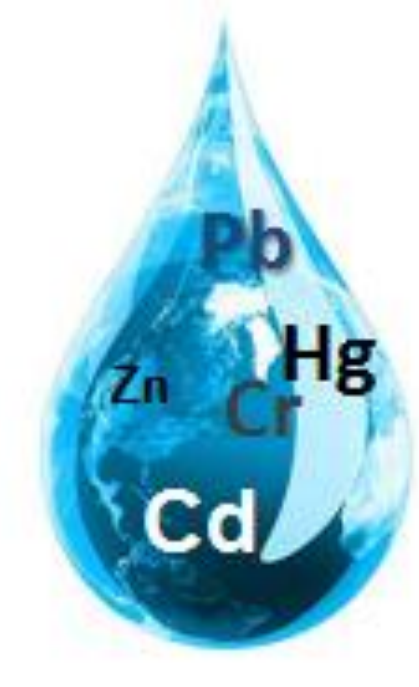




# ELEMENTAL DISTRIBUTION IN SURFACE WATERS FROM BREGALNICA RIVER BASIN



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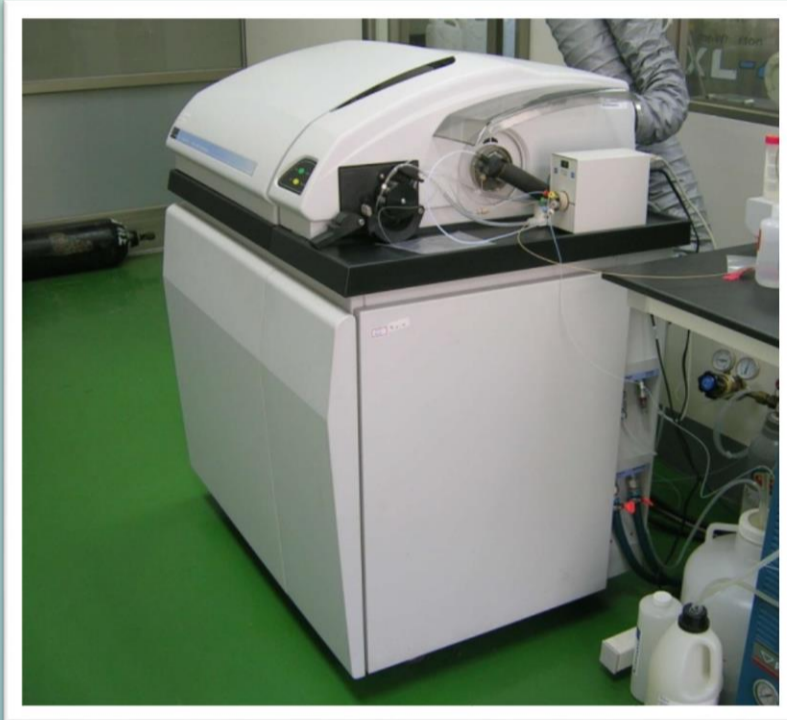
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## INTRODUCTION

The water quality and quantity of water resources worldwide is a subject of ongoing concern. The biggest threat for water systems is discharge of industrial waters, heavy industries, application of fertilizers and pesticides, waste disposals. Anthropogenic activity may add considerable amounts of pollution compounds, which will influence the on the quality of the aquatic system. In the region of the basin of the Bregalnica river, there are several significant emission sources of potentially toxic metals and other chemical elements in the environment, which are the following: the copper mine and flotation “Bučim” near Radoviš, the lead and zinc mines “Sasa” near Makedonska Kamenica and “Zletovo” near Probishtip.

The investigated area includes the basin of the Bregalnica river which is found in the area of the east planning region of the Republic of Macedonia. The investigated area covers ~200 km (W-E) x 200 km (S-N), that is, a total of ~4000 km<sup>2</sup>, within the following geographic coordinates N: 41°27'-42°09' and E: 22°55'-23°01' (Fig. 1). The total basin area of the river Bregalnica was divided into four zones: zone 1 (Z-1) which includes 5 locations (B1, B2, B3, B4, and P1), zone 2 (Z-2), which includes the following 5 locations: B5, B6, B7, B8 and P2, zone 3 (Z-3) which includes the following 5 locations: B9, B10, B11, B12, and B13 and zone 4 (Z-4) which includes the following locations: B14, B15, B16, B17 and B18. The areas of Kamenichka river (K), Zletovska river (Z) and Lakavica (L) were separately monitored.

### Determination of elements content



The investigated elements (Ag, As, Al, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Ti, Th, Tl, Tm, V, W, Y, Yb, Zn, Zr) were analyzed with application of mass spectrometry with inductively coupled plasma (ICP-MS).

For all measurements, a SCIEX Perkin Elmer Elan DRC II (Canada) inductively coupled plasma mass spectrometer (with quadrupole and single detector) was used. For 14 elements only were obtained concentrations that were quantified with the applied techniques, which are the following: Al, Ba, Ca, Fe, K, P, Ba, Li, Mn, Sb, Sc, Sr, and V.

