AN ASSESSMENT OF MULTIELEMENTAL COMPOSITION IN STREAM SEDIMENTS OF KUPA RIVER DRAINAGE BASIN, CROATIA FOR EVALUATING SEDIMENT QUALITY GUIDELINES

Stanislav Frančišković-Bilinski

Institute "Ruđer Bošković", POB 180, 10002 Zagreb, Croatia

SUMMARY

Levels and sources of 8 major and 45 trace elements in stream sediments of a non-mountain drainage basin of Kupa River, which is of supra-regional interest, is presented for the first time. It is a significant water resource for Croatia, Slovenia, and Bosnia and Herzegovina, but in its great part under mines from the war (1991-1995), and therefore difficult to sample.

Concentration of elements was determined in fine fraction (<63 μm) by ICP-MS. The drainage basin was delineated in such a way that each basin segment corresponded to the area upstream and upslope of each sampling site. Selected examples for Ca and Ba distributions are presented.

Cluster analysis of Q-modality, applied on a geochemical data set, was used to disaggregate it into three more homogenous subsets. Cluster 1 was interpreted as a region with significant anthropogenic Ba anomaly. Cluster 2 represents a part of the Supradinaric belt with ophiolites. Sedimentary formation was under the influence of mafic and ultramafic lavas, but also neutral and acid volcanism. Cluster 3 represents a part of the Dinaric carbonate platform, on which shallow water carbonate sedimentation occurred. The geochemistry of stream sediments belonging to the largest cluster 3 has been used to identify background geochemical signatures, related to geology of the mining-free area.

Assessment of sediment contamination with toxic elements was performed in comparison with existing criteria for sediment quality. Toxic effects are possible with respect to Ba, Mn, Ni, Pb, Zn, and P, on some locations. Two Ba anomalies were found. One is significant and of anthropogenic origin in the western part of the basin, whereas that in the eastern part of the basin is of natural origin. Concentrations of Ba can be followed far downstream in Kupa River. Therefore, Ba can be suggested as a suitable parameter to study sediment transport in the studied region.

KEYWORDS: stream sediments, mineral composition, chemical composition, anomalies` determination, cluster analysis, Kupa River drainage basin.

INTRODUCTION

There is an increasing interest in major and trace element geochemistry of stream sediments with numerous applications. Some of them will be mentioned.

The chemical composition of stream sediments can provide information on the presence of mineral deposits. Bonham-Carter and Goodfellow [1], Palinkaš and Šinkovec [2], and Palinkaš [3] have used stream sediment geochemistry of some selected Paleozoic regions in Croatia as an indicator of global tectonic events.

Borovec [4] has mapped a series of elements determined in stream sediments of Elbe River, and has used cluster analysis to find sources of contamination. Moon [5] has developed a quantitative relation between point source, soil geochemical anomalies, and their response in stream sediments. According to him, plots of productivity (area x concentration) provide an additional tool to detect areas of known metal enrichment in those of detailed sampling and upstream dilution. Oever [6] created a geochemical atlas from stream sediment geochemical data, and has established natural background values. He used a two-clusters model.

Rubio et al. [7] have examined pollution of the Ria de Vigo (NW Spain). Geo-accumulation indexes and enrichment factors have been calculated to assess whether the concentrations observed represent background or contaminated levels. They have found the maximum grade of pollution near Vigo harbor, as a consequence of anthropogenic activity. The same authors [8] critically evaluated the use of cluster analysis to distinguish contaminated and non-contaminated sediments. They have concluded that cluster analysis information can be used as a provenance indicator, but not to conclude with certainty about contamination status of sediments. It was studied how mining can modify stream sediment geochemistry by Ridgway et al. [9] and Avila et al. [10].

The geochemical data from the Soča River drainage basin performed on fraction <63 μm [11] were interpreted as a result of physical and chemical weathering of the pollution source. Sarkar et al. [12] have used geochemical data obtained on sediments of Hugli River (India), which can be used as a baseline, against which future anthropogenic effects may be assessed.

The aim of the present work

The aim of the work is to present geochemistry, mineralogy and contamination status in stream sediments of the Kupa River drainage basin, with respect to toxic elements, as a complementary study to organic pollutants determined in the same basin [13]. A complete picture about the current state of the important water resources of interest for Croatia, Slovenia and Bosnia and Herzegovina will be obtained from sediment data. The locations will be highlighted, where certain toxic elements should be measured in aqueous phase within the monitoring program of Croatian Waters.

STUDY AREA

Study area of the Kupa River drainage basin with numbers of sampling locations, where elements have been measured, is presented in Fig. 1. Kupa River is 296 km long, from its source under Risnjak Mountain in Gorski Kotar, till its inflow to Sava River in Sisak. Kupa River drainage basin covers 10,052 km^2. Most of its part is situated in Croatia, and minor parts are in Slovenia, and Bosnia and Herzegovina. Main tributaries flowing from south are Kupica, Dobra, Mrežnica, Korana, Glina and Petrinjčica. Tributaries flowing from north are Čabranka, Lahinja and Kupčina rivers.

Hydrogeological characteristics of Kupa River drainage basin were described in detail by Ivković et al. [14], Biondić et al. [15], have been recently summarized by Frančišković-Bilinski et al. [13], and will not be repeated here. Geological characteristics of the drainage basin will be briefly mentioned.

Kupa River springs in National Park Risnjak (Croatia) at the contact of Jurassic limestones with hornfels, dolomites and limestones from Tertiary and Permian clastic rocks. At Osilnica, Kupa has confluence with Čabranka River, which most of its course flows through argylloschists, sandstones, and partly conglomerates of Permian age. Above those rocks follow red Raibel clastites, and at the top are dolomites. Čabranka River source is at the contact of Triassic and Jurassic, where gray-layered limestones prevail. At Tršće in Gorski Kotar (Croatia), there are registered mineralogical occurrences of cinnabarite in Permian conglomerates, in upper layers of Raibel clastites and in upper Triassic dolomites, near fault areas. During the ore formation, a small amount of Hg was brought, so the degree of mineralization is low. At Ozalj, further downstream, Kupa River flows through unbound clastites and limestones from lower Pliocene, and then enters Holocene sediments, through which it flows till its inflow into Sava River at Sisak.

In the vicinity of Karlovac, the three biggest tributaries (Dobra, Mrežnica and Korana) flow into Kupa River. Dobra springs from the contact of Permian clastites with dolomites, limestones and clastites from middle till upper Triassic, through which it flows till Vrbovsko. From Vrbovsko to Ogulin, where it sinks, Dobra flows through Jurassic rocks, mostly limestones and dolomites. In its middle and lower course, Dobra flows mostly through limestones and clastites from Carbonian-Perm. Mrežnica and Korana flow mostly through Cretaceous limestones and dolomites. Radonja (tributary of Korana) springs from Petrova Gora and flows through Carboniferous rocks, mostly clastites.

From the area north from Kupa River, at the part of Kupa flow between Karlovac and Sisak, Kupčina River, which drains the Žumberak Mountains flows into Kupa. In this area, Triassic rocks are most abundant (mostly dolomites, limestones, clastites and marls, but also some Jurassic limestones and dolomites), while on southern slopes of Žubmerak Mountains some younger unbound sediments and clastites from Pliocene and Quaternary are also present.

In the lowest course of Kupa River, the inflowing river Glina with its tributaries drains the large and geologically very diverse areas of Banija and Western Bosnia till Cazin. In this region, besides Triassic and Cretaceous limestones and dolomites, also old clastites from Carbon and younger rocks from Miocene, Pliocene and Quaternary are present, together with different metamorphic and magmatic rocks.

Petrinjčica is the last tributary of Kupa River, before its inflow to Sava, flowing through sediments from Eocene, Oligocene, Miocene and Pliocene.

Field determinations performed in aqueous phase by Croatian Waters (name of the Croatian water authorities), include pH, alkalinity, specific conductance, oxygen parameters, nutrients, microbiological parameters, and only six elements (Cu, Zn, Cr, Ni, Pb and Hg). This chemical data of water composition within the Kupa River drainage basin are rather scarce. Up to now, concentrations of elements were below the detection limits of the used methods, mostly giving meaningless values, which were not suitable to be used in any modeling.

MATERIALS AND METHODS

Sampling and sample preparation

Sampling in the Kupa River drainage basin was performed in all parts of the basin in three countries (Croatia, Slovenia, and Bosnia and Herzegovina), during three summer months of 2003, June to August. The detailed description of sampling locations is presented in Table 1, in which information is given for sample number, the name of the river, to which river it flows, as well as its geographic coordinates and altitude.

The great part of this region is still under mines (since the war in 1991-1995), and, therefore, was difficult and dangerous to sample. In order to see the influence of Kupa drainage basin on Sava River (a tributary of Danube River), two sediments of Sava (42, 43) were sampled before and after inflow of Kupa River. Frančišković-Bilinski and Rantitsch [16] have studied the sediments of Sava River in its upper flow.

Sampling of stream sediments was performed further away from the river bank, to avoid contamination from the soil. Samples were air-dried in a shade for several days and then sieved, using three standard sieves (Fritsch, (Germany) with diameters 2000, 500 and 63 µm. Fine fraction (<63 µm), which is easily transported and usually used in environmental studies, was further analyzed.

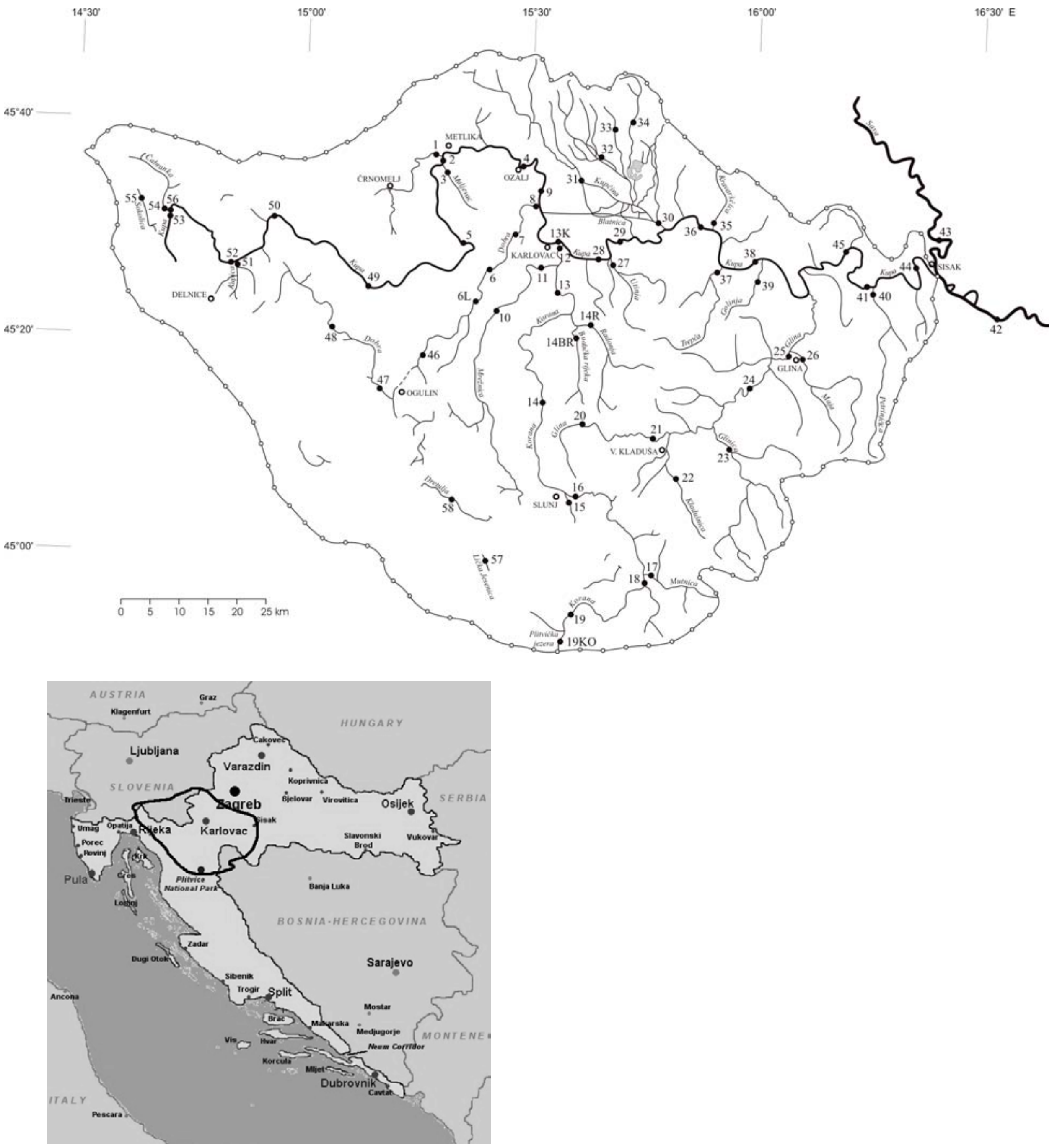

FIGURE 1 - A sketch map of Kupa River drainage basin with numbers of sampling locations, and location map for Slovenia, Croatia and Bosnia-Herzegovina with position of Kupa River drainage basin.

