ANALYSIS OF SEDIMENTS OF THE FOUR MAIN RIVERS (DRINI I BARDHË, MORAVA E BINÇËS, LEPENC AND SITNICA) IN KOSOVO

Fatbardh Gashi¹, Stanislav Frančišković-Bilinski²* and Halka Bilinski²

¹Faculty of Natural Science, Department of Chemistry, University of Pristina, 10000 Pristina, Kosovo ²Institute "Ruđer Bošković", Division for marine and environmental research, POB 180, HR-10002 Zagreb, Croatia

ABSTRACT

Mineralogical, geochemical and contamination status of stream sediments of the rivers Drini i Bardhë, Morava e Binçës, Lepenc and Sitnica, which are of supra-regional interest, are presented for the first time. From the results obtained by X-ray fluorescence spectroscopy (XRF), it was concluded that the sediments of Drini i Bardhë River are weathering products of sandstones; the sediments of Morava e Binçës, Sitnica and of the upper course of Lepenc are weathering products of magmatic rocks and sandstones; the sediments of the lower stretch of Lepenc are weathering products of magmatic rocks, sandstones and carbonates. The concentration of major and minor elements was determined by inductively coupled plasma mass spectroscopy (ICP-MS), the amounts of P and S by inductively coupled plasma in combination with optical emission spectrophotometry (ICP-OES), and the amounts of Hg by cold vapor in combination with adsorption atomic spectroscopy (CV-AAS). Assessment of sediment contamination with toxic elements was performed by comparison with the existing criteria for sediment quality. Results obtained by the box plot method showed the regions with determined anomalous element concentration values in stream sediments of Kosovo. Two locations in Sitnica River at Fushë Kosova (Kosovo Polje) and Mitrovica are significantly polluted as a result of Zn and Pb ore processing and Zn electrolysis. In the lower course of Morava River, sediments are contaminated with Cd. Increased concentrations of Mn were observed near the source of Drini i Bardhë River, suggesting natural origin. Continuation of sediment monitoring is recommended, particularly on Sitnica and Morava rivers, which flow through Serbia to enter ultimately the Black Sea.

KEYWORDS: Rivers of Kosovo, stream sediments, chemical composition, geochemical anomalies, pollution assessment

INTRODUCTION

Overexploitation of nature and uncontrolled use of natural resources, including inadequate processing of industrial wastes have caused large contamination of world ecosystems by toxic metals (Hg, Pb, Cd, Cu, Zn, Ni, Mn) which generally show considerable accumulation in river sediments. Decomposition of organic matter and pollution due to anthropogenic activity are the main sources of pollution of water and stream sediments [1]. Sediments (silt and clay) containing toxic heavy metals, inorganic and organic substances are important for studying water pollution [2]. Therefore, a multidisciplinary collaborative research is essential for understanding the processes of mechanical and chemical weathering of rocks, their products, the manner of release and consumption of CO₂, and other natural processes to better understand the geochemical cycles associated with various trace elements. Based on the results of such studies, it will be possible in the future to propose protection and detoxification measures of affected sediments and river waters and general protection and remediation of ecosystems. Considering more-lasting pollution in sediments in comparison to river water pollution, as well as adsorption of toxic elements, during last decades the interest for morphological and geochemical analysis of river sediments considerably increased, which is evident from increasing number of publications of this scope in many journals. This work is a continuation of earlier studies of sediments in the area of nearby countries of Croatia and Slovenia [3-10].

We could claim that the most polluted areas in the world are those with the densest population. It should therefore be the foremost goal of environmentalists to prevent such pollution, and to educate the population towards proper management of ecosystems [11].

The aim of the current work is to perform, for the first time, a research on mineralogical, geochemical and contamination status of the stream sediments (fraction $<63 \mu m$) of the rivers Drini i Bardhë, Morava e Binçës, Lepenc and Sitnica. These rivers, which belong to different watersheds, have drainage basins that cover a large area of Kosovo, being as well of supra-regional interest. The sampling sites in Kosovo Rivers are, for the first time, geographically posi-

tioned using GIS (Geographic Information System). The results were interpreted using modern statistical methods that can be used to locate pollution sources. Locations at which anomalous element concentration values have been determined, and where certain toxic elements should be monitored and sediments possibly remediated, were highlighted.

MATERIALS AND METHODS

Study Area

In terms of geotectonic setting, Kosovo is located within the Dinaric Mountains. All three divisions of rocks, namely magmatic, sedimentary and methamorphic, of Precambrian to Quaternary ages are present in the territory of Kosovo [12]. The sediments of the rivers in Kosovo are composed of alluvial deposits containing largely varying proportions of unconsolidated to semi consolidated sand and gravel materials [13]. The study area with the sampling locations is shown in Fig. 1. Details about all sampling sites are presented in Table 1. The area covers all four main drainage basins of Kosovo: the rivers Drini i Bardhë, Morava e Binçës, Lepenc and Sitnica. Kosovo is located between 41°51' - 43°16' N and 20°01' - 21°48' E. It is mainly situated on two plains, surrounded by mountains; the Dukagjin (Metohija) Plain at 330-550 m and the Kosovo Plain at 500-600 m above the sea level.

Sampling and sample preparation

Sampling of stream sediments within the drainage basins of Drini i Bardhë, Morava e Binçës, Lepenc and Sitnica was performed between 23^{rd} and 30^{th} September 2004. The weather was relatively warm and dry, with low water levels, which was very suitable for sampling. The sediments which were in contact with running water were sampled manually, using a metal bucket of the dimensions 25 x 8 x 3 cm. Sampling was performed at distance from the river banks to avoid possible contamination from the bank material. About 3-5 kg of sediment was collected at each sampling site to provide enough material of fraction <63 μ m for mineralogical and geochemical analysis. The material was transported in plastic bags. Samples were dried in air at 20-25° C for 3 weeks. Coarse material was separated using a sieve of 40 mesh, and afterwards with the standard sieve of 63 μ m, Fritsch (Germany).



FIGURE 1 - Study area with sampling stations.

TARLE 1 - Sampling	stations at the	rivers in Kosovo	with detailed local	ty description
TADLE I - Sampling	stations at the	I IVEIS III KUSUVU	o with detailed local	ty description.

