb
50	Savinja	Celje	15.26460	46.22810	-	-	B, S
79	Hudinja	Celje	15.28350	46.23400	Se	In, Cu, Co, Cd, Ba, B, K, Zn	B, Na, Al, K, Co, Ni, Cu, Zn, As, Se, Rb, Nb, Ag, Cd, In, Ba, Tl, Pb, U
80	Hudinja	Sp. Hudinja	15.28940	46.24670	-	Ba, K	K, Zn, As, Rb, Nb, Ba
81	Hudinja	Škofja Vas	15.29560	46.27030	-	K	K, Rb, Nb
82	Hudinja	Višnja Vas	15.30000	46.30120	-	K	K, Rb, Nb
83	Savinja	Debro	15.23890	46.16750	-	Ba	B, Zn, Cd, Ba
84	Savinja	Rimske Toplice	15.20840	46.12270	-	Ba	B, S, Zn, Cd, Ba
61	Krka	Krška Vas	15.57740	45.89110	-	-	Nb
62	Krka	Kostanjevica	15.42160	45.84760	-	Be, Nb, Y	Be, Al, V, Co, Ga, Y, Zr, Nb, La, Ce, Nd, Sm, Eu, Tb, Yb
63	Krka	Dobrava	15.33540	45.87440	-	Se	Se, Y, Nb
75	Krka	Fužine-Zagradec	14.83710	45.85960	Eu, La, V, Al, Y, Yb, Nb, Tb	Ga, Be, Sm, Zr, Lu, Nd	Be, Al, V, Ga, Rb, Y, Zr, Nb, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Tl, Th
76	Krka	Žužemberk	14.93550	45.82840	-	-	S, Ca, Y
77	Krka	Otočec	15.23430	45.83860	-	-	Ca, Zn, Y, Cd, Cs
S42	Sava	Lukavec Posavski	16.54000	45.40110	P	Bi, Na	Na, P, Zr, Bi
S43	Sava	Strelečko	16.40000	45.51720	-	-	P

Samples 1 – 6, 47 – 50, and 79 – 84 are from Frančišković-Bilinski et al. [5]
Samples S42 and S43 are from Frančišković-Bilinski [26]

The results of box plot evaluation and MAD method are presented in Table 3, including both toxic and lithogenic elements, as well as location description for each sample. According to box plot approach, anomalous concentrations (extremes or outliers) of Zn, Pb, In, Cu, Co, Se, Zr, Cd, As, K, Na, Tl, Ba and B were present in sediments of the Celje region (samples 49 and 79). Anomalies of Mn and Fe were found in Voglajna (sample 2), and of Fe in Ločnica (sample 48). In Sava Dolinka at Camping Šobec, downstream from Jesenice and Moste dam, concentrations of Cu, Pb, Cr, Ni, Mo, S and In showed anomalism. In the Sora River, near the closed uranium mine of Žirovski Vrh, U and Li showed anomalous values, and in Ljubljanica River, the highest concentration of Bi was found. Anomalous values of Hg were found in the Sava River at sampling stations 66 and 52, as well as of P in the Sava River, downstream the inflow of the Kupa River. Particularly interesting and not known before was the finding of a series of elements (Eu, La, V, Al, Y, Yb, Nb, Tb, Ga, Be, Sm, Zr, Lu and Nd), with high concentrations near to the source of the Krka River. There were also outliers of some lithogenic elements of minor importance for a pollution study.

The detection by the MAD method depicted the same regions as polluted ones, with many anomalies, which can be seen in Table 3.

DISCUSSION

The results will be discussed with specific emphasis on selected toxic elements and the concentration levels of elements that limit the quality of fresh water sediments [25].

The results of the box plot detection showed that the Sava River drainage basin has two heavily polluted sites. One is located in the vicinity of Celje, an industrial region of Slovenia, and the other one is downstream from Jesenice and Moste dam. In Jesenice, a heavy iron industry is located, and pollution is traced in Sava Dolinka at Camping Šobec. The remaining parts of this large drainage basin are unpolluted, with exception of two locations with higher mercury levels (samples 66 and 52 from Sava River). Anomaly of the non-toxic element series found in Krka River at location 75 can be assumed to be of geogenic origin, as there is no industrial pollution. Anomalous concentration of U, found in Sora River (sample 65) was below the median value (2 ppm), reported for stream sediments by FOREGS. It was also lower than the anomalous value of U (>4 ppm) discovered in Mrežnica River (belonging to Kupa River drainage basin) by Frančišković-Bilinski [26].