TABLE 1 - Description of sampling locations in Kupa River drainage basin

Sample No.	Locality	River	Flows into river	Coordinates	m above sea level
1	Primostek (SLO)	Lahinja	Kupa	45º38'51" N 15º17'57" E	136
2	Jurovo (river beach)	Kupa	Sava	45º36'38" N 15º18'40" E	135
3	Brihovo	Muljevac	Kupa	45º35'41" N 15º19'48" E	138
4	Ozalj (under hydropowerplant)	Kupa	Sava	45º36'57" N 15º29'09" E	122
5	Jakovci Netretički	Kupa	Sava	45º26'46" N 15º22'13" E	198
6	Jarče Polje	Dobra	Kupa	45º28'35" N 15º26'23" E	148
6L	Lipa	Dobra	Kupa	45º24'29" N 15º23'34" E	187
7	Donje Stative	Dobra	Kupa	45º30'01" N 15º27'18" E	121
8	Donje Pokupje – Priselci	Dobra	Kupa	45º32'15" N 15º30'50" E	114
9	Levkušje – Zorkovac	Kupa	Sava	45º35'54" N 15º31'40" E	116
10	Zvečaj	Mrežnica	Korana	45º21'57" N 15º27'40" E	191
11	Mala Švarča	Mrežnica	Korana	45º28'16" N 15º31'40" E	116
12	Ušće Korane u Kupu	Korana	Kupa	45º30'32" N 15º34'36" E	111
13	Belajske Poljice	Korana	Kupa	45º24'47" N 15º32'11" E	142
13K	Karlovac – Vodostaj	Kupa	Sava	45º31'28" N 15º33'57" E	111
14	Veljun	Korana	Kupa	45º15'08" N 15º32'47" E	133
14R	Zimić – Okić	Radonja	Korana	45º22'35" N 15º38'52" E	137
14BR	Donji Budački	Budačka Rijeka	Radonja	45º22'21" N 15º36'40"E	113
15	Slunj – Rastoke	Slunjčica (Slušnica)	Korana	45º07'14" N 15º35'10" E	210
16	Slunj (river beach)	Korana	Kupa	45º07'15" N 15º35'35" E	205
17	Pjanići (BiH)	Mutnica	Korana	44º58'39" N 15º49'04" E	275
18	Tržačka Raštela (BIH)	Korana	Kupa	44º58'27" N 15º46'59" E	276
19	Autokamp Korana	Korana	Kupa	44º56'19" N 15º38'36" E	395
19KO	Plitvička Jezera	Jezero Kozjak	Korana	44º52'46" N 15º37'04" E	553
20	Kestenovac	Glina	Kupa	45º13'29" N 15º39'32" E	164
21	Maljevac – Gejkovac	Glina	Kupa	45º12'10" N 15º47'39" E	151
22	Barake – Velika Kladuša (BiH)	Kladušnica	Glina	45º08'46" N 15º50'26" E	135
23	Glinica (BiH)	Glinica	Glina	45º11'52" N 15º56'47" E	143
24	Hrvatsko Selo	Glina	Kupa	45º17'19" N 15º59'41" E	137
25	Glina	Glina	Kupa	45º20'30" N 16º05'03" E	121
26	Glina – Majske Poljane	Maja	Glina	45º19'44" N 16º06'28" E	122
27	Brežani	Utinja	Kupa	45º28'30" N 15º41'33" E	110
28	Donja Rečica	Kupa	Sava	45º28'51" N 15º39'60" E	122
29	Zamršlje – Gorenjski Kraj	Kupa	Sava	45º30'24" N 15º41'42" E	121
30	Gornje Selo (Donja Kupčina)	Kupčina	Kupa	45º32'01" N 15º47'24" E	117
31	Lazina	Kupčina	Kupa	45º37'14" N 15º36'36" E	116
32	Domagović	Volavčica	Kupčina	45º34'58" N 15º40'32" E	116
33	D. Desninec – Breznik Plešiv.	Stošinec (Rakovac)	Bukovac	45º41'09" N 15º40'49" E	116
34	Klinča Sela	Okićnica	Crna Mlaka	45º41'37" N 15º42'01" E	120
35	Lijevo Sredičko	Kravaršćica	Kupa	45º32'20" N 15º54'26" E	102
36	Lijevo Sredičko	Kupa	Sava	45º31'49" N 15º53'04" E	100
37	Trepča	Trepča	Kupa	45º27'39" N 15º54'53" E	104
38	Pokupsko (Sunčani Brijeg)	Kupa	Sava	45º29'16" N 16º00'35" E	90
39	Donje Taborište	Golinja	Kupa	45º27'08" N 16º00'13" E	98
40	Petrinja	Petrinjčica	Kupa	45º26'05" N 16º16'22" E	101

TABLE 1 - continued

Sample No.	Locality	River	Flows into river	Coordinates	m above sea level
41	Petrinja (river beach)	Kupa	Sava	45º26'41" N 16º16'10" E	91
42	Lukavec Posavski (ferry)	Sava	Dunav	45º24'04" N 16º32'24" E	90
43	Strelečko	Sava	Dunav	45º31'02" N 16º23'60" E	92
44	Sisak (Zibel beach)	Kupa	Sava	45º28'33" N 16º21'35" E	108
45	Letovanić	Kupa	Sava	45º30'15" N 16º12'03" E	108
46	Trošmarija	Dobra	Kupa	45º19'26" N 15º16'38" E	180
47	Ogulin (Puškarić Selo)	Dobra	Kupa	45º16'07" N 15º11'55" E	325
48	Vrbovsko (Kamačnik)	Dobra	Kupa	45º22'03" N 15º04'21" E	368
49	Severin na Kupi	Kupa	Sava	45º25'30" N 15º09'27" E	158
50	Žaga (SLO)	Kupa	Sava	45º31'41" N 14º55'24" E	223
51	Brod na Kupi	Kupica	Kupa	45º27'49" N 14º51'22" E	249
52	Brod na Kupi	Kupa	Sava	45º27'53" N 14º51'22" E	246
53	Hrvatsko	Kupa	Sava	45º31'26" N 14º42'02" E	262
54	Osilnica – Sela (SLO)	Čabranka	Kupa	45º31'32" N 14º41'31" E	276
55	Tršće – Sokoli	Sokolica	sinks	45º33'32" N 14º37'05" E	768
56	Osilnica (SLO) (at Čabranka inflow)	Kupa	Sava	45º31'34" N 14º42'04" E	271
57	Lička Jesenica	Lička Jesenica	Slunjčica (sinks)	45º59'35" N 15º26'41" E	477
58	Plaški	Dretulja	Mrežnica (sinks)	45º05'05" N 15º21'59" E	396

Determination of mineralogical composition

Mineralogical composition was determined with an X-ray diffractometer Philips, X-Pert MPD (start position: 82Q: 4.01; end position: 82Q: 62.99; generator settings: 40 kV, 40 mA). Crystalline phases were identified using a Powder Diffraction File [17], and the computer program X'Pert High score 2002, Philips. Semi-quantitative mineralogical composition was determined as described by Boldrin et al. [18].

Determination of elements

Determination of elements was carried out in ACT-LABS commercial laboratory, Ontario, Canada in fraction <63 µm, using ICP-MS (Inductively Coupled Plasma Mass Spectroscopy), with program "Ultratrace 2". The procedure was as follows: 0.5 g of sample is dissolved in aqua regia at 90 ºC in a microwave digestion unit. The solution is diluted and analyzed using 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 analyzing each series of samples.

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 [19].

Statistical methods

Program Statistica 6.0 [20] has been used for all statistical calculations in this work. Cluster analysis of Q-modality was applied on the total data set, in order to disaggregate it into more homogenous subsets [21]. Basic statistical parameters were determined for the subset, which did not contain significant anomalies. Correlation analysis was performed to find mutual dependence of elements.

RESULTS

Mineralogical composition

Semi-quantitative mineralogical composition of sediment fraction <63 µm from the Kupa River drainage basin is presented in Table 2. According to abundance, minerals were divided in four groups: >30%, 10-30%, 5-10%, and <5%. The most abundant minerals (>30%) are quartz, calcite, and dolomite group minerals (dolomite, ankerite and dolomite ferroan). In the amount, 10-30% are minerals from feldspar group (albite, anorthite) and from mica group (muscovite). In concentrations, 5-10% are present besides feldspar plagioclase in some samples, but also different phyllosilicates from mica group and some chlorites. Some inosilicates and nesosilicates, several manganese and iron oxides, and hydroxides were identified as trace minerals (<5%). It should be mentioned that trace minerals present at concentrations <5% are near the detection limit of XRD. They are very probable, not completely certain, and need further investigation.

Geochemical characterization of stream sediments in Kupa River drainage basin

In stream sediments of Kupa River drainage basin, 51 chemical elements were determined. Results are presented in Table 3 for all 61 sampling stations. This database is from

Frančišković-Bilinski [22]. It can be used for present and future statistical calculations. In Fig. 2, distribution of Ca in sediments of the whole Kupa River drainage basin is presented, to illustrate the predominance of carbonates in the middle transect of the basin. In parts of it, tufa is formed, as described by Frančišković-Bilinski et al. [23].

There are significant differences in downstream distribution of elements in various river valleys of the same drainage basin. To illustrate these differences, the downstream distribution of 8 elements is presented in Fig. 3 (a – Kupa River, b – Dobra River, c – Korana River).

Q-modality cluster analysis

On total set of geochemical data, Q-modality cluster analysis was performed. Sampling stations were grouped in 3, 4 and 5 clusters. In Fig. 4, the cluster map for the simplest case with 3 clusters is shown. Cluster 1 has only one sampling location (No. 51) with the largest Ba-anomaly. This sample will distort the multivariate analysis and should be removed in further calculations. The preliminary results describing the origin of anthropogenic Ba-anomaly in the western part of the Kupa River drainage basin were recently reported by Frančišković-Bilinski [24].

TABLE 2 - Mineralogical composition of sediment fraction <63 µm from Kupa River drainage basin, estimated according to Boldrin et al. [18] from X-ray diffraction patterns.

sample	SiO_2 group	calcite group	dolomite group	feldspar plagioclase	feldspar ortoclase	mica dioctah.	mica trioctah.	chlorite trioctah.	clay minerals	oxide and hydroxide
1	+++	+++	(+)	-	-	(+)	-	-	-	-
2	+++	+++	++	++	-	+	++	+	-	-
3	+++	++	-	+	-	(+)	-	(+)	-	(+)
4	+++	++	-	+	-	+	-	-	(+)	-
5	+++	+++	++	+	-	+	-	(+)	-	-
6	+++	+++	-	++	(+)	-	-	-	-	-
6L	++	+++	(+)	-	-	-	-	-	-	-
7	+++	+++	++	+	(+)	+	-	-	-	-
8	+++	++	(+)	(+)	-	(+)	-	(+)	-	-
9	+++	+++	+	-	-	+	-	(+)	-	-
10	+	+++	-	-	-	-	-	-	-	-
11	++	+++	-	-	-	-	(+)	-	-	-
12	++	+++	-	(+)	-	(+)	-	-	-	-
13	+++	+++	(+)	-	-	-	(+)	-	(+)	-
13K	+++	+++	+	(+)	-	(+)	(+)	-	-	-
14	+++	+++	+	+	-	-	+	-	-	-
14R	+++	-	-	+	-	++	-	(+)	-	-
14BR	+++	+	-	+	+	(+)	-	-	-	-
15	+++	+++	++	-	(+)	(+)	-	-	-	-
16	+++	+++	++	(+)	-	+	-	-	-	(+)
17	+++	-	-	++	-	+	-	(+)	(+)	-
18	+++	+++	++	++	-	-	-	-	(+)	(+)
19	++	+++	+	-	-	-	-	-	-	-
19KO	+++	+++	+++	-	-	-	-	-	-	-
20	+++	++	(+)	-	(+)	(+)	-	(+)	-	-
21	+++	++	+++	(+)	-	(+)	-	-	-	(+)
22	+++	-	-	-	(+)	+	-	(+)	-	-
23	+++	+	(+)	-	(+)	++	(+)	(+)	-	-
24	+++	+	(+)	++	(+)	(+)	-	+	(+)	-
25	+++	-	-	(+)	-	(+)	-	(+)	-	-
26	+++	(+)	-	++	(+)	(+)	-	(+)	-	(+)
27	+++	-	-	(+)	(+)	(+)	-	(+)	-	-
28	+++	++	-	(+)	-	(+)	-	-	+	-
29	+++	++	++	(+)	-	+	-	-	-	-
30	+++	-	++	(+)	-	(+)	(+)	(+)	-	-
31	+++	+	++	(+)	-	+	-	(+)	-	-
32	+++	+	++	(+)	-	(+)	-	(+)	-	-
33	+++	+	(+)	-	-	(+)	-	-	(+)	+
34	+++	-	(+)	+	+	(+)	(+)	-	-	-
35	+++	(+)	-	(+)	(+)	+	-	(+)	-	-
36	+++	++	-	(+)	-	+	-	-	-	-
37	+++	-	-	(+)	-	(+)	-	(+)	-	-
38	+++	(+)	+	(+)	(+)	(+)	-	-	(+)	-
39	+++	(+)	-	(+)	-	(+)	-	(+)	-	-
40	+++	++	(+)	++	-	-	(+)	-	-	-
41	+++	+	(+)	(+)	-	-	(+)	-	-	-
42	+++	++	+++	+	-	+	-	(+)	-	-
43	+++	++	+++	-	-	+	-	(+)	-	-
44	+++	+	-	(+)	-	(+)	(+)	(+)	-	-
45	+++	++	+	+	-	(+)	(+)	-	-	-
46	+++	+++	+++	++	-	-	+	-	-	-
47	+++	++	++	(+)	-	+	-	(+)	-	-
48	+++	++	+++	(+)	(+)	+	-	(+)	-	-
49	+++	++	+	(+)	-	(+)	-	(+)	-	-
50	+++	(+)	++	+	(+)	++	-	(+)	-	-
51	+++	++	+	-	-	++	-	+	-	-
52	+++	++	++	(+)	-	++	-	+	-	-
53	+++	++	+	+	-	-	+	(+)	-	-
54	+++	-	++	-	(+)	++	-	+	-	-
55	++	++	+++	-	-	-	-	-	-	-
56	+++	-	++	+	-	++	-	++	-	-
57	(+)	+++	-	-	-	-	-	-	-	-
58	+++	-	+++	+	-	(+)	-	-	-	-