G 1	D'	T 1.		XX7 4 1 1 6		
Sample	River	Locality	Flowing to river	watershed of	Coordinates	Height above sea level (m)
\mathbf{D}_1	Drini i Bardhë	Radavc	Fierza (Albania)	Adriatic Sea	42°44'12" N; 20°18'19" E	734
D ₂	Drini i Bardhë	Katundi i ri	Fierza (Albania)	Adriatic Sea	42°34'36" N;20°19'37" E	487
D ₃	Drini i Bardhë	Klina	Fierza (Albania)	Adriatic Sea	42°42'36" N; 20°34'26" E	348
D ₄	Drini i Bardhë	Bridg Fsheji Gjakovë	Fierza (Albania)	Adriatic Sea	42°22'08" N; 20°32'50" E	319
D ₅	Drini i Bardhë	Nashec, Prizren	Fierza (Albania)	Adriatic Sea	42°14'21" N; 20°38'52" E	287
M ₁	Morava e Binçës	Binçë	J. Morava (Serbia)	Black Sea	42°17'01" N; 21°21'44" E	538
M ₂	Morava e Binçës	Kllokot	J. Morava (Serbia)	Black Sea	42°22'15" N; 21°24'14" E	477
M ₃	Morava e Binçës	Partesh	J.Morava (Serbia)	Black Sea	42°23'58" N; 21°28'03" E	471
M4	Morava e Binçës	Dobërçan	J.Morava (Serbia)	Black Sea	42°28'02" N; 21°34'56" E	450
M ₅	Morava e Binçës	Kormini i ulët	J.Morava (Serbia)	Black Sea	42°29'41" N; 21°35'39" E	421
L ₁	Lepenc	Brod	Vardar (Macedonia)	Aegean Sea	42°16'17" N; 21°07'51" E	646
L_2	Lepenc	Kovaçec	Vardar (Macedonia)	Aegean Sea	42°14'25" N; 21°14'24" E	478
L ₃	Lepenc	Kaqanik	Vardar (Macedonia)	Aegean Sea	42°12'59" N; 21°15'12" E	466
L_4	Lepenc	Elez Han	Vardar (Macedonia)	Aegean Sea	42°09'07" N; 21°17'34" E	399
L ₅	Lepenc	Elez Han	Vardar (Macedonia))	Aegean Sea	42°08'27" N; 21°17'49" E	361
S ₁	Sitnicë	Lipjan	Ibri (Kosovo)	Black Sea	42°31'23" N; 21°06'09" E	535
S ₂	Sitnicë	Fushë Kosovë	Ibri (Kosovo)	Black Sea	42°37'14" N; 21°04'11" E	528
S ₃	Sitnicë	Obiliq	Ibri (Kosovo)	Black Sea	42°46'00" N; 21°00'23" E	510
S ₄	Sitnicë	Vuqiternë	Ibri (Kosovo)	Black Sea	42°50'15" N; 20°55'35" E	492
S ₅	Sitnicë	Mitrovicë	Ibri (Kosovo)	Black Sea	42°53'48" N; 20°52'58" E	480



Determination of mineralogical composition

Mineralogical composition was determined by the XRD method, using a Philips PW 1050 X-ray diffractometer with a proportional counter and Cu-K_a irradiation at the Faculty of Mining and Geology in Sofia, Bulgaria. For interpretation, Powder Diffraction File [14] was used. Mineralogical composition was determined semi-quantitatively as described by Boldrin et al. [15].

Geochemical characterization

Determination of major elements in stream sediments (fraction <63 µm) was performed in commercial laboratory ACTLABS, Ontario, Canada, using FUS-XRF method and equipment for irradiation beam (WDS, XRF, ARL 8410) as well as program 4C. Concentrations are expressed as percentages of the corresponding oxides. Following standards were used: DNC-1, W2, SY-3, SGR-1 and BE-N.

Multielemental analysis of the samples (<63 μ m) by ICP-MS was carried out by ACTLABS laboratory with the program "Ultratrace 2". The procedure was as follows: 0.5 g of sample was dissolved in aqua regia at 90 °C in a microwave digestion unit. The solution was diluted and analyzed with a Perkin Elmer SCIEX ELAN 6100 ICP-MS instrument. For analysis, the following reference materials were used: USGS GXR-1, GXR-2, GXR-4 and GXR-6, which were analyzed at the beginning and after each series of samples. Elements Ti, P and S were analyzed with ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) using a Perkin Elmer OPTIMA 3000 ICP spectrophotometer.

Although this digestion is not total, its use is justified because the international standard methods for determining action limits are based on aqua regia leach [16].

Mercury was determined also in ACTLABS, using the same solution as prepared from the sediment fraction <63 µm for ICP-MS analysis. The program 1G-Hg-CV was used as well as international standards SO-2, GXR-4, GXR-2 and GXR-1. Determination was performed using CV-AAS method (Cold Vapor Atomic Adsorption Spectrometry). Hg was oxidized in the solution till the state of stable divalent ions has been reached. Their concentration was determined using Hg vapor, which is adsorbed at the wavelength of 253.7 nm, along with the reducing of Hg (II) in evaporating state (Hg⁰), using SnCl₂. Argon was run through the mixture of the sample and the reducing solution, which transported Hg atoms into adsorption cell situated in beam of atomic adsorption spectrophotometer. According to

Beer's law, adsorbed emission intensity is proportional to the concentration of Hg atoms in emission beam of $\lambda = 253.7$ nm.

Statistical methods

Program Statistica 6.0 [17] has been used for all statistical calculations in this work: cluster analysis of Qmodality, determination of basic statistical parameters and anomalies (extremes and outliers).

RESULTS

Mineralogical composition

Results of semi-quantitative mineralogical analysis of the selected sediment samples (fraction <63 μ m) are presented in Table 2. Quartz is the most abundant mineral, followed by different minerals from feldspar group (albite, microcline, plagioclase), mica group (muscovite, biotite), chlorite group, calcite group and hornblende group (amphibole).

XRF analysis of major components

Results of XRF analysis of major components, expressed as percentages of the corresponding oxides, are presented in Table 3. In all samples prevail SiO₂ (36.38 – 82.58 %), Al₂O₃ (5.12 – 13.87 %), CaO (1.28 – 22.69 %) and Fe₂O₃ (2.18 – 8.32 %). Other oxides are less abundant. In Table 3 are also presented the data for Loss of Ignition (LOI, ω / %). For better comparison, Fig. 2 (a-d) presents the distribution of major component oxides and LOI in each river.

ICP-MS and ICP-OES analyses of major and trace elements

Table 4 presents concentrations of major and trace elements in stream sediments (fraction $<63 \mu m$). The results represent the first database of stream sediment analysis in Kosovo. The database will be used in statistical calculation and in physico-chemical assessment of sediment quality.

CV-AAS analysis of Hg

Table 4 includes also the concentrations of Hg (ppm) in sediments (fraction <63 μ m) at all sampling stations. Concentrations range from 0.247 ppm in Lepenc River (station L₃) to the highest concentration of 11.900 ppm observed in Sitnica River (station S₅). Fig. 3 shows Hg concentrations in the region for all sampling sites.

TABLE 2 - Minerological composition of stream sediments (fraction <63 μm) of the rivers of Kosovo, estimated according to Boldrin et al. [15] from X-ray diffraction patterns.