With the MAD method, the same pollution sites were detected with positive anomalies, but with higher number of anomalies. Negative anomalies, not listed in Table 3, prevailed in samples 74, 72, 43 and 44, and can be explained with low abundance of particular elements at those locations, where carbonate mineralogy predominates. Higher numbers of positive anomalies found for toxic elements determined by MAD method show the regions of threshold concentrations causing lower to significant toxic effects, or close to it. Elements Zn and Cd showed their downstream transport in Savinja River (samples 83 and 84). When using the first method (box plot), no anomalies were detected in Savinja sub-system in samples 83 and 84 by Frančišković-Bilinski et al. [5]. Using the total data set from Table1 of this work and box plot method, Ba was detected as outlier in samples 79, 80, 83 and 84. Using the MAD method, Ba was detected to be anomalous in samples 2, 5, 79, 80, 83 and 84.

In the present study, elevated concentrations of Pb were found in all cases, comparable to those of Štern and Förstner [1] and Kotnik et al. [3] in the Moste region. One difference was only noticed with respect to Cd. It was reported earlier [1, 3] in the Moste region, but not detected herein to be anomalous in sample 70 (located a few km downstream from Moste dam), using both statistical methods. The concentration of Cd (0.7 ppm) may cause the lowest toxic effects. In the same sample, Zn was not detected as anomalous by box plot method, while it showed positive anomaly determined by MAD method.

From solution data of Van der Meulen et al. [11], no evidence was found for introduction of sulphate into the rivers from factories. However, an extreme value for S has been detected in the present study at location 70 (Camping Šobec) by the box plot method, whereas 6 anomalous values of S were found by MAD method (locations 70, 4, 5, 50, 84 and 76), which indicates a possible anthropogenic introduction of S to the sediments.

Both statistical methods showed 2 anomalous values for Hg (samples 52 and 66) in Sava River, near Kranj and Zagorje. The concentrations were much higher than those causing significant toxic effects >>2 ppm. This supports the finding of Halamić et al. [8] that Hg in the topsoil of NW Croatia originates from mining upstream in Litija. In comparison with the Soča River, the concentration of Hg found in it by Frančišković-Bilinski et al. [27], after the confluence with polluted Idrijca River, was significantly higher as measured down to the border of Slovenia and Italy.

Distribution of Mg and Ca in the sediments is the result of natural processes, such as weathering of carbonates. A similar situation exists in sediments near the source of the Soča River. Sample 32S from Soča River was characterized as a good leverage point outlier, as well as indicator of an unpolluted data population [27].

In sample S42 (Sava River below Kupa River inflow), P was found as an extreme, but its concentration was below the reported value, causing the lowest toxic effects (<600 ppm).

It is also interesting to compare the two locations (S42 and S43) of Sava River in Croatia, which show a very clean environment with respect to trace elements, although Sava River passed the big cities of Zagreb and Sisak. The results clearly indicate self-purification mechanisms in the lowland part of the Sava River. In comparison with Soča

River, which flows from the same Julian Alps, but toward the Adriatic Sea, there was a difference. The self-purification mechanism was less effective in the Alpine Soča River, as observed down to the border of Slovenia/Italy [27]. In addition, results supported those of Hanesch et al. [24], who studied magnetic susceptibility and recommended the box plot method as a standard method, showing problematic regions. For the purpose of early detection of changes in the environment, the MAD method can be used successfully.

CONCLUSIONS

From the sediment analysis, it can be concluded that the Sava River drainage basin in Slovenia has three main pollution sites: Celje region, Moste dam (pollution traced down to Camping Šobec), and Litija-Zagorje mining region. Sediments taken in Croatia, downstream Zagreb and Sisak, have shown an unpolluted environment, with respect to trace elements (except P), which is the evidence for acting self-purification mechanism.

Two statistical methods have been applied on a total geochemical data-set. The box plot method shows locations with extreme and outlier values. It can be either an anthropogenic pollution or because of the influence of geological setting. The MAD method is more sensitive giving more locations with anomalous values above threshold ones for toxicity, and can be applied for early detection of changes in the environment.

A similar future sediment study is recommended for middle and lower Sava drainage basin, being of interest for Croatia, Bosnia and Herzegovina and Serbia, to detect possible pollution centers. In the case of significant pollution in sediments and waters, some remediation techniques and management measures should be applied.

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