TABLE 3 - Concentration of elements in ppm = mg/kg (all elements without other sign), and in % and ppb = µg/kg, in stream sediments (fraction <63 µm) from Kupa River drainage basin and 2 sediments from Sava River (negative values (-) mean: under detection limit).

Sample	Li	Be	B	Na%	Mg%	Al%	P%	S%	K%	Ca%	Sc	Ti%	V	Cr	Mn	Fe%	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Rb	Sr	Y	Zr	Nb	Mo	Ag
1	8.5	0.5	-1	0.012	0.57	1.10	0.056	0.115	0.08	12.1	1.9	0.01	23	22.3	194	1.31	6.2	19.2	14.2	58.9	2.85	-0.1	3.7	0.5	12.2	64.1	8.22	0.8	0.5	0.76	0.035
2	17.9	0.7	-1	0.017	1.32	1.26	0.035	0.103	0.12	9.47	2.7	-0.01	23	20.0	293	2.25	8.4	25.2	14.7	58.6	4.00	-0.1	4.8	0.6	12.6	53.7	6.46	0.9	0.4	0.83	0.031
3	20.4	1.2	-1	0.015	0.40	2.69	0.043	0.050	0.16	4.31	5.0	0.01	53	41.4	610	3.30	15.5	36.2	20.4	102	7.09	0.1	6.4	0.6	24.3	17.0	13.2	2.8	0.9	1.30	-0.002
4	18.7	0.8	-1	0.017	1.23	1.39	0.040	0.062	0.16	8.19	3.3	-0.01	26	26.4	593	2.32	21.2	38.7	21.4	65.3	4.28	-0.1	4.0	0.5	14.5	44.5	8.07	0.7	0.4	0.71	-0.002
5	13.6	0.6	-4	0.056	1.37	0.87	0.038	0.081	0.18	16.9	1.4	0.01	15	18.3	330	1.62	4.8	23.6	14.1	47.3	2.10	-0.4	-0.4	0.6	13.2	68.8	5.42	1.5	0.5	0.76	-0.008
6	7.9	0.4	-1	0.017	1.54	0.83	0.031	0.054	0.07	15.9	1.2	-0.01	11	13.5	289	1.07	4.4	17.8	8.49	35.8	2.06	-0.1	0.5	0.5	9.0	79.5	5.34	0.8	0.4	0.61	-0.002
6L	3.4	0.2	-1	0.015	0.60	0.36	0.031	0.060	0.04	18.3	0.6	-0.01	7	8.0	363	0.61	3.1	13.1	4.24	22.0	0.95	-0.1	3.0	0.6	3.9	81.8	6.62	0.6	0.2	0.31	-0.002
7	12.7	0.6	-1	0.019	1.54	1.36	0.031	0.090	0.12	15.2	2.1	0.01	22	19.7	323	1.55	6.9	23.6	12.3	45.0	3.36	-0.1	2.7	0.7	14.5	80.5	7.16	0.7	0.6	0.71	-0.002
8	21.4	1.0	-1	0.016	0.82	2.43	0.035	0.044	0.16	5.04	3.7	0.01	37	32.5	969	2.72	14.9	36.6	18.0	69.4	5.96	-0.1	5.7	0.5	20.5	30.6	9.97	0.9	0.7	0.89	-0.002
9	17.6	0.7	-1	0.015	1.18	1.52	0.054	0.102	0.14	7.04	2.8	-0.01	21	21.7	408	2.24	8.4	26.6	17.6	67.9	4.43	-0.1	3.2	0.4	13.3	42.2	6.71	0.6	0.4	0.56	-0.002
10	4.0	0.2	-1	0.012	0.25	0.41	0.017	0.053	0.05	24.0	0.1	-0.01	12	7.2	225	0.50	2.5	13.4	5.89	14.8	1.14	-0.1	6.2	0.9	5.1	53.5	2.96	0.7	0.2	0.35	-0.002
11	12.2	0.7	-1	0.026	0.57	1.42	0.047	0.157	0.10	24.9	3.4	0.04	39	35.5	498	2.60	9.4	57.4	31.2	59.5	3.68	-0.1	8.8	1.2	9.8	149	12.8	4.0	1.1	1.97	-0.002
12	8.6	0.7	-1	0.024	0.53	1.14	0.056	0.111	0.07	18.0	1.8	0.02	27	28.7	662	1.96	11.4	42.4	19.3	92.6	2.51	-0.1	7.2	0.8	6.9	103	9.54	1.7	0.7	1.79	0.046
13	11.3	0.7	-1	0.016	0.62	1.19	0.037	0.076	0.08	24.6	2.2	-0.01	28	23.9	1640	1.78	10.4	38.1	14.0	45.7	2.81	-0.1	11.6	0.9	11.7	119	12.4	1.8	0.6	0.84	0.093
13K	15.9	-1.0	-10	0.082	1.16	1.21	0.088	0.108	0.22	10.2	-1.0	0.02	27	62.8	333	2.18	7.8	29.4	32.9	96.2	3.61	-1.0	-1.0	1.2	16.9	51.4	7.44	1.4	-1.0	1.46	-0.020
14	6.5	0.3	-1	0.014	0.68	0.73	0.029	0.096	0.06	19.7	1.0	-0.01	14	14.0	253	0.96	4.3	23.2	8.30	27.2	1.71	-0.1	4.2	0.8	8.1	87.1	5.59	1.0	0.4	0.40	-0.002
14R	23.7	0.8	-1	0.014	0.58	1.65	0.076	0.063	0.13	1.01	2.1	0.01	20	23.3	2640	3.01	13.3	25.3	17.6	134	4.38	-0.1	9.4	0.4	15.9	17.4	6.18	1.4	0.6	0.54	-0.002
14BR	14.6	0.7	-1	0.014	1.12	1.59	0.042	0.063	0.13	2.87	2.2	0.02	21	22.7	574	2.10	10.0	19.6	13.9	74.1	3.87	-0.1	2.7	0.4	16.4	17.9	7.99	0.7	0.7	0.45	-0.002
15	9.6	0.6	-1	0.013	1.39	1.11	0.032	0.061	0.09	18.6	1.2	0.01	24	16.3	314	1.23	5.2	23.3	11.4	32.7	2.56	-0.1	6.1	1.0	11.5	73.6	6.02	1.3	0.7	0.95	0.005
16	11.7	0.6	-1	0.015	1.25	1.43	0.043	0.164	0.11	12.4	2.2	0.02	21	26.0	460	1.46	7.7	34.9	14.6	42.4	3.22	-0.1	3.4	0.5	13.5	93.6	6.78	0.9	0.5	0.67	-0.002
17	19.3	0.9	-1	0.015	0.73	2.10	0.062	0.072	0.16	2.79	4.7	0.02	38	55.7	1380	2.77	31.8	105	25.7	74.9	5.56	-0.1	4.2	0.5	17.4	42.5	13.1	2.0	0.9	0.42	-0.002
18	7.4	0.4	-1	0.014	2.08	0.76	0.024	0.081	0.07	17.8	1.0	-0.01	19	15.8	426	1.08	5.8	25.1	10.1	26.3	1.84	-0.1	4.3	0.6	7.9	96.5	6.06	0.9	0.4	0.57	0.031
19	6.9	0.4	-1	0.010	1.60	0.62	0.016	0.066	0.06	27.2	0.3	-0.01	18	11.0	93	0.66	2.9	16.6	6.89	25.0	1.61	-0.1	8.1	0.9	7.5	61.9	3.67	1.2	0.4	0.31	0.021
19KO	0.9	-0.1	-1	0.010	7.75	0.09	0.005	0.041	0.01	20.3	-0.1	-0.01	9	2.5	37	0.21	0.8	10.3	4.65	11.8	0.20	0.1	6.1	0.2	0.8	63.5	0.99	0.7	-0.1	0.31	0.022
20	12.0	0.8	-1	0.009	0.58	1.31	0.053	0.070	0.08	5.76	1.7	0.01	25	23.1	991	2.17	11.5	25.8	16.2	54.2	3.49	-0.1	5.5	0.6	11.1	37.5	9.17	1.2	0.7	0.69	-0.002
21	6.7	0.6	-1	0.010	3.72	0.74	0.048	0.206	0.07	7.61	1.1	-0.01	15	15.6	618	1.39	6.7	14.4	19.9	42.9	2.22	-0.1	5.2	0.3	6.3	55.8	5.98	1.1	0.6	0.79	-0.002
22	19.7	1.0	-1	0.011	1.50	1.96	0.078	0.067	0.12	2.48	2.6	0.02	33	35.0	1080	2.71	13.5	43.8	37.5	116	5.09	-0.1	4.9	0.5	15.4	24.9	9.05	0.9	1.0	0.72	-0.002
23	20.8	0.8	-1	0.012	0.99	2.00	0.051	0.042	0.19	2.73	4.9	0.13	45	40.5	2260	2.80	16.5	47.6	29.9	77.2	5.61	-0.1	5.4	0.3	14.6	26.0	9.77	3.0	2.1	0.60	-0.002
24	23.6	0.8	-5	0.046	1.73	1.94	0.062	0.045	0.19	4.17	9.9	0.35	125	44.1	1470	3.87	19.3	39.8	50.0	72.5	7.85	-0.5	1.0	0.7	11.5	37.6	14.3	7.6	0.9	0.47	-0.010
25	11.9	0.4	-1	0.010	0.45	0.97	0.037	0.163	0.08	1.26	1.9	0.07	20	32.9	435	1.60	12.2	34.3	14.4	44.0	2.88	-0.1	1.0	0.2	7.9	21.4	5.57	1.7	1.2	0.32	-0.002
26	17.8	0.6	-1	0.010	0.68	1.36	0.045	0.074	0.12	1.56	3.3	0.04	33	48.6	1090	2.31	16.1	78.7	23.4	58.0	4.08	-0.1	4.2	0.4	10.5	63.8	8.43	0.8	0.7	0.65	0.008
27	11.5	0.4	-1	0.008	0.32	0.65	0.028	0.042	0.06	0.42	1.0	0.01	16	20.7	443	1.63	8.1	20.5	8.91	38.1	2.15	-0.1	6.2	0.4	8.0	14.1	5.80	0.7	0.4	0.27	-0.002
28	17.0	0.8	-1	0.009	1.05	1.09	0.052	0.071	0.09	6.80	2.1	-0.01	21	36.6	343	1.96	9.1	24.1	14.6	71.8	3.26	-0.1	3.3	0.6	10.8	37.1	7.99	0.6	0.5	0.42	-0.002
29	9.9	0.5	-1	0.007	1.18	0.78	0.048	0.067	0.04	9.36	1.6	-0.01	18	28.4	267	1.86	8.3	22.7	11.1	57.6	2.34	-0.1	4.0	0.4	5.6	50.3	7.50	0.8	0.3	0.47	0.049
30	15.9	0.9	-1	0.011	1.06	1.65	0.064	0.234	0.08	1.66	3.1	-0.01	33	28.4	570	2.55	11.8	30.3	23.7	89.1	4.87	-0.1	4.8	0.6	13.4	21.3	10.7	1.5	0.7	0.48	0.232
31	10.6	0.8	-1	0.011	4.33	1.09	0.038	0.041	0.07	9.16	2.1	-0.01	28	21.1	391	1.83	9.0	21.7	17.6	50.6	2.93	-0.1	4.8	0.7	8.8	40.5	8.56	1.4	0.6	0.41	0.136
32	11.0	0.5	-1	0.009	1.76	1.22	0.074	0.096	0.09	6.29	1.6	-0.01	20	20.7	300	1.46	6.4	21.9	30.7	67.1	3.00	-0.1	2.7	0.5	11.3	86.0	7.06	1.8	0.5	0.30	0.039
33	16.5	0.7	-1	0.013	0.59	1.40	0.041	0.075	0.13	5.26	2.8	-0.01	25	23.1	904	2.05	10.2	29.3	19.0	50.5	3.96	-0.1	6.6	0.7	14.1	207	8.95	1.3	0.5	0.43	-0.002
34	18.7	0.7	-1	0.009	0.66	1.33	0.036	0.033	0.13	1.38	2.5	0.01	26	24.0	858	2.13	11.8	31.0	21.0	47.1	3.94	-0.1	5.2	0.5	12.9	37.0	7.30	0.7	0.4	0.35	-0.002
35	12.1	0.7	-1	0.010	0.36	1.19	0.033	0.049	0.07	1.62	2.3	0.02	23	21.2	810	2.29	11.6	22.2	12.3	46.4	3.48	-0.1	6.1	0.3	10.8	16.5	8.32	0.8	0.6	0.44	-0.002
36	17.1	0.6	-1	0.011	0.80	1.46	0.066	0.128	0.15	6.84	3.3	-0.01	25	32.4	608	2.37	13.2	33.5	28.3	90.9	4.25	-0.1	4.8	0.5	13.2	47.9	7.16	0.7	0.4	0.61	0.007
37	12.4	0.6	-1	0.028	0.35	0.96	0.046	0.076	0.14	0.79	1.3	0.03	20	29.9	877	2.22	14.0	37.9	16.7	45.1	2.66	-0.1	1.5	0.5	12.9	28.3	7.21	1.4	0.7	0.68	-0.002
38	8.1	0.3	-1	0.007	1.13	0.59	0.033	0.024	0.04	4.47	1.7	-0.01	12	17.0	367	1.35	6.5	16.3	7.49	33.3	1.87	-0.1	1.8	0.1	5.0	30.4	6.29	0.7	0.3	0.27	-0.002
39	14.8	0.6	-1	0.007	0.33	1.10	0.031	0.303	0.09	1.14	2.4	-0.01	25	27.5	244	1.73	9.5	29.4	20.2	59.7	3.68	-0.1	6.9	1.0	13.9	87.7	8.52	1.7	0.6	0.48	-0.002
40	8.9	0.5	-1	0.011	0.35	0.88	0.036	0.134	0.07	9.89	2.9	0.01	27	25.5	703	1.73	9.5	36.1	22.0	49.3	3.10	-0.1	4.5	0.7	6.8	226	8.72	1.1	0.6	0.82	-0.002
41	8.0	0.4	-1	0.007	0.70	0.66	0.034	0.080	0.04	3.62	1.8	-0.01	14	19.3	291	1.42	7.0	20.9	8.88	42.2	2.12	-0.1	2.0	0.3	5.3	29.6	5.59	0.6	0.3	0.32	-0.002
42	8.1	-1.6	-16	0.079	3.34	0.65	0.335	0.176	-0.16	9.80	-1.6	0.03	-16	27.2	1370	2.92	6.5	23.4	23.1	116	1.26	-1.6	1.9	-1.6	7.7	75.7	5.10	2.5	-1.6	0.62	-0.032
43	17.0	0.6	-1	0.012	2.43	1.31	0.108	0.177	0.12	8.05	2.4	0.01	23	52.0	494	2.08	9.3	37.7	54.5	229	3.55	-0.1	6.1	0.7	11.6	94.2	8.46	0.6	0.5	0.77	0.870
44	12.2	0.6	-1	0.010	0.70	1.14	0.047	0.134	0.09	6.00	3.3	0.02	28	29.5	793	2.55	15.0	36.6	14.6	57.6	3.45	-0.1	13.0	0.5	10.4	48.5	12.3	0.9	0.7	0.54	0.199
45	10.6	0.6	-1	0.010	0.65	0.97	0.054	0.092	0.09	8.08	2.5	0.02	22	27.8	1680	2.06	14.2	32.9	12.4	50.5	3.11	-0.1	6.0	0.6	9.7	63.9	8.97	0.5	0.6	0.49	0.080
46	8.9	0.6	-1	0.012	2.18	0.86	0.052	0.060	0.09	16.3	1.3	0.02	20	16.8	632	1.34	7.2	21.4	13.2	46.2	2.35	-0.1	3.8	0.6	10.6	69.8	7.17	0.6	0.6	0.98	-0.002
47	19.6	0.7	-1	0.011	2.19	1.50	0.047	0.072	0.12	9.42	2.1	0.01	32	22.4	253	1.82	7.7	28.7	18.3	68.8	3.95	-0.1	5.4	0.7	14.8	41.9	6.18	0.8	0.7	1.38	-0.002
48	19.1	0.7	-1	0.011	2.33	1.32	0.045	0.062	0.11	9.27	2.2	-0.01	28	21.7	481	2.03	8.7	30.0	32.0	79.2	3.49	-0.1	6.6	0.7	12.2	51.7	6.52	1.0	0.6	1.51	0.004
49	16.4	0.4	-1	0.009	1.74	0.85	0.039	0.072	0.07	6.02	2.1	-0.01	15	13.4	238	2.00	6.8	19.1	11.9	51.4	1.62	-0.1	4.8	0.3	6.5	43.0	5.49	0.6	0.2	0.45	-0.002
50	22.4	0.8	-1	0.010	1.59	1.13	0.042	0.078	0.09	6.11	2.8	-0.01	23	20.9	391	2.65	9.4	29.5	21.4	73.0	2.80	-0.1	8.6	0.7	9.3	46.9	6.65	0.5	0.4	0.99	-0.002
51	22.6	1.0	-7	0.045	1.41	1.23	0.051	0.171	0.21	4.38	1.9	0.01	34	29.1	451	2.73	9.9	30.7	25.0	71.7	-0.14	-0.7	9.5	-0.7	15.5	93.7	7.07	0.8	-0.7	1.24	-0.014
52	20.7	0.7	-1	0.011	2.10	1.10	0.047	0.074	0.10	7.20	2.4	-0.01	24	22.6	366	2.32	8.9	31.3	23.1	70.9	3.06	-0.1	8.0	1.1	9.7	45.5	5.92	0.6	0.4	1.40	-0.002
53	23.7	1.0	-1	0.011	1.63	1.39	0.042	0.065	0.14	7.31	3.1	-0.01	28	21.0	791	2.34	10.5	29.9	18.1	60.7	4.02	-0.1	7.9	0.8	13.4	32.6	7.98	0.9	0.5	0.85	-0.002
54	22.1	0.8	-1	0.014	1.54	1.21	0.058	0.084	0.13	9.37	2.2	-0.01	22	22.3	399	2.37	9.7	32.1	24.9	76.3	3.41	-0.1	9.9	0.8	13.2	63.3	5.89	0.4	0.3	1.25	-0.002
55	11.7	0.2	-1	0.015	10.9	0.63	0.011	0.031	0.10	17.3	0.7	-0.01	24	10.3	121	0.60	2.5	20.3	8.31	19.8	1.63	-0.1	6.8	0.5	7.4	72.5	2.26	1.0	0.2	3.99	-0.002
56	23.9	0.9	-1	0.017	1.50	1.47	0.055	0.089	0.20	6.60	3.7	-0.01	28	32.9	481	2.87	10.9	39.9	28.0	85.1	4.58	-0.1	12.6	1.3	16.8	49.7	6.82	0.5	0.4	2.13	0.014
57	3.0	0.2	-1	0.010	0.45	0.36	0.009	0.088	0.04	24.7	0.3	-0.01	9	6.6	41	0.35	1.3	15.7	6.17	15.8	0.82	-0.1	6.2	0.6	3.8	87.0	2.89	1.2	0.2	0.29	0.051
58	8.6	0.4	-1	0.014	6.07	0.74	0.019	0.040	0.10	9.95	0.8	0.02	18	11.5	74	0.71	2.5	14.1	5.19	15.9	1.78	-0.1	1.5	0.5	8.8	46.9	3.89	0.5	0.4	1.51	-0.002