Sampling locations	Quartz	Feldspar group	Mica group	Chlorite group	Calcite group	Hornblende group
D2	+++	++	(+)	(+)	++	-
M_2	+ + +	++	++	+	(+)	-
L ₂	+ + +	+ +	++	+	-	(+)
S ₁	+ + +	+ +	(+)	(+)	-	-
S ₂	+++	++	(+)	(+)	+	-
S ₃	+ + +	++	+	(+)	(+)	-
S_4	+ + +	++	+	+	(+)	-
S ₅	+ + +	+	+	+	(+)	-

Explanations: +++ (> 30 %); ++ (10 - 30 %); + (5 - 10 %); (+) (< 5 %); - not detected

Station	SiO ₂	Al_2O_3	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P_2O_5	Cr_2O_3	LOI*	Total
	%	%	%	%	%	%	%	%	%	%	%	%	%
D ₁	64.43	11.19	4.57	0.556	1.89	4.45	0.81	2.11	0.58	0.13	0.03	7.340	98.09
D ₂	58.11	11.59	4.85	0.280	1.92	4.79	0.95	1.97	0.67	0.16	0.02	11.770	97.08
D ₃	62.03	10.05	4.27	0.133	1.40	6.27	1.20	1.50	0.67	0.11	0.07	10.420	98.12
D ₄	56.27	9.10	4.66	0.141	2.77	9.80	1.72	1.14	0.64	0.17	0.21	11.480	98.11
D ₅	70.53	9.31	4.25	0.147	1.65	2.99	2.07	1.11	0.71	0.17	0.08	5.096	98.11
M ₁	65.95	11.86	4.73	0.107	1.98	2.54	1.67	1.93	0.87	0.13	0.04	7.569	99.38
M ₂	61.04	12.78	5.31	0.164	1.80	2.84	1.78	2.45	0.91	0.24	0.04	8.482	97.85
M ₃	58.52	13.37	6.15	0.162	2.34	3.35	2.06	2.14	1.03	0.23	0.04	8.804	98.20
M ₄	63.64	12.80	4.46	0.121	1.47	4.07	2.85	2.26	0.89	0.23	0.02	4.926	97.74
M ₅	58.51	13.87	5.55	0.154	1.88	4.10	2.38	2.30	1.01	0.24	0.02	7.506	97.52
L ₁	59.57	12.52	7.90	0.152	3.49	3.45	2.31	1.66	1.40	0.26	0.18	5.306	98.20
L ₂	58.86	12.35	6.99	0.187	4.00	3.80	1.74	1.66	0.96	0.16	0.10	7.729	98.54
L ₃	82.58	5.12	2.18	0.048	0.76	1.28	0.87	0.83	0.70	0.06	0.04	2.901	97.37
L_4	41.32	6.98	3.42	0.078	2.12	21.12	0.85	0.92	0.63	0.13	0.03	20.010	97.61
L ₅	36.38	6.74	3.60	0.088	2.56	22.69	0.82	0.92	0.62	0.16	0.04	21.830	96.45
S ₁	61.13	12.34	6.44	0.289	1.77	2.21	1.14	1.81	0.77	0.30	0.04	9.780	98.02
S ₂	64.08	9.35	5.79	0.384	2.49	2.73	1.09	1.37	0.76	0.27	0.27	8.414	97.00
S ₃	62.21	11.80	5.13	0.217	2.05	3.33	1.26	1.70	0.76	0.17	0.06	9.304	97.99
S4	63.67	12.03	5.12	0.191	1.73	2.66	1.45	1.75	0.82	0.19	0.06	8.042	97.71
S ₅	61.37	11.47	8.32	0.285	1.49	2.79	0.86	1.92	0.67	0.27	0.05	8.394	7.75

TABLE 3 - Results of XRF analysis of major components of sediments (fraction <µm) of the rivers Drini i Bardhë, Morava e Binçës, Lepenc and Sitnica, expressed as weight % of oxides.

* LOI - loss upon ignition at 900° C



FIGURE 2 - Distribution of oxides and of LOI (in %) in stream sediments of rivers Drini i Bardhë (a), Morava e Binçës (b), Lepenc (c) and Sitnica (d).

STATISTICAL ANALYSIS Determination of basic statistical parameters

Table 5 presents basic statistical parameters for 56 elements in 20 samples of stream sediments (fraction <63 μ m) which can be considered as preliminary values until a larger dataset has been collected. For each element, the values are given as arithmetic mean, geometric mean, median,

minimal and maximal concentration, variance, standard deviation, skewness and curtosis.

Determination of anomalies (extremes and outliers)

Table 6 presents the identified anomalous geochemical data (extremes and outliers) both for the toxic and lithogenic elements, using experimental data from Table 4 and box plot approach [18].



Cluster analysis of Q-modality

Cluster analysis of Q-modality was performed on the total set of geochemical data from Table 4. Sampling stations were grouped in 3 and 4 clusters. In Table 7 are pre sented the results of Q-modality cluster analysis, with the distances given in parenthesis, using 4 clusters. In the case

of 3 clusters, clusters 1 and 3 remain the same, with only 2 locations, and cluster 2 is composed of 16 locations. Samples L_4 and L_5 show strong anomaly of lithogenic elements Ca and Sr. Samples D_3 and D_4 show strong anomaly of Sr.

TABLI	E 4 - Conce	ntrations of	63 elements	(ppm) in str	eam sediments	(fraction
<63 µm) of	the rivers of	of Kosovo (l	Drini i Bardhë	ė, Morava e	Binçës, Lepenc	and Sitnica).