TABLE 3 – continued.

Sample	Cd	In	Sn	Sb	Te	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Au (ppb)	Tl	Pb	Bi	Th	U	Hg (ppb)
1	0.8	0.02	2.39	0.15	0.07	1.1	52.9	12.6	25.7	3.1	11.6	2.4	0.5	2.1	0.3	1.6	0.3	0.7	-0.1	0.6	-0.1	-0.1	-0.05	0.1	0.001	31.1	0.21	16.7	0.21	1.4	0.6	141
2	0.3	0.03	0.31	0.10	0.03	1.3	386	7.2	15.3	1.9	7.56	1.8	0.4	2.1	0.3	1.5	0.3	0.7	-0.1	0.5	-0.1	-0.1	-0.05	-0.1	-0.001	18.9	0.22	33.5	0.24	2.4	1.0	104
3	0.5	0.04	0.48	0.18	0.05	2.0	77.4	22.2	47.2	5.2	18.9	4.0	0.8	3.7	0.5	2.4	0.5	1.2	0.2	0.9	0.1	-0.1	-0.05	-0.1	0.001	31.3	0.39	21.5	0.32	6.7	1.0	105
4	0.3	0.03	0.48	0.12	0.05	1.4	341	9.3	25.4	2.4	10.2	2.3	0.5	2.6	0.3	1.8	0.3	0.8	0.1	0.6	-0.1	-0.1	-0.05	-0.1	-0.001	21.4	0.30	20.1	0.32	2.9	0.8	101
5	-0.4	-0.08	-0.20	0.20	-0.02	1.5	548	8.2	18.5	2.1	8.31	1.9	-0.4	1.9	-0.4	1.3	-0.4	0.6	-0.4	-0.4	-0.4	-0.4	-0.20	-0.4	-0.004	-0.8	0.15	11.9	0.46	2.2	0.6	22
6	0.3	0.03	0.42	0.11	-0.02	0.7	38.3	9.5	18.5	2.3	8.56	1.8	0.3	1.7	0.2	1.1	0.2	0.5	-0.1	0.4	-0.1	-0.1	-0.05	-0.1	0.001	16.0	0.15	9.64	0.76	1.4	0.8	84
6L	0.5	0.02	0.06	0.08	0.03	0.4	26.7	8.2	13.9	1.9	7.26	1.5	0.3	1.5	0.2	1.1	0.2	0.5	-0.1	0.4	-0.1	-0.1	-0.05	-0.1	0.001	15.3	0.09	7.05	0.30	0.7	0.4	29
7	0.4	0.02	0.33	0.18	0.06	1.4	46.8	13.9	27.9	3.2	12.1	2.6	0.5	2.4	0.3	1.5	0.3	0.7	-0.1	0.5	-0.1	-0.1	-0.05	-0.1	0.001	10.4	0.24	13.6	0.14	2.6	0.9	56
8	0.6	0.04	0.41	0.18	0.05	1.6	90.8	19.5	42.7	4.6	18.1	3.5	0.7	3.5	0.4	2.1	0.4	1.0	0.1	0.8	0.1	-0.1	-0.05	-0.1	0.002	10.7	0.34	23.3	0.26	4.5	0.9	93
9	0.3	0.03	0.37	0.10	-0.02	1.2	468	7.6	16.5	1.9	7.73	1.9	0.4	2.1	0.3	1.5	0.3	0.7	-0.1	0.5	-0.1	-0.1	-0.05	-0.1	0.001	23.8	0.23	16.3	0.23	2.6	0.7	130
10	0.3	-0.02	0.14	0.09	0.06	0.5	25.4	3.7	7.35	1.0	3.82	0.7	0.2	0.7	-0.1	0.5	0.1	0.3	-0.1	0.2	-0.1	-0.1	-0.05	-0.1	-0.001	8.2	0.10	4.99	0.39	0.3	0.3	26
11	0.5	-0.02	2.41	0.56	0.04	2.0	90.4	13.0	24.7	3.3	12.6	2.6	0.5	2.6	0.4	2.3	0.4	1.2	0.2	1.1	0.2	-0.1	-0.05	0.2	0.003	16.0	0.12	23.8	0.22	1.6	4.3	134
12	0.4	-0.02	0.67	0.20	0.06	0.9	68.5	9.3	18.4	2.3	9.17	1.9	0.4	2.2	0.3	1.7	0.4	0.9	0.1	0.8	0.1	-0.1	-0.05	0.1	0.001	15.1	0.13	13.4	0.20	0.8	2.4	88
13	0.6	0.02	0.41	0.21	0.08	1.0	84.6	12.7	23.6	3.3	12.7	2.8	0.6	2.8	0.4	2.2	0.4	1.0	0.1	0.9	0.1	-0.1	-0.05	-0.1	0.001	12.6	0.21	17.3	0.25	1.4	0.6	44
13K	-1.0	-0.20	3.61	0.46	-0.20	2.0	262	11.7	30.3	3.0	11.2	2.6	-1.0	2.7	-1.0	1.8	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-0.50	-1.0	0.022	1.9	0.26	37.7	0.85	2.8	0.7	23
14	0.3	-0.02	0.18	0.12	0.02	0.7	37.7	7.7	15.3	2.0	7.67	1.6	0.3	1.5	0.2	1.1	0.2	0.5	-0.1	0.4	-0.1	-0.1	-0.05	-0.1	0.001	3.4	0.13	8.61	0.10	0.8	0.5	38
14R	0.4	0.03	0.58	0.27	0.04	1.7	158	15.9	34.7	3.8	14.0	2.9	0.5	2.6	0.3	1.5	0.3	0.6	-0.1	0.6	-0.1	-0.1	-0.05	-0.1	0.001	15.3	0.17	51.5	0.25	3.6	0.8	120
14BR	0.3	0.02	0.32	0.28	0.04	1.3	76.0	21.3	43.4	5.0	18.1	3.6	0.6	3.1	0.4	1.8	0.3	0.8	-0.1	0.7	-0.1	-0.1	-0.05	-0.1	0.001	6.1	0.23	32.4	0.17	4.7	0.9	104
15	0.6	-0.02	0.33	0.26	0.06	1.2	41.9	10.6	20.0	2.6	9.71	1.9	0.4	1.8	0.2	1.2	0.2	0.6	-0.1	0.5	-0.1	-0.1	-0.05	-0.1	0.001	7.3	0.27	14.9	0.17	1.0	0.8	42
16	0.3	-0.02	0.26	0.14	0.03	1.0	70.3	10.2	21.1	2.6	10.0	2.1	0.5	2.0	0.3	1.5	0.3	0.7	-0.1	0.6	-0.1	-0.1	-0.05	-0.1	0.001	5.1	0.17	11.5	0.16	1.7	0.8	60
17	0.3	0.03	0.40	0.12	0.08	1.0	101	18.5	40.4	4.8	18.5	4.1	0.9	3.9	0.5	2.8	0.5	1.4	0.2	1.0	0.1	-0.1	-0.05	-0.1	-0.001	1.0	0.22	17.9	0.23	4.6	0.7	97
18	0.4	-0.02	0.17	0.14	0.09	0.7	41.0	8.5	16.0	2.1	8.13	1.6	0.3	1.6	0.2	1.1	0.2	0.5	-0.1	0.5	-0.1	-0.1	-0.05	-0.1	0.001	3.6	0.14	7.55	0.17	1.2	1.0	26
19	0.3	-0.02	0.14	0.10	0.09	0.7	30.7	5.1	10.8	1.3	4.96	1.0	0.2	0.9	0.1	0.7	0.1	0.3	-0.1	0.3	-0.1	-0.1	-0.05	-0.1	0.002	25.3	0.12	9.16	0.17	0.3	0.5	25
19KO	0.2	-0.02	-0.05	0.03	0.05	-0.1	12.3	1.2	2.99	0.3	1.06	0.2	-0.1	0.2	-0.1	0.2	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.05	-0.1	-0.001	2.9	0.03	9.16	0.16	0.1	1.0	15
20	1.2	0.02	1.00	0.21	0.02	0.7	59.1	15.6	34.2	4.0	15.3	3.2	0.6	2.9	0.4	2.0	0.4	0.9	0.1	0.7	0.1	-0.1	-0.05	-0.1	0.001	16.3	0.16	18.7	0.27	2.2	0.5	60
21	0.6	-0.02	0.73	0.27	0.05	0.5	204	10.6	23.8	2.6	9.85	2.1	0.4	1.9	0.2	1.4	0.3	0.6	-0.1	0.5	-0.1	-0.1	-0.05	-0.1	-0.001	12.9	0.14	24.5	0.22	2.6	1.0	99
22	0.4	0.03	2.01	0.24	0.04	1.6	119	17.1	35.5	4.0	15.1	3.2	0.6	3.0	0.4	2.0	0.4	0.9	0.1	0.7	0.1	-0.1	-0.05	0.1	-0.001	25.7	0.43	32.0	0.32	3.5	1.0	109
23	0.3	0.03	0.38	0.22	-0.02	1.1	112	17.7	37.3	4.3	16.7	3.4	0.7	3.2	0.4	2.2	0.4	1.0	0.1	0.9	0.1	-0.1	-0.05	-0.1	-0.001	9.2	0.17	18.6	0.21	3.3	0.6	58
24	-0.5	-0.10	-0.25	0.26	-0.10	1.7	272	11.4	28.9	3.3	14.3	3.6	0.9	3.7	0.6	3.3	0.6	1.5	-0.5	1.2	-0.5	-0.5	-0.25	-0.5	-0.005	-1.0	0.12	15.3	0.43	2.9	0.5	21
25	0.2	-0.02	0.19	0.22	0.03	0.7	101	13.3	28.3	3.2	12.3	2.5	0.5	2.3	0.3	1.4	0.2	0.6	-0.1	0.5	-0.1	-0.1	-0.05	-0.1	-0.001	-0.2	0.11	22.9	0.07	3.6	0.5	89
26	0.4	0.02	0.40	0.19	0.08	0.8	105	12.9	30.1	3.3	13.8	2.9	0.6	2.8	0.3	1.9	0.3	0.8	0.1	0.6	-0.1	-0.1	-0.05	-0.1	0.001	1.2	0.14	13.5	0.16	3.0	0.5	132
27	0.1	-0.02	0.20	0.13	0.04	1.2	51.8	15.8	34.5	4.0	15.0	3.0	0.5	2.4	0.3	1.4	0.2	0.5	-0.1	0.4	-0.1	-0.1	-0.05	-0.1	-0.001	24.6	0.08	12.3	0.12	4.0	0.7	83
28	0.4	-0.02	0.98	0.07	0.04	1.1	199	10.0	22.4	2.6	10.5	2.5	0.5	2.4	0.3	1.8	0.3	0.8	0.1	0.6	-0.1	-0.1	-0.05	-0.1	0.002	31.4	0.15	18.6	0.21	2.3	0.6	164
29	0.3	-0.02	0.54	0.09	0.05	0.6	74.5	7.6	16.7	2.1	8.20	1.9	0.4	2.1	0.3	1.6	0.3	0.7	-0.1	0.6	-0.1	-0.1	-0.05	-0.1	-0.001	5.6	0.13	14.5	0.16	1.9	0.6	112
30	0.7	0.03	0.61	0.19	0.03	1.0	139	15.1	32.6	3.9	15.1	3.3	0.7	3.3	0.4	2.3	0.4	1.0	0.1	0.9	0.1	-0.1	-0.05	-0.1	0.001	16.3	0.22	20.5	0.25	3.8	1.2	143
31	0.3	-0.02	0.50	0.15	0.07	0.7	58.7	13.2	30.6	3.4	13.1	2.8	0.5	2.6	0.3	1.8	0.3	0.8	0.1	0.7	-0.1	-0.1	-0.05	-0.1	0.001	7.3	0.10	15.5	0.17	3.0	0.9	67
32	0.3	-0.02	0.30	0.16	0.04	0.9	70.0	11.1	23.5	2.8	11.0	2.3	0.5	2.2	0.3	1.4	0.3	0.7	-0.1	0.6	-0.1	-0.1	-0.05	-0.1	-0.001	25.5	0.14	15.0	0.22	1.9	0.7	162
33	0.3	0.02	0.30	0.14	0.04	1.4	120	14.3	30.0	3.7	14.5	3.2	0.6	2.7	0.4	1.9	0.4	0.9	0.1	0.7	-0.1	-0.1	-0.05	-0.1	0.001	24.2	0.15	16.6	0.21	3.8	0.7	108
34	0.2	0.02	0.47	0.13	0.02	1.0	88.8	15.3	34.4	4.1	15.4	3.3	0.6	2.9	0.3	1.9	0.3	0.8	0.1	0.5	-0.1	-0.1	-0.05	-0.1	0.001	18.8	0.10	18.1	0.19	3.9	0.6	86
35	0.2	-0.02	0.17	0.14	0.02	0.9	61.5	19.0	41.3	4.7	18.0	3.6	0.7	3.3	0.4	1.9	0.4	0.9	0.1	0.7	-0.1	-0.1	-0.05	-0.1	-0.001	0.7	0.14	15.3	0.18	4.9	0.7	89
36	0.2	0.03	0.53	0.11	0.06	1.3	122	8.3	18.7	2.2	8.80	2.2	0.5	2.3	0.3	1.6	0.3	0.7	-0.1	0.5	-0.1	-0.1	-0.05	-0.1	0.001	7.0	0.15	17.0	0.22	2.7	0.6	127
37	0.3	0.02	1.00	0.19	0.05	1.1	129	17.4	41.6	4.5	16.9	3.4	0.7	3.2	0.4	1.8	0.3	0.8	-0.1	0.6	-0.1	-0.1	-0.05	0.2	0.006	3.5	0.11	19.1	0.37	3.8	0.9	13
38	0.2	-0.02	0.15	0.07	0.04	0.5	78.4	12.0	25.2	3.0	11.6	2.5	0.4	2.5	0.3	1.5	0.3	0.6	-0.1	0.5	-0.1	-0.1	-0.05	-0.1	-0.001	-0.2	0.08	8.43	0.07	4.4	0.8	61
39	0.3	0.03	0.28	0.15	0.03	0.8	81.4	13.6	29.2	3.4	12.9	2.6	0.6	2.3	0.3	1.8	0.3	0.8	0.1	0.7	-0.1	-0.1	-0.05	-0.1	0.001	74.1	0.14	15.7	0.23	2.9	1.1	98
40	0.4	0.02	0.20	0.16	0.07	0.5	147	10.1	22.7	2.6	10.5	2.3	0.5	2.3	0.3	1.8	0.3	0.9	0.1	0.7	-0.1	-0.1	-0.05	-0.1	0.001	9.7	0.12	10.4	0.10	1.7	0.7	45
41	0.2	-0.02	0.14	0.09	0.04	0.5	54.4	7.7	15.9	1.9	7.50	1.7	0.3	1.7	0.2	1.2	0.2	0.5	-0.1	0.4	-0.1	-0.1	-0.05	-0.1	-0.001	5.3	0.10	9.07	0.07	2.3	0.5	67
42	-1.6	-0.32	-0.80	-0.32	-0.32	-1.6	169	9.5	30.3	2.6	10.1	2.0	-1.6	1.9	-1.6	-1.6	-1.6	-1.6	-1.6	-1.6	-1.6	-1.6	-0.80	-1.6	-0.016	-3.2	-0.32	22.0	0.86	3.4	-1.6	17
43	0.8	0.03	1.03	0.42	0.03	1.3	140	10.6	21.4	2.6	10.1	2.4	0.5	2.5	0.3	1.7	0.3	0.8	0.1	0.7	0.1	-0.1	-0.05	0.2	0.003	48.8	0.17	65.1	0.52	1.4	1.1	697
44	0.4	0.02	0.45	0.14	-0.02	0.8	65.0	15.7	35.2	4.1	16.3	3.5	0.7	3.6	0.4	2.5	0.5	1.1	0.1	0.9	0.1	-0.1	-0.05	-0.1	0.001	2.4	0.15	17.6	0.14	3.5	1.0	145
45	0.3	-0.02	0.24	0.13	0.02	0.9	99.2	12.6	28.5	3.2	12.8	2.5	0.6	2.7	0.3	1.9	0.3	0.8	0.1	0.7	-0.1	-0.1	-0.05	-0.1	-0.001	1.5	0.14	14.2	0.10	2.5	0.5	59
46	0.5	0.03	1.56	0.21	0.06	0.8	48.4	12.4	24.2	3.0	11.9	2.4	0.4	2.2	0.3	1.5	0.3	0.6	-0.1	0.5	-0.1	-0.1	-0.05	0.1	0.002	15.1	0.19	19.0	0.62	1.6	1.0	41
47	0.4	0.03	0.84	0.35	0.04	1.2	58.1	9.5	21.8	2.4	9.47	2.1	0.4	2.1	0.3	1.4	0.3	0.6	-0.1	0.5	-0.1	-0.1	-0.05	-0.1	-0.001	36.2	0.22	19.9	0.46	1.7	1.0	86
48	0.4	0.03	0.94	0.32	0.04	1.0	69.2	9.1	19.1	2.3	9.79	2.2	0.4	2.1	0.3	1.5	0.3	0.6	-0.1	0.5	-0.1	-0.1	-0.05	0.2	0.002	33.0	0.20	25.3	0.37	1.7	1.1	152
49	0.2	0.02	0.37	0.12	0.03	0.8	1060	5.7	12.5	1.6	6.60	1.7	0.4	2.0	0.3	1.5	0.2	0.6	-0.1	0.4	-0.1	-0.1	-0.05	-0.1	0.001	11.2	0.10	13.1	0.20	3.2	0.8	75
50	0.2	0.03	0.19	0.17	0.04	1.2	1070	4.8	10.9	1.5	6.10	1.8	0.4	2.3	0.3	1.7	0.3	0.7	-0.1	0.5	-0.1	-0.1	-0.05	-0.1	-0.001	23.3	0.17	17.6	0.33	2.2	0.8	130
51	-0.7	-0.14	-0.35	0.22	-0.14	2.3	5790	7.7	19.8	2.1	8.48	2.3	-0.7	2.8	-0.7	1.8	-0.7	-0.7	-0.7	-0.7	-0.7	-0.7	-0.35	-0.7	0.011	-1.4	0.26	24.5	0.62	3.0	0.9	20
52	0.3	0.03	0.29	0.30	0.04	1.2	75.2	5.1	10.7	1.4	5.87	1.7	0.4	2.1	0.3	1.4	0.3	0.6	-0.1	0.5	-0.1	-0.1	-0.05	-0.1	0.002	20.9	0.16	20.6	0.38	1.4	0.9	154
53	0.4	0.03	0.23	0.26	0.03	1.3	98.2	7.6	16.7	2.2	9.02	2.4	0.5	2.6	0.3	1.8	0.3	0.8	0.1	0.6	-0.1	-0.1	-0.05	-0.1	0.001	19.7	0.24	16.5	0.29	2.6	0.8	73
54	0.3	0.03	0.28	0.29	0.05	2.0	107	4.8	11.1	1.4	5.84	1.6	0.4	2.2	0.3	1.5	0.3	0.6	-0.1	0.5	-0.1	-0.1	-0.05	0.2	0.001	23.8	0.16	20.3	0.37	1.3	0.8	171
55	0.3	0.02	0.06	0.28	-0.02	0.7	21.8	3.2	8.16	0.9	3.50	0.8	0.1	0.8	-0.1	0.5	-0.1	0.2	-0.1	0.2	-0.1	-0.1	-0.05	-0.1	0.002	16.5	0.15	6.68	0.37	0.7	2.3	128
56	0.2	0.03	0.39	0.28	0.07	2.0	106	6.6	14.1	1.8	7.42	2.0	0.4	2.5	0.3	1.7	0.3	0.7	-0.1	0.5	-0.1	-0.1	-0.05	-0.1	-0.001	10.9	0.16	20.3	0.36	2.6	0.8	206
57	0.3	0.03	-0.05	0.06	0.08	0.4	24.2	3.3	6.79	0.8	3.13	0.6	0.1	0.6	-0.1	0.5	-0.1	0.3	-0.1	0.2	-0.1	-0.1	-0.05	-0.1	0.001	4.6	0.13	5.49	0.60	0.3	0.4	14
58	0.2	-0.02	0.16	0.08	0.05	0.7	20.9	7.1	15.2	1.8	6.91	1.4	0.3	1.1	0.2	0.8	0.1	0.4	-0.1	0.3	-0.1	-0.1	-0.05	-0.1	0.004	32.8	0.12	5.48	0.18	1.1	1.5	23