Element										Sta	tion									
(ppm)	D.	D.	D.	D.	D.	М.	М.	М.	М.	м.	L.	L	L	L	L	S.	S.	S.	S.	S.
	D 1	D ₂	D ₃	D ₄	D5	1011	1412	1413	1414	1415	1.1	1.2	1.3	1.4	1.5	51	52	53	54	55
Ca	29500	33100	46600	64400	17800	14900	16500	15300	20400	19900	15200	20200	7500	161000	160000	13800	16800	20400	14200	18000
Fe	25600	28500	24700	25100	23700	26100	31200	34500	22400	28700	35800	33600	11700	20600	17800	41900	33000	27300	30300	45700
Al	15700	17500	17600	12600	12300	12500	15200	18800	11100	18900	14400	18800	6300	10000	8000	23500	15100	17000	16200	11700
Mn	3790	2050	1040	977	1040	8300 765	1180	1010	5200	/100	707	13000	246	428	479	2200	2990	1660	1400	2120
K	1300	1500	1800	1300	1300	1100	2100	2200	1800	2900	1000	1400	800	1600	1200	3100	1800	1800	1700	1200
Р	380	480	330	510	550	360	770	730	800	750	800	480	190	410	480	950	840	510	580	710
S	210	380	180	210	270	200	430	400	240	340	550	160	90	230	310	400	920	300	370	3300
Na	90	100	140	120	120	70	130	160	160	160	210	210	110	130	80	180	150	150	150	130
Zn Ni	/5.50	85	38.9	163	49.7 82.4	130	91.5	91.9 80.6	40.6	66.4	107.00	220	41.3	40.6	41.1	130	329	204	172	2280
Pb	44.90	51.3	23.4	19.3	18.4	188	57.8	46.6	136	102	72.50	37.8	11.5	16.1	19.2	210	576	75.6	132	2210
Ba	109.00	93.3	98.2	74	81.8	96.10	137	128	71.4	111	80.30	76.1	31.7	55.6	66	203	258	133	149	112
Cr	45.00	73	81.4	84	58.3	72.40	70.9	76.6	39.1	61.5	75.30	152	35.7	60.2	58.7	104	154	133	114	58.5
Sr	24.70	35.9	85.5	121	43.3	26.40	50.1	48.5	43	47.4	30.70	42.7	12	93.6	98.3	46	46.1	55.9	52.7	53.1
Cu Co	91.20	03.5	/1.9	42.5	22.3	39.50	38.5	34.3	31.8	54.5	41.40	45.4	26.1	21	23.1	50.20	57.4	53.9	57.7	24.1
Co	26 40	20.7	19.4	19.2	42.5	15 30	17.3	18.6	42.4	15.5	19.80	25.8	6.3	11.7	17.8	33.20	49.4	24.5	21.6	24.1
V	27.00	35	39	40	34	29.00	42	73	41	60	48.00	54	17	32	24	63.00	47	40	43	30
La	13.80	8.8	17.1	12.8	18.7	14.50	23.9	21.4	20.3	25	22.70	18.2	12.8	12.9	9.1	31.10	22.8	19.9	21.3	9.8
Ti	100.00	200	100	1000	800	200.00	400	900	900	1000	1200.00	1100	400	500	300	300.00	300	200	300	100
Li	26.30	30.2	22.4	14.3	13.4	23.80	25.1	21.3	10.1	17.9	17.70	19.4	5.1	10.7	9	26.10	16.4	20.3	17.4	23.3
Y Nd	9.55	8.99	10.5	13.9	91.2	15.10	23.6	20.7	14.9	23.6	9.70 21.60	10.5	4.55	8.77	7.52 8.59	29.60	22.1	10.5	19.5	/.91
Au	0.0276	0.0174	0.0005	0.0005	0.0005	0.0166	0.0159	0.463	0.0012	0.0048	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	0.0157	0.0066	0.0029	0.0059	0.0323
Th	2.60	2.1	4.1	3.3	3.9	3.10	6	6.3	6.4	7.5	5.20	4.7	2.5	3.2	2.4	5.90	4.5	4.6	5.2	4
Ga	4.60	5.21	4.3	3.96	3.58	3.81	4.5	5.67	3.67	5.91	4.71	5.47	1.94	6.28	2.47	6.43	4.4	4.4	4.38	3.46
As	6.30	7.4	6.8	4.5	6	17.20	12.1	9.2	12.2	16.3	8.10	9.6	2.3	4.2	4.7	27.10	113	15.4	18.1	252
Sc Dv	2.40	3.4	4.1	3.8	2.8	2.60	3.4	6.2	3.3	2.62	3.60	6.2 2.38	1.3	2.8	1.9	5.30	3.7	2 21	4.1 2.47	2.2
Dy Sn	6.94	2.00	5.37	3.45	1.77	2.57	2.04	1.92	3.66	2.86	2.44	1.28	0.61	0.83	1.44	2.16	3.17	4.92	3.83	8.24
Sm	3.80	3.1	4.3	3.3	4	3.10	4.7	4.3	4.1	4.9	4.40	3.9	2.3	2.5	1.9	5.90	4.7	4	4.1	2.7
Rb	12.00	13.4	20.3	10.8	11.4	10.50	20.6	23.3	18.7	27.2	8.40	12.5	7.7	14.9	10.9	32.80	17.8	17.4	17.6	106
Gd	3.30	2.9	3.5	2.9	3.4	2.70	4	3.8	3.6	4.3	3.60	3.2	1.8	2.2	1.8	5.10	4.1	3.5	3.5	2.7
Pr sh	4.00	2.5	4.8	3.5	4.8	4.00	6.1	5.3	5.2	6.3	5.70	4.7	3.2	3.1	2.3	1.32	5.8	5.2	5.2	2.7
Cs	1.44	1.5	1.34	0.32	0.23	0.81	2.8	3.01	1.93	3.07	0.72	0.4	0.61	1.12	0.25	3.28	1.88	2	2.36	1.68
Er	0.90	0.9	1.1	1.2	1	0.80	1.2	1.4	1.6	1.8	1.10	1.2	0.5	0.9	0.8	1.70	1.4	1.1	1.1	0.9
Zr	0.60	0.5	0.6	0.7	0.9	0.50	1.2	3	1.5	1.6	0.60	1.3	0.8	0.7	0.6	1.60	1	0.8	1	1.1
Cd	0.65	0.49	0.2	0.19	0.14	0.26	0.27	0.3	4.24	21.3	0.25	0.14	< 0.01	0.27	0.29	0.38	1.82	0.51	0.58	96.2
Be	0.90	1	0.8	0.6	0.6	0.60	1	1.1	0.7	1.1	0.40	0.6	0.2	0.5	0.3	1.60	1	0.8	0.9	0.7
ь Ня	0.94	0.557	0.502	0 799	0.598	0.665	0 629	0 749	0.812	1 26	0 441	0 471	0 247	0 269	0 423	1.00	2 65	2.09	1 43	11.9
Mo	0.68	0.61	0.25	0.2	0.41	0.29	0.43	0.37	0.44	0.41	0.49	0.39	0.11	0.24	0.24	0.50	0.48	0.47	0.39	1.15
Nb	0.30	0.4	0.3	0.5	0.6	0.40	0.8	0.7	0.6	0.8	0.50	0.3	0.3	0.5	0.3	0.80	0.5	0.4	0.3	0.3
Ho	0.40	0.4	0.4	0.4	0.4	0.30	0.5	0.5	0.6	0.6	0.40	0.4	0.2	0.3	0.3	0.70	0.5	0.4	0.4	0.3
Se En	0.40	0.7	0.4	0.5	0.3	0.30	0.4	0.6	0.3	0.5	0.40	0.3	<0.1	0.6	0.3	0.60	0.6	0.3	0.2	0.6
ги Tb	0.80	0.7	0.8	0.0	0.8	0.80	0.9	0.9	0.7	0.9	0.90	0.8	0.4	0.3	0.4	0.70	0.9	0.8	0.8	0.0
Yb	0.50	0.6	0.6	0.8	0.7	0.60	0.8	1	1.2	1.5	0.80	0.9	0.4	0.7	0.6	1.30	0.9	0.8	0.9	0.6
TI	0.18	0.14	0.17	0.1	0.12	0.12	0.19	0.23	0.19	0.29	0.08	0.13	0.09	0.13	0.1	0.54	0.34	0.21	0.28	0.38
U	0.40	0.4	0.4	0.4	0.4	0.40	0.8	0.9	1.1	1.2	0.70	0.5	0.4	0.5	0.4	0.60	0.6	0.6	0.8	0.9
Bi	0.37	0.26	0.19	0.14	0.11	0.49	0.24	0.23	23	33	0.15	0.14	0.07	0.11	0.13	0.53	0.69	0.32	0.42	8.5
LU Hf	<0.10	<0.1	<0.1	<0.1	<0.1	<0.10	<0.1	0.1 <0.1	<0.2	<0.2	<0.10	0.1 <0.1	<0.1	<0.1	<0.1	<0.10	<0.1	<0.1	<0.1	<0.1
W	<0.10	<0.1	<0.1	<0.1	<0.1	<0.10	<0.1	<0.1	<0.1	<0.1	<0.10	<0.1	0.2	0.1	0.1	<0.10	0.8	0.2	0.2	1.3
Tm	0.10	0.1	0.1	0.1	0.1	0.10	0.1	0.2	0.2	0.2	0.10	0.2	< 0.1	0.1	< 0.1	0.20	0.2	0.1	0.2	0.1
Ge	< 0.10	< 0.1	< 0.1	< 0.1	< 0.1	< 0.10	< 0.1	< 0.1	< 0.1	< 0.1	0.10	0.1	< 0.1	< 0.1	< 0.1	0.10	0.1	< 0.1	< 0.1	< 0.1
In	0.04	0.03	0.03	0.02	< 0.02	0.05	0.03	0.03	0.03	0.06	0.02	0.02	< 0.02	< 0.02	< 0.02	0.05	0.13	0.03	0.05	0.86
Ag To	0.08	0.123	0.055	0.199	0.041	0.168	0.14	0.258	0.16	0.212	0.107	0.085	0.047	0.046	0.047	0.586	0.413	0.268	0.315	4.35
те Та	<0.26	0.15	0.06	0.04	0.06	0.05	<0.07	<0.04	0.06	0.06	0.08	<0.05	<0.04	<0.05	0.06	<0.12	<0.12	0.08	<0.08	<0.07
Re	<0.0010	< 0.001	0.001	0.001	0.001	< 0.001	< 0.001	0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	< 0.001	0.001	< 0.001	< 0.001	0.002