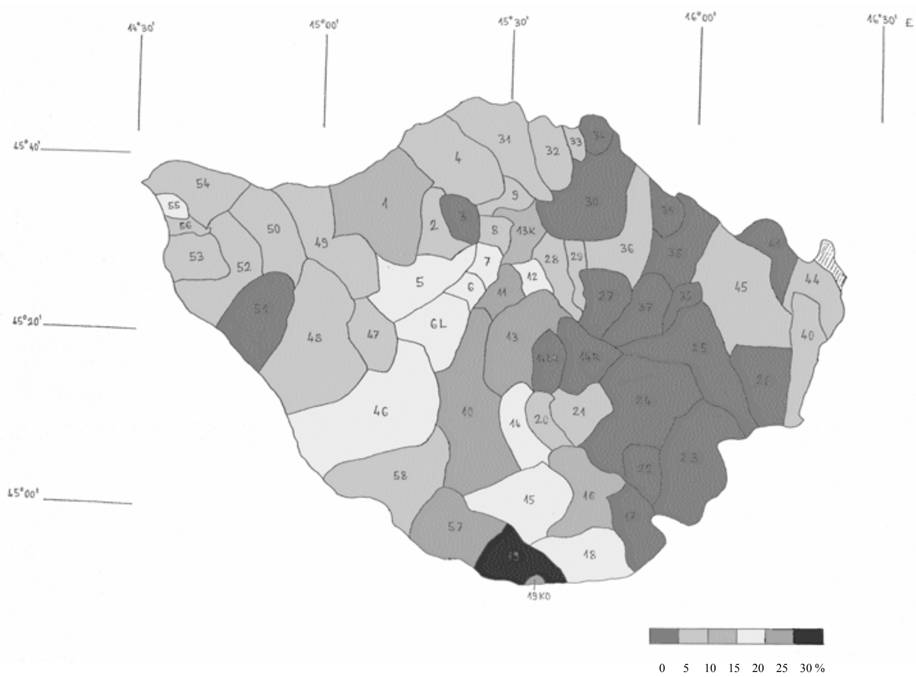

FIGURE 2 - Distribution of Ca in sediments (f <63 µm) of Kupa River drainage basin.

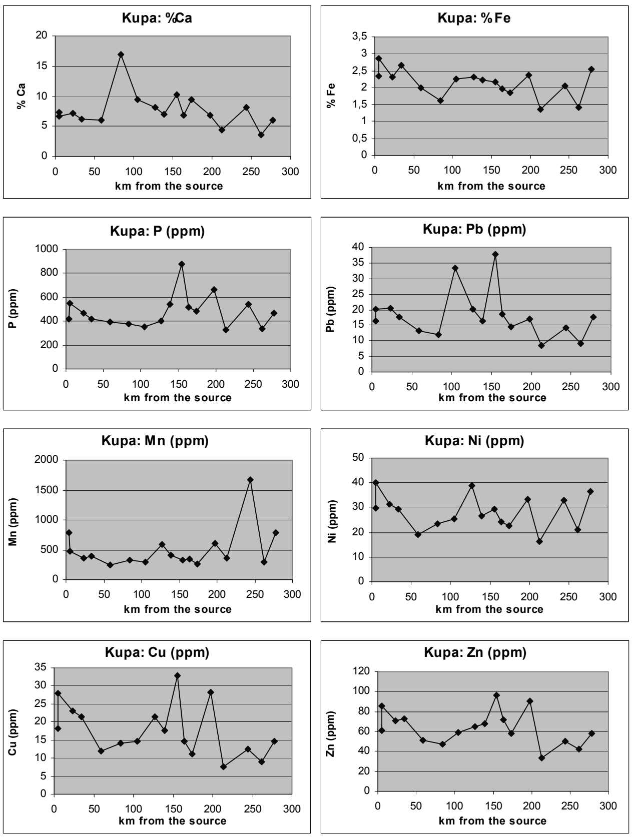

FIGURE 3a - Concentrations of 8 selected elements vs. flow direction in km for f <63 µm in Kupa River.

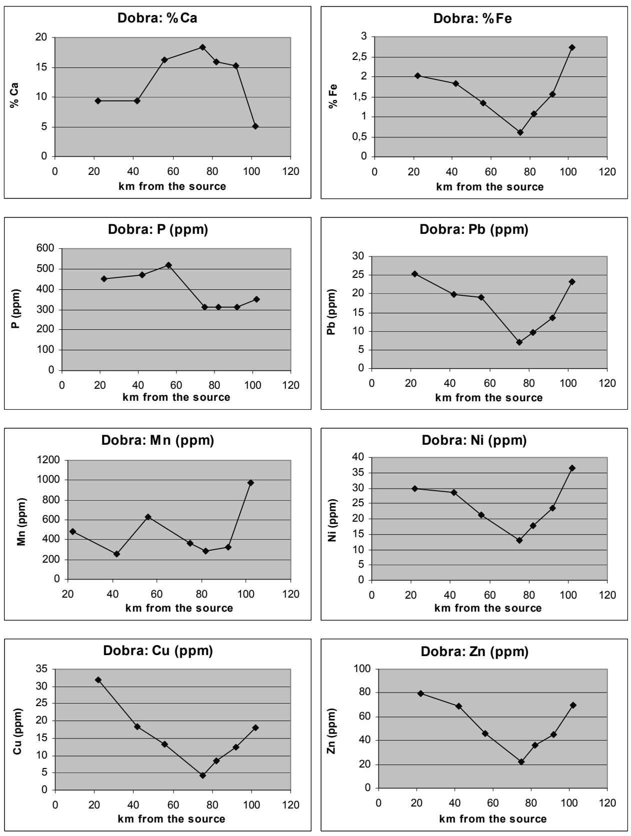

FIGURE 3b - Concentrations of 8 selected elements vs. flow direction in km for f <63 µm in Dobra River.

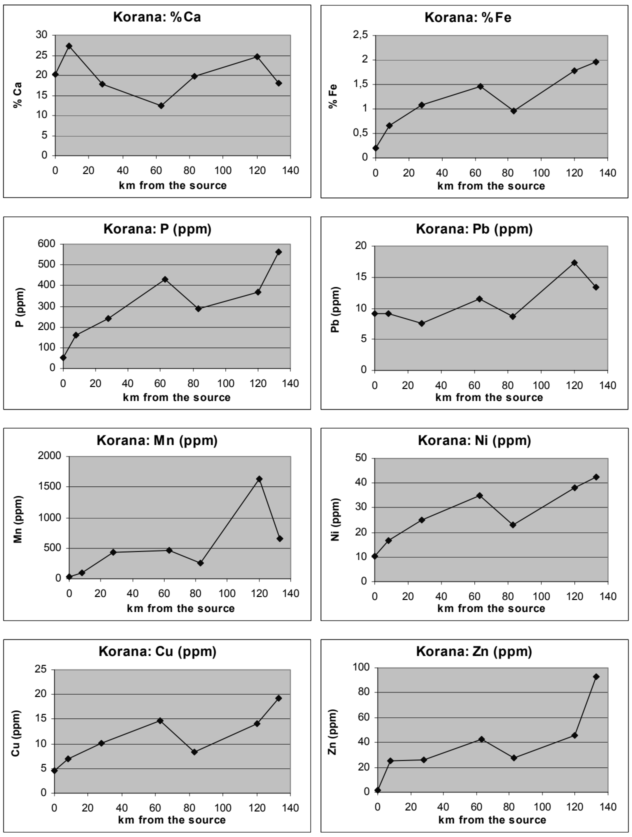

FIGURE 3c - Concentrations of 8 selected elements vs. flow direction in km for f <63 µm in Korana River.

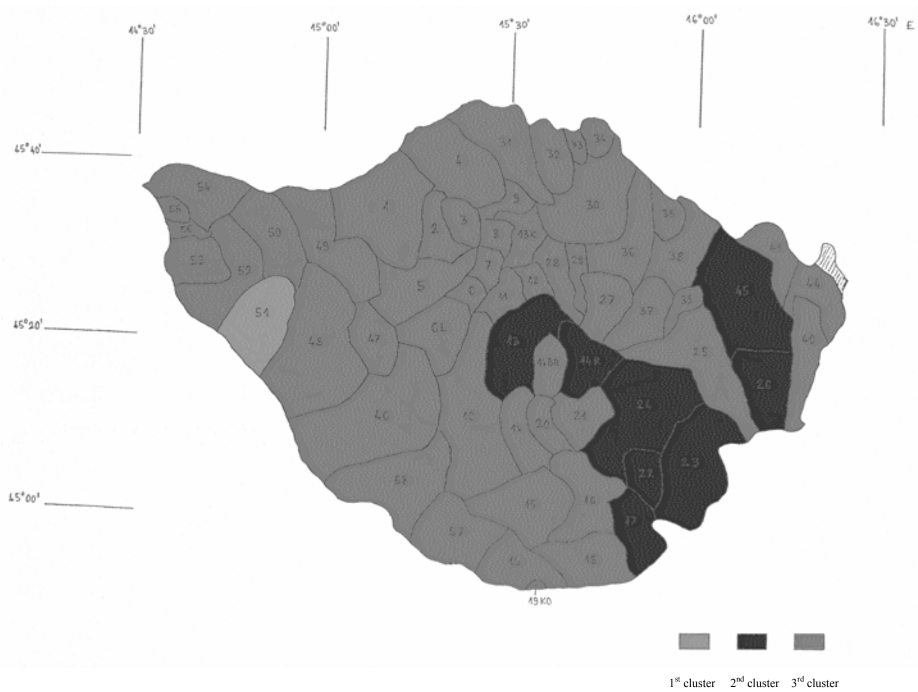

FIGURE 4 - Map with 3 clusters obtained from geochemical data in Kupa River drainage basin.