TABLE 5 - Basic statistical parameters for 9 major a	and 47 minor elements
in 20 samples of stream sediments (fraction <63 µm) of	of the rivers of Kosovo.

Descriptive Statistics									
	Mean	Geometric	Median	Minimum	Maximum	Variance	Std.Dev.	Skewness	Kurtosis
Ca	36275.00	24425.22	18950.00	7500.00	161000.0	1.971339E+09	44399.76	2.498057	5.37483
Fe	28410.00	27283.16	27900.00	11700.00	45700.0	6.222937E+07	7888.56	0.206890	0.65138
Al	14660.00	14032.28	15150.00	6300.00	23500.0	1.728779E+07	4157.86	-0.088528	0.04435
Mg	8840.00	8358.76	8300.00	3400.00	15600.0	8.994105E+06	2999.02	0.686579	0.51685
Mn	1338.65	1089.54	1040.00	245.00	3790.0	8.101519E+05	900.08	1.361514	1.74861
K	1645.00	1556.14	1550.00	800.00	3100.0	3.457632E+05	588.02	1.146582	1.29398
Р	580.50	542.82	530.00	190.00	950.0	4.096289E+04	202.39	0.024572	-0.82324
S	474.50	325.11	305.00	90.00	3300.0	4.737629E+05	688.30	4.021336	17.00767
Na	137.50	132.29	135.00	70.00	210.0	1.440789E+03	37.96	0.201698	-0.09793
Zn	219.61	102.21	83.85	32.00	2280.0	2.472091E+05	497.20	4.153524	17.78716
Ni	124.24	108.62	104.50	40.60	329.0	4.870201E+03	69.79	1.470977	2.62240
Pb	202.42	67.17	54.55	11.50	2210.0	2.393024E+05	489.19	4.037021	16.99005
Ba	108.73	98.56	97.15	31.70	258.0	2.653451E+03	51.51	1.465576	2.93629
Cr	80.38	74.17	72.70	35.70	154.0	1.180037E+03	34.35	1.025951	0.32022
Sr	52.85	46.76	46.75	12.00	121.0	7.276152E+02	26.97	1.146029	1.09987
Cu	138.98	48.59	41.95	11.60	1930.0	1.781137E+05	422.04	4.455558	19.89581
Ce	39.17	36.97	41.10	17.80	71.2	1.747959E+02	13.22	0.379573	0.29638
Со	20.34	18.61	19.55	6.30	49.4	8.471945E+01	9.20	1.643727	4.53070
V	40.90	38.70	40.00	17.00	73.0	1.908316E+02	13.81	0.627564	0.34067
La	17.85	16.85	18.45	8.80	31.1	3.546471E+01	5.96	0.236001	-0.35921
Ti	465.50	340.68	300.00	100.00	1200.0	1.293839E+05	359.70	0.800348	-0.83978
Li	18.51	17.12	18.65	5.10	30.2	4.361884E+01	6.60	-0.289013	-0.52334
Y	10.60	10.18	10.40	4.55	16.7	9.011796E+00	3.00	0.489622	0.50256
Nd	17.68	16.89	18.65	8.59	29.6	2.794670E+01	5.29	0.176770	-0.11391
Au	0.03	0.00	0.00	0.00	0.5	1.060515E-02	0.10	4.438727	19.78218
Th	4.38	4.11	4.30	2.10	7.5	2.337763E+00	1.53	0.297481	-0.77020
Ga	4.31	4.16	4.39	1.94	6.4	1.234830E+00	1.11	-0.143408	0.14803
As	27.63	11.74	9.40	2.30	252.0	3.350027E+03	57.88	3.557489	13.13403
Sc	3.62	3.38	3.50	1.30	6.2	1.809342E+00	1.35	0.481103	-0.17743
Dy	2.39	2.30	2.38	1.12	3.9	4.610892E-01	0.68	0.429657	0.53631
Sn	3.07	2.51	2.56	0.61	8.2	3.994927E+00	2.00	1.234850	1.30962
Sm	3.80	3.67	4.00	1.90	5.9	9.663158E-01	0.98	-0.122266	-0.02258
Rb	15.94	14.81	14.15	7.70	32.8	4.274147E+01	6.54	1.058957	0.90749
Gd	3.29	3.19	3.45	1.80	5.1	6.678684E-01	0.82	-0.060071	0.36670
Pr	4.61	4.38	4.80	2.30	7.7	2.026816E+00	1.42	0.109427	-0.35781
Sb	2.68	0.84	0.66	0.15	31.8	4.903478E+01	7.00	4.184749	18.07650
Cs	1.64	1.43	1.47	0.61	3.3	7.598197E-01	0.87	0.617410	-0.88634
Er	1.13	1.08	1.10	0.50	1.8	1.053684E-01	0.32	0.439890	0.09992
Zr	1.03	0.92	0.85	0.50	3.0	3.422105E-01	0.58	2.170546	6.11568
Cd	6.42	0.52	0.29	0.01	96.2	4.687318E+02	21.65	4.166766	17.84224
Be	0.77	0.70	0.75	0.20	1.6	1.043158E-01	0.32	0.529255	1.03523
Hg	1.47	0.85	0.71	0.25	11.9	6.447837E+00	2.54	4.019696	17.05039
Mo	0.43	0.38	0.41	0.11	1.2	4.805132E-02	0.22	1.858310	5.67155
Nb	0.48	0.45	0.45	0.30	0.8	3.326316E-02	0.18	0.675543	-0.81751
Ho	0.42	0.40	0.40	0.20	0.7	1.431579E-02	0.12	0.598157	0.52934
Se	0.42	0.38	0.40	0.10	0.7	2.589474E-02	0.16	-0.023577	-0.78658
Eu	0.75	0.72	0.80	0.40	1.2	3.736842E-02	0.19	-0.024287	0.54896
Tb	0.41	0.39	0.40	0.20	0.7	1.463158E-02	0.12	0.384610	0.83646
Yb	0.82	0.78	0.80	0.40	1.5	7.326316E-02	0.27	0.985911	1.04092
Tl	0.20	0.18	0.17	0.08	0.5	1.354184E-02	0.12	1.548997	2.57397
U	0.62	0.58	0.55	0.40	1.2	6.378947E-02	0.25	0.991366	0.00855
Bi	0.68	0.27	0.23	0.07	8.5	3.412125E+00	1.85	4.415446	19.64050
Tm	0.14	0.13	0.10	0.10	0.2	2.394737E-03	0.05	0.681161	-1.71946
In	0.08	0.04	0.03	0.02	0.9	3.451158E-02	0.19	4.343530	19.14970
Ag	0.39	0.16	0.15	0.04	4.4	8.904732E-01	0.94	4.315059	18.98710
Te	0.20	0.18	0.17	0.08	0.5	1.354184E-02	0.12	1.548997	2.57397

Sample	Extremes of elements (Ω) (ppm)	Outliers of elements (o) (ppm)
\mathbf{D}_1	-	Mn (3790.0)
	_	Sn(6.94)
		$T_{-}(0.2(1))$
	-	10(0.20)
D_2	-	-
D3	-	Sr (85.5)
 D	Sr(1210)	$C_{2}(64400.0)$
D4	31 (121.0)	Ca (04400.0)
D_5	-	-
M_1	-	-
M.	_	_
1112	A (0, 4(2)	V(72.0)
IVI 3	Au (0.405)	V (73.0)
	-	Sc (6.2)
	-	Zr (3.0)
M.	Cd(424)	<u> </u>
1114	Sh(5.76)	
	SD (5.76)	-
M5	Cd (21.3)	K (2900.0)
	-	Y (18.5)
		Yh(15)
T		10(1.5)
L_1	-	-
L_2	-	Sc (6.2)
		Cr (152.0)
L.	_	_
13	C (1(1000.0.)	8 (02 ()
L_4	Ca (161000.0)	Sr (93.6)
L_5	Ca (160000.0)	Sr (98.3)
S.	-	Y (16.7)
~1	_	$D_{V}(3.91)$
	-	Dy(3.91)
	-	KD (32.8)
	-	Gd (5.1)
	-	T1 (0.54)
		K(31000)
C.	$C_{-}(40.4)$	NE (220.0.)
\mathbf{S}_2	Co (49.4)	N1 (329.0)
	As (113.0)	Ba (258.0)
	Cd (1.82)	Cr (154.0)
	Ph (576.0)	Hg (2.65)
	70(5480)	S(0200)
	ZII (548.0)	3 (920.0)
	Sb (4.4)	In (0.13)
S_3	-	-
S4	-	-
S	Δμ(0.0323)	Sn(8.24)
35	Au(0.0525)	511(0.24)
	Ag (4.55)	1e(0.27)
	In (0.86)	-
	As (252.0)	-
	Sh (31.8.)	-
	Cd(962)	
	Cu(90.2)	-
	Cu (1930.0)	-
	Pb (2210.0)	-
	Zn (2280.0)	-
	$H_{\alpha}(11.9)$	
	11g(11.7)	-
	S (3300.0)	-
	Bi (8.5)	
	Mo(1.15)	

TABLE 6 - Samples of stream sediments of the rivers ofKosovo (fraction < 63 μ m) with anomalous values (extremesand outliers) of concentrations for particular elements (ppm).

 TABLE 7 - Grouping of 20 samples of sediments

 from the rivers of Kosovo by cluster analysis of Q-modality.

Clusters	Samples
Cluster 1	L ₄ (242.9091)*
Cluster I	L ₅ (242.9091)
	D ₁ (1291.178)
	D ₂ 1860.526)
	D ₅ (427.5001)
Cluster 2	M ₁ (832.6213)
Cluster 2	M ₄ (518.9352)
	M ₅ (919.9263)
	L ₃ (2662.329)
	S ₃ (637.7465)
Cluster 3	D ₃ (1300.929)
Cluster 3	D ₄ (1300.929)
	M ₂ (712.0915)
	M ₃ (452.0736)
	L ₁ (715.4406)
Cluster 4	L ₂ (996.2620)
Cluster 4	S ₁ (1305.292)
	S ₂ (487.3896)
	S ₄ (842.3110)
	S ₅ (1642.505)

* In parenthesis is the distance of a cluster member (sample) from the centre of the respective cluster group. TABLE 8 - Weathering indices A and B and compositional maturity index (M), calculated from XRF data from Table 3.

Location	Index A	Index B	М
D ₁	0.8651645	0.3970905	4.9259259
D ₂	0.8502777	0.3994819	4.7247387
D ₃	0.8760025	0.4716088	4.4423077
D_4	0.8833782	0.5818015	2.2806236
D ₅	0.8917568	0.3985788	2.8010753
M ₁	0.8587254	0.3411111	3.7780822
M ₂	0.8420077	0.3561713	4.2541899
M ₃	0.8316969	0.3608987	3.5250000
M_4	0.8505022	0.4176524	3.4861111
M ₅	0.8291030	0.387638	3.7957746
L_1	0.8425355	0.3721163	2.4448276
L_2	0.8424946	0.3682864	2.4407666
L_3	0.9435377	0.3679012	3.6503067
L_4	0.9019525	0.7663207	2.6599327
L_5	0.9002221	0.7837664	2.2662722
S ₁	0.8430624	0.2948571	4.8625430
S_2	0.8810735	0.3569464	2.9944134
S_3	0.8530511	0.3477059	4.0785498
S_4	0.8525012	0.3275573	4.3333333
S_5	0.8537176	0.3268779	5.6978723

DISCUSSION

Discussion of mineralogical composition

Mineralogical analysis has shown that the most abundant mineral is quartz (>30%), followed by the minerals from feldspar group (10 – 30%), except for the station S_5 (5 – 10%). Mica group, chlorite group and calcite group are less abundant (5 – 10%), except at stations M₂ and L₂ (10 – 30%). Hornblende group was detected at the station L₂ (<5%). However, due to the limitation of XRD method, this hornblende group is less certain. Other sediments from Lepenc River have not been studied by XRD method. Mineral composition of stream sediments is similar to the results obtained for sediments of Hugli River, northeast India [19].

From Table 2, one can get an idea about mineralogical maturity, which is commonly expressed by the quartz / feldspar ratio [20]. The high content of feldspars in all cases, except for S_5 , suggests mineralogical immaturity. Only the sediment in S_5 can be considered to be submature, because lower feldspar concentrations give higher ratio of quartz to feldspar (stable to unstable mineral).

Discussion of XRF analysis

Results of XRF analysis presented in Table 3 can be used for comparison of sediment composition with average values of different rock types using the plot log (SiO₂/ Al₂O₃) vs. log (CaO+Na₂O)/K₂O, which is shown in Fig. 4, a modified figure 10-2 in Prohić [21]. Samples D₁–D₅ plot in the region of sandstones. It has recently been reported by Bilinski [10] that Kupa River stream sediments were the weathering products of sandstones. To make comparison with the present work, data from Kupa River are presented as triangles in Fig. 4. Samples M₁ – M₅, L₁ – L₃ and S₁ – S₅ plot in the region between magmatic rocks and sandstones. Samples L₄ and L₅ plot in the region between average magmatic rocks, sandstones and carbonates.



FIGURE 4 - Composition of stream sediments from this work and from Kupa River, Croatia (fraction <63 µm) in comparison with the composition of sandstones, shales and carbonates (Average values of each rock type are presented by dots).