Cluster 2 has 8 sampling locations, No. 13, 14R, 17, 22, 23, 24, 26 and 45. Total number of locations in cluster 2 is too small to perform further statistical calculations. This region is mostly mined and dangerous to sample. It is under the influence of metallogenic regions of Petrova and Trgovska Gora, studied earlier by several authors [3, 25, 26]. In this region, natural Ba and Mn anomalies were observed.

Cluster 3 has 52 sampling locations, where strong anomalies have not been observed. Therefore, this region was suitable for further statistical analysis of basic statistical parameters, as presented in Table 4. For each element, the values are given for arithmetic mean, geometric mean, median, minimal and maximal concentration, variance (σ^2), standard deviation, skewness and kurtosis. The value for arithmetic mean ± standard deviation can be considered as baseline value for each element studied in this region.

Shapiro-Wilk-W test of normality showed that within cluster 3 the following 24 elements evidenced normal distribution: P, K, Fe, Li, Sc, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Y, Cs, La, Ce, Pr, Nd, Sm, Gd, Th and Hg.

TABLE 4 - Basic statistical parameters for 51 element in sediments of 52 sampling locations (Cluster 3) from Fig. 4

Element	Mean	Geometr. mean	Median	Minimum	Maximum	Variance	Std. Dev.	Skewness	Kurtosis
Ca %	10.1350	7.3436	8.6730	0.42300	27.170	48.97	6.9981	0.72633	-0.31384
Na %	0.0149	0.0129	0.0115	0.00700	0.082	0.00	0.0121	4.30651	20.94946
Mg %	1.6078	1.0953	1.1700	0.24800	10.945	3.64	1.9077	3.33467	12.67612
Al %	1.0976	0.9855	1.1080	0.08700	2.689	0.21	0.4606	0.86800	2.71292
P %	0.0404	0.0366	0.0403	0.00520	0.088	0.00	0.0156	0.25056	1.08288
S %	0.0886	0.0775	0.0745	0.02374	0.303	0.00	0.0523	2.06229	5.44018
K %	0.0981	0.0878	0.0890	0.01100	0.220	0.00	0.0430	0.59280	0.30107
Fe %	1.7618	1.5684	1.8460	0.20700	3.296	0.49	0.6965	-0.36154	-0.33478
Li (ppm)	12.9919	11.4017	12.1340	0.93800	23.868	32.10	5.6661	0.08749	-0.69261
Be (ppm)	0.5578		0.6060	-1.00000	1.161	0.10	0.3189	-2.34425	10.46876
Sc (ppm)	1.9497		2.0770	-1.00000	5.017	1.24	1.1134	-0.03874	0.54911
V (ppm)	22.3066	20.8815	22.2925	6.67100	52.856	64.54	8.0340	1.00123	3.23468
Cr (ppm)	22.4081	20.0614	21.7140	2.45600	62.801	98.62	9.9308	1.19763	4.33094
Mn (ppm)	448.6493	370.0779	395.0440	37.04500	991.023	58677.87	242.2352	0.51713	-0.35374
Co (ppm)	8.4501	7.2929	8.4250	0.76600	21.184	15.76	3.9704	0.47558	1.00436
Ni (ppm)	26.4748	25.0068	25.1380	10.27400	57.400	80.54	8.9747	0.74647	1.34201
Cu (ppm)	16.2064	14.3991	14.6810	4.23900	32.902	55.88	7.4756	0.46523	-0.36442
Zn (ppm)	53.3664	47.7970	51.0020	11.83800	101.630	506.66	22.5091	0.10538	-0.53222
Ga (ppm)	3.0029	2.6702	3.0290	0.19700	7.091	1.61	1.2677	0.51462	1.31506
As (ppm)	5.0361		4.8040	-1.00000	12.960	8.00	2.8289	0.46447	0.95692
Se (ppm)	0.6102	0.5552	0.5825	0.11800	1.265	0.07	0.2555	0.68730	0.53352
Rb (ppm)	10.7188	9.6299	10.8230	0.76800	24.327	18.92	4.3492	0.43271	0.99855
Sr (ppm)	61.2855	51.5919	50.8695	14.07000	226.078	1672.44	40.8955	2.29948	6.88068
Y (ppm)	6.9855	6.4912	6.8005	0.98900	13.181	5.64	2.3742	0.25086	1.22620
Zr (ppm)	1.0409	0.9270	0.8590	0.36500	4.049	0.38	0.6145	2.85483	11.22839
Nb (ppm)	0.4726		0.4690	-1.00000	1.221	0.09	0.3040	-1.89558	10.63547
Mo (ppm)	0.8166	0.6614	0.6395	0.27000	3.987	0.42	0.6444	2.74488	10.69901
Cd (ppm)	0.3189		0.3295	-1.00000	1.186	0.08	0.2805	-1.67102	10.88880
Sn (ppm)	0.5230		0.3260	-0.20000	3.608	0.44	0.6639	2.96084	10.16234
Sb (ppm)	0.1790	0.1560	0.1500	0.03300	0.561	0.01	0.0999	1.59843	3.61857
Te (ppm)	0.0357		0.0420	-0.20000	0.093	0.00	0.0422	-3.60930	18.85822
Cs (ppm)	1.0214		0.9895	-0.10000	2.040	0.22	0.4698	0.42469	0.14493
Ba (ppm)	144.1184	84.0571	74.8520	12.32900	1070.000	46512.41	215.6674	3.36857	11.94570
La (ppm)	10.4824	9.2935	9.7685	1.21300	22.198	22.28	4.7206	0.47218	-0.04908
Ce (ppm)	22.5733	19.9942	21.4285	2.99100	47.232	107.27	10.3569	0.48218	-0.30178
Pr (ppm)	2.6519	2.3767	2.4930	0.31200	5.151	1.28	1.1294	0.34006	-0.38214
Nd (ppm)	10.2892	9.2697	9.8220	1.06000	18.889	17.43	4.1743	0.22381	-0.35202
Sm (ppm)	2.2375	2.0353	2.1875	0.21600	3.985	0.68	0.8243	-0.05709	-0.02758
Eu (ppm)	0.3929		0.4300	-1.00000	0.753	0.08	0.2805	-2.90878	12.13853
Gd (ppm)	2.1997	2.0107	2.2080	0.22300	3.678	0.57	0.7521	-0.45022	0.56160
Tb (ppm)	0.2281		0.2830	-1.00000	0.450	0.05	0.2337	-3.48464	15.22077
Dy (ppm)	1.5057	1.3891	1.5230	0.15900	2.456	0.23	0.4838	-0.62557	0.77006
Ho (ppm)	0.2300		0.2765	-1.00000	0.469	0.05	0.2298	-3.62429	16.56166
Er (ppm)	0.6436		0.6745	-1.00000	1.232	0.11	0.3342	-2.40446	10.99600
Yb (ppm)	0.4961		0.5295	-1.00000	1.069	0.10	0.3212	-2.35133	9.36173
Re (ppm)	0.0011		0.0010	-0.00400	0.022	0.00	0.0033	4.94707	30.96605
Au (ppb)	15.5025		15.0539	-0.80000	74.090	170.59	13.0609	1.85310	6.55216
Tl (ppm)	0.1628	0.1498	0.1470	0.03200	0.385	0.00	0.0680	1.14878	1.69453
Pb (ppm)	16.2822	14.7565	16.4380	4.98800	37.734	49.66	7.0467	0.75441	1.04697
Bi (ppm)	0.2683	0.2299	0.2205	0.06600	0.849	0.03	0.1624	1.72664	3.54031
Th (ppm)	2.3516	1.8687	2.2500	0.10400	6.702	1.87	1.3679	0.69119	0.67060
U (ppm)	0.9100	0.8072	0.8135	0.27700	4.258	0.37	0.6088	3.89950	18.63947
Hg (ppb)	86.8511	70.6596	87.0817	13.44265	206.168	2320.26	48.1691	0.25962	-0.65936

Determination of anomalous values

Elements, which show extreme and/or outlier values in particular locations, are listed in Table 5. Anomalous values were obtained using experimental data from Table 3, and two-dimensional scatter box diagrams [20].

TABLE 5 - Elements with extreme and/ or outlier values in particular locations.

Element	Extreme sample	Outlier sample
Fe		24
Al		3, 8
Mg	55, 19KO, 58	31, 21
S	39, 30, 21	11, 16, 25, 51
P		13K
Na	13K, 5, 24, 51	37, 11, 12
Sc	24	
V	24	3, 23
Cr	13K	17, 26
Mn	14R	23, 45, 13
Co	17	4
Ni	17, 26	11
Cu		24, 22
Zn		14R, 22
Ga		24, 3
As		44, 56, 13
Se		56, 13K, 11
Rb		3
Sr	40, 33	11
Y		24, 3, 11, 17
Zr	24, 11	11, 23
Nb	23	25, 11
Mo	55	56, 1, 12
Cd	20	1, 13K, 30
Sn	13K, 11, 1, 22, 46	
Sb	11	13K
Cs		51
Ba	51, 50, 49, 5, 9	2, 4, 13K
Au	39	
Tl		22, 3
Pb	14R	13K, 2, 14BR
Bi	13K	6, 46, 51, 57
Th		3
U	11, 12, 55	58

Mutual correlation of elements

At this stage of the work, only simple classical correlation analysis was performed, excluding sample 51 with its large Ba-anomaly. Correlation matrix *n x n* (n=53) showed mutual relationship among elements. From 8 major elements, Ca, Mg, S and Na did not show significant correlation with any element. P was significantly correlated with Fe (0.68), Cr (0.68), Cu (0.72), Zn (0.84) and Pb (0.65), whereas Fe was with Al (0.83), P (0.68), K (0.68), Li (0.85), Sc (0.79), V (0.67), Cr (0.73), Co (0.79), Cu (0.75), Zn (0.81), Ga (0.89), Rb (0.69), Y (0.75), Cs (0.72), Sm (0.74), Gd (0.86), Dy (0.87) and Th (0.67). Al showed significant correlation with K (0.72), Fe (0.83), Li (0.77), Be (0.63), Sc (0.73), V (0.63), Cr (0.68), Co (0.73), Cu (0.66), Zn (0.75), Ga (0.95), Rb (0.89), Y (0.72), Cs (0.71), La (0.65), Ce (0.66), Pr (0.66), Nd (0.68), Sm (0.74), Gd (0.78), Dy (0.76), Tl (0.71) and Th (0.65), and K with Al (0.72), Fe (0.68), Li (0.77), Cr (0.66), Cu (0.65), Ga (0.75), Rb (0.81) and Cs (0.80).

DISCUSSION

When cluster analysis of Q-modality was performed on stream sediment geochemistry, the whole drainage basin was divided in three clusters, comprising 1, 8 and 52 locations. **Cluster 1** presents a single location 51. It has a significant Ba-anomaly, and the only Cs outlier in the whole drainage basin. Ba entered the aquatic environment due to uncareful handling of waste during barite ore processing in Homer, Lokve, Gorski Kotar, (Croatia), what is further studied and described by Frančišković-Bilinski [24]. Other sources of barium, relating to the use of barite in drilling muds [27], as well as in oil and gas wells [28], can be excluded in the region of Gorski Kotar, because there are no such exploitation activities. Cluster 2 with 8 locations is mostly composed of older sediments, under the influence of Petrova Gora, Zrinjska Gora and Trgovska Gora. The ore deposits from these regions were firstly studied by Jurković [25, 29], and later continued by Palinkaš and Šinkovec [2], Palinkaš [3] and Palinkaš and Borojević-Šoštarić [30]. Locations 13 and 45 are outside the ancient region, but there is an inflow of Radonja River to Korana River above location 13, and of Glina River to Kupa River above location 45, causing similarity in composition of sediments. The samples within this cluster 2 had different anomalies and/ or outliers, shown in parenthesis: 13 (Mn, As); 14R (Mn, Pb, Zn); 24 (Sc, V, Zr, Na, Fe, Cu, Ga, Y); 22 (Sn, Tl, Cu, Zn); 23 (Nb, V, Mn, Zr); 17 (Co, Ni, Cr, Y); 26 (Cr, Ni); 45 (Mn). The largest cluster 3 was composed of 52 locations, and samples within it either showed fewer anomalies, mostly of lower intensity, or anomalies were not present. The most interesting samples were 11 (U, Zr, Sn, Sb, S, Na, Ni, Se, Sr, Y, Zr, Nb); 13K (Na, Sn, Cr, Bi, P, Se, Cd, Sb, Pb); 20 (Cd); 39 (S, Au); 40 (Sr) and 55 (Mg, Mo, U). To explain the meaning of clusters 3 and 2, results of Herak [31] were used. Clusters 3 and 2 represent two different proveniences of sediments. The largest cluster 3 was a part of Dinaric carbonate platform within Adriatic paleodynamic and paleostructural belt, on which shallow water carbonate sedimentation occurred, whereas cluster 2 was a part of Supradinaric belt. In this part of platform, sedimentation was under the influence of penetration of mafic and ultramafic lavas, and also of younger neutral and acid volcanism. It can be assumed that this area belongs to the ophiolitic belt. Ophiolites provide models for processes at mid-ocean ridges.