The data in Table 3 were used to calculate weathering indices after Kronberg and Nesbitt [22], using the following equations:

 $Index A = (SiO_2+CaO+K_2O+Na_2O)/$ $(Al_2O_3+SiO_2+CaO+K_2O+Na_2O)$

Index $B = (CaO+K_2O+Na_2O) / (Al_2O_3+CaO+K_2O+Na_2O)$

Indices A and B reflect the degree of silicate hydrolysis and accumulation of Al-/Si-oxides with simultaneous release of alkali and earth alkali cations. The lowest range of weathering was observed in samples L_4 and L_5 . Sediments of Drini i Bardhë River (D₁-D₅) plot close to the locations of basalt, terrestrial crust and granite, similarly as observed for the Kupa River by Bilinski [10]. Other sediments plot close to the less developed towards highly developed soils in Nepal. The highest degree of weathering was observed in sediments of Sitnica River.

The data in Table 3 were also used to calculate compositional maturity index, defined by Björlykke [23]:

$M = (Al_2O_3 + K_2O) / (MgO + Na_2O)$

Compositional maturity is basically a reflection of mineralogical maturity. It is a type of sedimentary maturity in which sediment approaches the textural end product. The results indicate the highest degree of weathering in Sitnica River at location S_2 , which is in agreement with the conclusion obtained from weathering indices after Kronberg and Nesbitt [22]. In Table 8 are presented calculated weathering and compositional maturity indices.

Discussion of ICP analyses and toxicity

Geochemical data (Table 4) can be used for the assessment of sediments' contamination by toxic elements. Chemical analyses were used to compare the obtained amounts of the selected toxic elements (As, Cd, Cr, Cu, Pb, Zn, Mn, Hg, Ni, P and Ag) with the existing criteria for sediment quality by SMSP, Falconbridge NC, SAS [24], referred in further discussion.

Concentrations of As above those causing significant toxic effects (33 ppm) were found in sediment samples at locations S_2 and S_5 . The concentrations below 6 ppm, causing the lowest toxic effects, were found at locations D_4 , L_3 , L_4 and L_5 . Other stations are moderately contaminated with As.

The concentrations of Cd above those causing significant toxic effects (10 ppm) were found only at locations M_5 and S_5 . In most stations, the concentrations are below the value causing the lowest toxic effects (0.6 ppm).

The concentrations of Cr above 110 ppm, causing significant toxic effects, were found at stations L_2 , S_2 , S_3 and S_4 . At all other locations, the concentrations were above the level of the lowest toxic effects (26 ppm), representing moderately contaminated sediments. Besides the total concentration, the valence state of Cr and its bioavailability should be studied as well in future experiments.

The concentration of Cu above the value causing significant toxic effects (110 ppm) was determined only at station S_5 . The concentrations below the value causing

minimal toxic effects (28 ppm) were found at stations D_5 , L_3 , L_4 and L_5 . All other locations are moderately contaminated.

The concentrations of Pb above the value of significant toxic effects (250 ppm) were present only at stations S_2 and S_5 . Very clean environment, where the concentrations of Pb were below the value of minimal toxic effect (31 ppm), was found at locations D_3 , D_4 , D_5 , L_3 , L_4 and L_5 . All other locations are moderately contaminated with Pb.

Zn levels above the value causing significant toxic effects (200 ppm) were found at stations S_2 and S_5 . Concentrations of Zn below 90 ppm, representing non-contaminated sediments, were found at M_4 and at all stations of Lepenc and of Drini i Bardhë rivers.

The concentrations of Mn above 1100 ppm, possibly causing significant toxic effects, were found at stations D_1 , D_2 , L_2 , M_2 and in S_1 - S_5 . The highest concentration was found at station D_1 (3790 ppm), which is significantly higher than the concentration present in average earth crust (1000 ppm) or in basalt (1700 ppm). Concentration of Mn measured at D_1 is higher than that found in the eastern part of the Kupa River drainage basin by Frančišković-Bilinski [5, 7], where the influence of mining was observed. This highest value of Mn at D_1 is supposed to come from ore mineralization. The concentrations below the lowest toxic effects (460 ppm) were found only at stations L_3 and L_4 . In future studies, determination of valence states of manganese and its bioavailability are recommended.

Sediments contaminated with Hg in which the values are exceeding 2 ppm were found only at locations S_2 and S_5 . All other sediments are moderately contaminated with Hg, because the concentrations are above 0.2 ppm, which is the limit for the lowest toxic effects.

The concentrations of Ni are above 75 ppm, causing significant toxic effects, and were found at most of the stations: D_1 - D_5 , M_1 - M_3 , L_1 , L_2 , L_4 , L_5 , S_1 - S_5 . The highest value was obtained at S_2 (329 ppm). All Ni values are higher than those found in the Kupa River drainage basin by Frančišković-Bilinski [7], and at most locations of the upper Sava River drainage basin by Frančišković-Bilinski [8].

The concentrations of P slightly above 600 ppm, indicating minimal toxic effects, were found at locations M_2 - M_5 , L_1 , S_1 , S_2 and S_5 . The highest value (950 ppm) was found at S_1 . These values are below those in average earth crust (1100 ppm) and are far from 2000 ppm, which causes significant toxic effects.

Elevated concentrations of Ag were found at two locations. At S_1 the concentration is slightly above 0.5 ppm, indicating minimal toxic effects. It is significantly higher at S_5 (4.35 ppm), almost double than maximal concentrations reported for the polluted sites of the upper Sava River [8].

Discussion of anomalies

Results of the box plot detection of anomalies, presented in Table 5, show several contaminated areas in Kosovo. The most contaminated, with a number of toxic elements, is Sitnica River at the locations S_2 and S_5 , as the result of anthropogenic pollution due to the industrial processes in the adjacent Kishnica and in Mitrovica towns. Locations M_4 and M_5 are contaminated with Cd. Location D_1 shows increased concentration of Mn, and location M_3 of Au. They deserve further investigation and looking for possible Mn and Au ores in the vicinity.

CONCLUSIONS

Mineralogical, geochemical and statistical investigation of the stream sediments of main rivers in Kosovo have been described for the first time. Their drainage basins are of supra-regional interest, because in the lower courses these rivers flow through Albania (Drini i Bardhë), Serbia (Morava e Binçës and Sitnica) and Macedonia (Lepenc).

Mineralogical analysis has shown that the most abundant minerals are quartz and feldspars, less abundant are mica, chlorite and calcite. Mineralogical maturity, expressed by the quartz/feldspar ratio, suggests mineralogical immaturity of all sediments, with the exception of sediment S_5 (from Sitnica River), considered to be submature.

For better understanding of sediments as weathering products, XRF analysis results were used for the comparison with average rock types from the literature. All sediments from Drini i Bardhë plot in the region of sandstones. All sediments of Morava e Binçës and Sitnica and three sediments of the upper course of Lepenc plot in the region between magmatic rocks and sandstones. Sediments from the lower course of Lepenc plot between average magmatic rock, sandstones and carbonates, and show the lowest degree of weathering. The highest degree of weathering shows the sediment from Sitnica River. Compositional maturity shows the highest degree of weathering in Sitnica River, which is in agreement with calculated weathering indices.

By comparing the concentrations of toxic elements with the existing criteria for sediment quality, it was found that two sites in Sitnica River are significantly polluted. These are the locations in Fushë Kosova (Kosovo Polje) (S₂) and in Mitrovica (S₅). Near location S₂, there is ore (containing Zn, Pb) processing by flotation. Near location S₅, there is a factory for Zn electrolysis. In Morava e Binçës River, two sites are polluted with Cd: Dobrqan (M₄) and Kormini i ulët (M₅). Locations with increased Mn (D₁) and Au (M₃) concentrations can be suggested for future investigations with regard of ore deposits.

The authors of this paper suggest future monitoring of sediments and possibly remediation of Sitnica and Morava e Binçës rivers, which ultimately flow into the Black Sea.

© by PSP Volume 18 – No 8. 2009



ACKNOWLEDGEMENTS

This paper is a part of PhD Thesis of Fatbardh Gashi, defended at the University of Pristina, Kosovo, in June 2006 (supervisor Dr. Halka Bilinski, from the Ruđer Bošković Institute, Zagreb, Croatia). MSc Florim Isufi from the Department of Geography, University of Pristina is thanked for his assistance with geographical positioning of sampling stations using GIS and drawing maps. Special thanks go to the collaborators of the Faculty of Natural Science, Department of Chemistry and Geography, University of Pristina: Dr. Naser Troni, Dr. Mustafë Bacaj, Dr. Selim Jusufi and Dr. Valdet Pruthi for useful discussions and for participation in this work. Mrs. Marija Kumbatović, linguist, is thanked for her kind help in editing of English language of the paper. Part of the work and preparation of the manuscript was partly financed through the projects of Croatian Ministry of Science Education and Sport No. 0098041 and No. 098-0982934-2720.

REFERENCES

- Montgomery, J.M. (1996). Water Treatment, Principles and Design. John Wiley & Sons, New York
- [2] Halamić, J., Bukovec, D., Miko, S. and Galović, L. (2001). A factor model of the relationship between stream sediment geochemistry and adjacent drainage basin lithology, Medvednica Mt., Croatia. *Geologia Croatica* 54(1), 37-51.
- [3] Frančišković-Bilinski, S., Bilinski, H., Tibljaš, D. and Rantitsch, G. (2005). Effects of mercury mining regions from NW Dinarides on quality of stream sediments. *Fresenius Environmental Bulletin* 14(10), 913-927.
- [4] Frančišković-Bilinski, S., Bilinski, H., Tibljaš, D. and Hanžel, D. (2006). Sediments from Savinja, Voglajna and Hudinja rivers (Slovenia), reflecting anomalies in an old metallurgic area. *Fre*senius Environmental Bulletin 15(3), 220-228.
- [5] Frančišković-Bilinski, S. (2005). Geochemistry of stream sediments in Kupa River drainage basin, Dissertation. University of Zagreb, 197 pp.
- [6] Frančišković-Bilinski, S. (2006). Barium anomaly in Kupa River drainage basin. *Journal of Geochemical Exploration* 88(1-3), 106-109.
- [7] Frančišković-Bilinski, S. (2007). An assessment of multielemental composition in stream sediments of Kupa River drainage basin, Croatia for evaluating sediment quality guidelines. *Fresenius Environmental Bulletin* 16(5), 561-575.
- [8] Frančišković-Bilinski, S. (2008). Detection of geochemical anomalies in stream sediments of the upper Sava River drainage basin (Slovenia, Croatia). *Fresenius Environmental Bulletin* 17(2), 188-196.
- [9] Frančišković-Bilinski, S. (2008). Detection of coal combustion products in stream sediments by chemical analysis and magnetic susceptibility measurements. *Mineralogical Magazine* 72(1), 43-48.
- [10] Bilinski, H. (2008). Weathering of sandstones studied from the composition of stream sediments of the Kupa River (Croatia). *Mineralogical Magazine* 72(1), 23-26.
- [11] Šajn, R., Bidovec, M., Andjelov, M., Pirc, S. and Gosar, M. (1998). Geokemični atlas Ljubljane in okolice. Geološki Zavod Slovenije, Ljubljana.

- [12] Sikošek, B. (1971). Explanation for Geological map of Yougoslavia, scale 1:500000, Federal Geological Institute, Belgrade.
- [13] Ivković, A., Šarin, A. and Komatina, M. (1983). Explanation for the Hydrogeological Map of SFR Yugoslavia 1:500000, Federal Geological Institute, Belgrade.
- [14] Powder Diffraction File (1997). International Center for Diffraction Data, Newtown Square, PA, USA.
- [15] Boldrin, A., Juračić, M., Mengazzo Vitturi, L., Rabitti, S. and Rampazzo, G. (1992). Sedimentation of river-borne material in a shallow shelf sea: Adiga River, Adriatic Sea. *Marine Geology* 103, 473-485.
- [16] Salminen, R. and Tarvainen, T. (1997). The problem defining geochemical baselines. A case study of selected elements and geological materials in Finland. *Journal of Geochemical Exploration* **60**, 91-98.
- [17] StatSoft, Inc. (2001). STATISTICA (data analysis software system), version 6. http://www.statsoft.com
- [18] Tukey, J.W. (1977). Exploratory data analysis. Reading: Addison-Wesley.
- [19] Sarkar, S.K., Frančišković-Bilinski, S., Bhattacharya, A., Saha, M., Bilinski, H. (2004). Levels of elements in the surficial estuarine sediments of the Hugli River, northeast India and thier environmental implications. *Environment International* **30**, 1089-1098.
- [20] Dockal, J.A. (2006). Sedimentary petrology: Sediment or sand observation and description (lectures). University of North Carolina, Wilmington. Available at: http://people.uncw.edu/dockal/ GLY312/grainsize/grainsize.htm
- [21] Prohić, E. (1998). Geokemija. Manualia Universitatis Studiorum Zagrebiensis, Targa, Zagreb, Croatia, 554 pp (in Croatian).
- [22] Kronberg, B.I. and Nesbitt, H.W. (1981). Quantification of weathering, soil geochemistry and soil fertility. *Journal of Soil Science* 32, 453-459.
- [23] Björlikke, K. (1974). Geochemical and mineralogical influence of Ordovician Island Arcs on epicontinental clastic sedimentation. A study of Lower Paleozoic sedimentation in the Oslo Region, Norway. Sedimentology 21, 251-272.
- [24] SMSP and FALCONBRIDGE NC SAS (2005). Koniambo project, Environmental and Social Impact Assessment, Chapter 4 Mine, 4.2-7 Quality criteria for freshwater sediment. Available at:http://www.falconbridge.com/documents/koniambo_esia/vol2/ Chapter04/4_2_7/4_2_7.pdf

Received: December 22, 2008 Revised: February 16, 2009 Accepted: March 23, 2009

CORRESPONDING AUTHOR

Stanislav Frančišković-Bilinski

Institute "Ruđer Bošković" Division of Marine and Environmental Research POB 180 10002 Zagreb CROATIA

E-mail: francis@irb.hr

FEB/ Vol 18/ No 8/ 2009 – pages 1462 - 1471