Geochemical data can be used also for assessment of contamination of sediments with toxic elements. There was no unique “best method”. Chemical analysis (Table 3) was used to compare the obtained concentrations of selected toxic elements in comparison with existing criteria for sediment quality [32]. Comparison with other criteria (US NOAA), used by Long et al. [33, 34] was not possible, because the criteria considering Effect Range-Low (ER-L) and Effect Range-Median (ER-M) were described for marine and estuarine sediments.

It was found that levels of Sb, Cd, Cr, Co, Cu, Fe, Hg, Mo, Se and Ag were relatively low, thus not presenting a danger for environment and human health. Toxic effects could be possible at some locations, with respect to Ni, Pb, Zn, Mn and P. At two locations (17 and 26), the values for Ni were above those causing significant toxic effects. At other locations, Ni did not present any danger. With respect to Pb, Zn and P, there were only a few locations with minimal toxic effects. Concentrations of manganese above the level causing significant toxicity were found in 6 locations: 13, 14R, 17, 23, 24, 45 and 42. There were natural concentrations coming from ore mineralization in Petrova Gora. But toxicity of manganese depends also on valence (II, III, IV or VII) and bioavailability. Therefore, in future investigations, pH, redox potential and concentration of manganese in sediments and water should be measured at the above 6 locations.

The most significant result was the distribution of Ba in sediments (Fig. 5). Anthropogenic Ba-anomaly in Kupica and Kupa rivers was observed in the western part of the drainage basin. There was another smaller Ba-anomaly in Glina River, in the eastern part, which was caused by ore mineralization in Petrova Gora. It can be suggested that Kupa River and Ba, measured in sediments and water, can be used as a future model to study sediment transport processes.

In comparison with the elemental composition of stream sediments of Savinja River [35] and Soča River [11] drainage basins, that of Kupa River was less contaminated, with exception of barium and manganese.

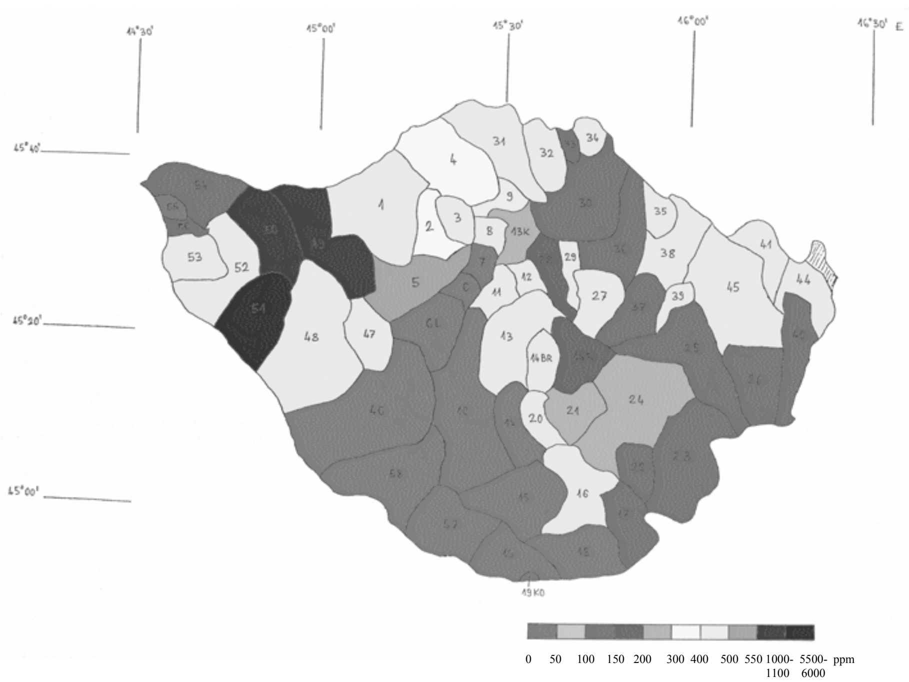

FIGURE 5 - Distribution of Ba in sediments f <63 µm of Kupa River drainage basin.

CONCLUSIONS

The described mineralogical, geochemical and statistical investigation of stream sediments of the complete Kupa River drainage basin, which is of supra-regional interest, led to the following conclusions:

- Mineralogical analysis has shown that the most abundant minerals are quartz, calcite, and minerals from the dolomite group. Feldspars-plagioclase, mica, chlorite, Mn and Fe oxides and hydroxides are less abundant. It was possible to determine with certainty a class and a group of minerals. Minor minerals (<5%) are possible, but not proved, due to the limitation of XRD method.
- Geochemical characterization showed different distributions of elements between different river valleys within the same drainage basin, due to different bedrock lithologies.
- Q-modality cluster analysis of geochemical data was used to disaggregate the total data set into more ho-

mogenous subsets. From this result, one can conclude that Q-modality cluster analysis is suitable as pollution and provenance indicator. Cluster 1 showed a region with significant anthropogenic Ba-anomaly. Cluster 2 represented a part of Supradinaric belt with ophiolites. Sedimentation was under the influence of mafic and ultramafic lavas, but also neutral and acid volcanism. Cluster 3 represented a part of Dinaric carbonate platform, on which shallow water carbonate sedimentation occurred. In this largest cluster, without significant anomalies, it was possible to calculate baseline values for 51 elements in the studied region.

- Comparing the concentrations of toxic elements and existing criteria for sediment quality, it was found that the region is relatively uncontaminated. This is an especially important conclusion, because, according to Biondić et al. [15], the karstic aquifers are highly vulnerable and at risk. A most significant contamination was found only with Ba and Mn. There were also a few locations where toxic effects might be possible, due to Ni, Pb, Zn and P.
- With some exceptions, in comparison with Savinja and Soča River drainage basins, the trans-boundary Kupa River drainage basin was less contaminated.
- Experimental data presented for sediments can be combined in the future with solution data, and used in any advanced geo-statistical models.

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REFERENCES

[1] Bonham-Carter, G.F. and Goodfellow, W.D. (1986). Background corrections to stream geochemical data using digitized drainage and geological maps: application to Selwyn Basin, Yukon and Northwest Territories. Journal of Geochemical Exploration 25, 139-155.

[2] Palinkaš, A.L. and Šinkovec, B. (1987). Stream sediment geochemistry of some selected Paleozoic regions in Croatia, as an indicator of global-tectonic-metallogenic events. 5th Meeting of the European Geological Societies, Dubrovnik.

[3] Palinkaš, A.L. (1988). Geochemical characteristics of Paleozoic metallogenic regions: Samoborska Gora, Gorski Kotar, Lika, Kordun and Banija. Dissertation, University of Zagreb.

[4] Borovec, Z. (1996). Evaluation of the concentrations of trace elements in stream sediments by factor and cluster analysis and the sequential extraction procedure. The Science of the Total Environment 177, 237-250.

[5] Moon, C.J. (1999). Towards a quantitative model of downstream dilution of point source geochemical anomalies. Journal of Geochemical Exploration 65, 111-132.

[6] Oever van den, F. (2000). Aruba – a geochemical baseline study. Geologie en Mijnbouw / Netherlands Journal of Geosciences 79(4), 467-477.

[7] Rubio, B., Nombela, M.A. and Vilas, F. (2000). Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution. Marine Pollution Bulletin 40(11), 968-980.

[8] Rubio, B., Nombela, M.A. and Vilas, F. (2001). A critical evaluation of the use of cluster analysis to identify contaminated sediments in the Ria de Vigo (NW Spain). Ciencias Marinas 27(2), 175-208.

[9] Ridgway, J., Breward, N., Langston, W.J., Lister, R., Rees, J.G. and Rowlatt, S.M. (2003). Distinguishing between natural and anthropogenic sources of metals entering the Irish Sea. Applied Geochemistry 18, 283-309.

[10] Ávila, P.F., Oliveira, J.M.S., Da Silva, E.F. and Fonseca, E.C. (2005). Geochemical signatures and mechanisms of trace elements dispersion in the area of the Vale das Gatas mine (Northern Portugal). Journal of Geochemical Exploration 85, 17-29.

[11] 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.

[12] Sarkar, S.K., Frančišković-Bilinski, S., Bhattacharya, A., Saha, M. and 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.

[13] Frančišković-Bilinski, S., Bilinski, H. and Širac, S. (2005). Organic pollutants in stream sediments of Kupa River drainage basin. Fresenius Environmental Bulletin 14(4), 282-290.

[14] Ivković, A., Šarin, A. and Komatina, M. (1983). Explanation for the Hydrogeological Map of SFR Yugoslavia 1:500.000, Belgrade.

[15] Biondić, B., Biondić, R. and Kapelj, S. (2006). Karst groundwater protection in the Kupa River catchment area and sustainable development. Environment International 49, 828-839.

[16] Frančišković-Bilinski, S. and Rantitsch, G. (2003). Geochemical and mineralogical dispersion in the upper Sava River (Slovenia), a preliminary report. First Conference on Applied Environmental Geology (AEG'03) in Centraln and Eastern Europe Abstract volume, Umweltbundesamt GmbH, Vienna, 58-59.

[17] Powder Diffraction File (1997). International Center for Diffraction Data, Newtown Square, PA, USA.

[18] 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.

[19] 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.

[20] StatSoft, Inc. (2001). STATISTICA (data analysis software system), version 6. www.statsoft.com

[21] Davis, J.C. (1986). Statistics and data analysis in geology, Second edition. John Wiley & Sons, New York.

[22] Frančišković-Bilinski, S. (2005). Geochemistry of stream sediments in Kupa River drainage basin, Dissertation. University of Zagreb, 197 pp.

[23] Frančišković-Bilinski, S., Barišić, D., Vertačnik, A., Bilinski, H. and Prohić, E. (2004). Characterization of tufa from the Dinaric karst of Croatia: mineralogy, geochemistry and discussion of climate conditions. Facies 50, 183-193,

[24] Frančišković-Bilinski, S. (2006). Barium anomaly in Kupa River drainage basin. Journal of Geochemical Exploration 88(1-3), 106-109.

[25] Jurković, I. (1958). Metallogeny of Petrova Gora in Southwestern Croatia. Geološki Vjesnik 9, 143-228.

[26] Šinkovec, B. (1979). Investigations of nuclear sources in Croatia, basic studies, presentation of occurrences and deposits of mineral sources of Petrova Gora and Lika (in Croatian), Report No. 268/79, Institute for geology and mineral resources, archive of Faculty of mining, geology and petroleum engineering 33, Zagreb, University of Zagreb.

[27] Sharma, V.K., Rhudy, K.B., Koening, R., Vazquez, F.G. (1999). Metals in sediments of the Upper Laguna Madre. Marine Pollution Bulletin 38, 1221-1226.

[28] Holmes, C.W., Slade, E.A., Mickerran, C.J. (1974). Migration and redistribution of zinc and cadmium in marine estuarine system. Environmental Science & Technology 8, 254-259.

[29] Jurković, I. (1961). Investigation of Iron-ore deposits Ljubija near Prijedor in Bosnia. Geološki Vjesnik 14, 161-220.

[30] Palinkaš, A.L. and Borojević-Šoštarić, S. (2003). Stratabound barite deposit, Sabkha depositional environment, Permian-Triassic boundary (Lokve locality in the Gorski Kotar, Central Croatia). Field trip guidebook, 22nd IAS Meeting of Sedimentology, Opatija, Croatia.

[31] Herak, M. (1986). A new concept of geotectonics. Acta Geologica 16(1), 1-42.

[32] SMSP and FALCONBRIDGE NC SAS (2005). Koniambo project, Environmental and Social Impact Assesment, 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

[33] Long, E.R., MacDonald, D.D., Smith, S.C., Calder, F.D. (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environmental Management 19(1), 81-97.

[34] Long, E.R., Field, L.J., MacDonald, D.D. (1997). Predicting toxicity in marine sediments with numerical sediment quality guidelines. Environmental Toxicology and Chemistry 17(4), 714-727.

[35] Frančišković-Bilinski, S., Bilinski, H., Tibljaš, D., Hanžel, D. (2006). Sediments from Savinja, Voglajna and Hudinja Rivers (Slovenia), reflecting anomalies in an old metallurgic area. Fresenius Environmental Bulletin 15(3), 220-228.

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CORRESPONDING AUTHOR

Stanislav Frančišković-Bilinski
Institute "Ruđer Bošković"
POB 180
10002 Zagreb
CROATIA

E-mail: francis@irb.hr