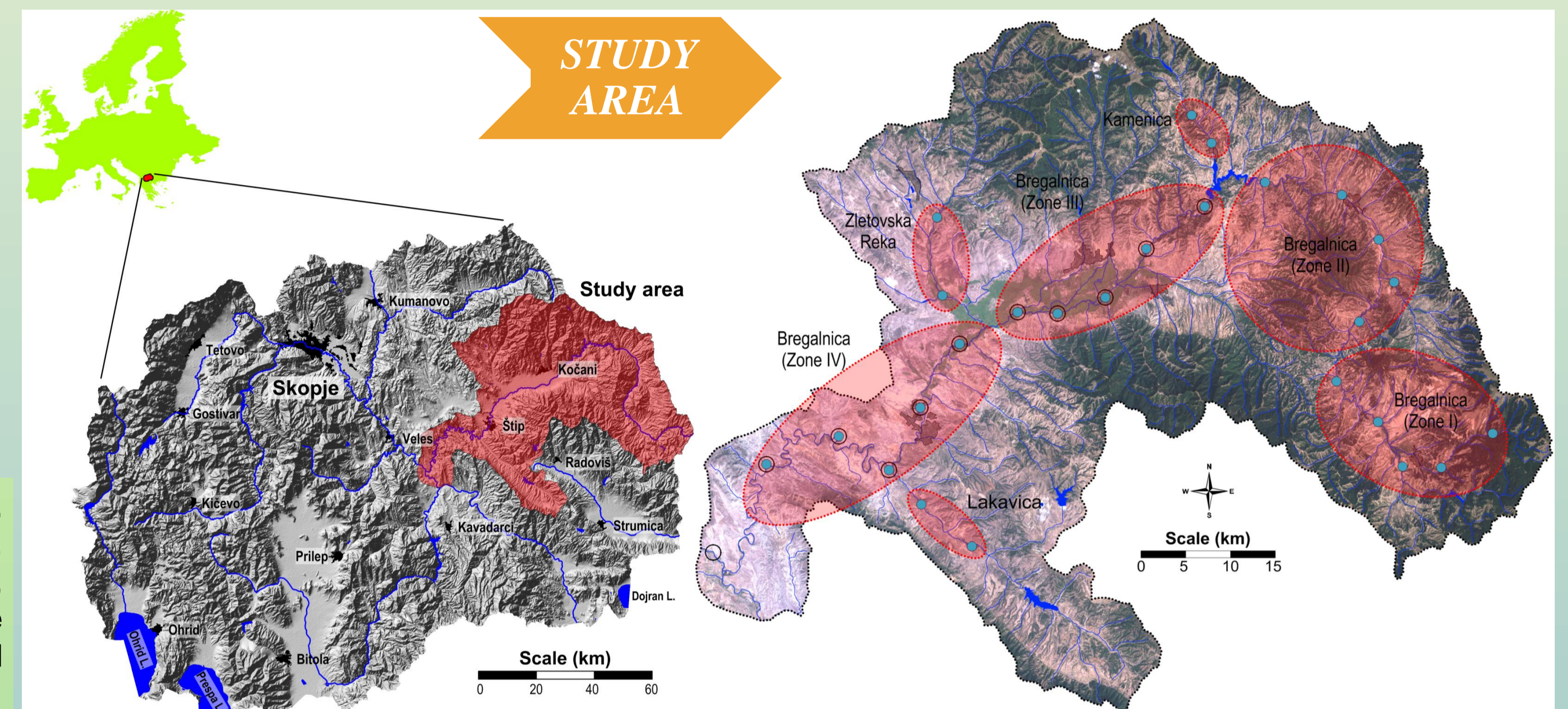


Fig. 1. The investigated area on the territory of the Republic of Macedonia

### Sampling

Along the whole course of the river Bregalnica a total of 18 samples of surface water were collected. Additionally, such samples were also collected from another 13 locations from the tributaries: Ratevska river, Ochipalska river, Kamenichka river, Kochanska river, Orizarska river, Zletovska river, the river Lakavica and Sveti Nikolska river.

## RESULTS

Table 1. Values of medians of the analyzed elements in 4 zones along the course of the Bregalnica river and its tributaries

Element	ME	Z1	Z2	Z3	Z4	K	Z	L
N		5	5	5	5	3	2	2
Al	mg L <sup>-1</sup>	0.26	1.4	0.20	0.42	0.83	0.32	0.076
Ca	µg L <sup>-1</sup>	18	33	43	61	31	28	66
Fe	mg L <sup>-1</sup>	0.081	0.19	0.41	0.25	0.08	0.059	0.034
K	mg L <sup>-1</sup>	2.4	2.6	4.4	5.7	1.5	2.5	2.6
Mg	mg L <sup>-1</sup>	5.4	10	12	17	4.6	6.1	15
Na	µg L <sup>-1</sup>	4.4	7.6	19	21	2.1	4.1	10
P	mg L <sup>-1</sup>	0.018	0.026	0.049	0.11	0.01	0.01	0.01
Ba	µg L <sup>-1</sup>	2.9	19	37	51	5.4	25	72
Li	µg L <sup>-1</sup>	0.89	1.8	9.9	9.7	0.99	1.4	4.2
Mn	mg L <sup>-1</sup>	0.01	3.2	190	180	380	6.3	96
Sb	µg L <sup>-1</sup>	0.10	0.087	0.062	0.01	0.43	0.23	0.24
Sc	µg L <sup>-1</sup>	0.92	0.84	0.93	1.9	0.43	0.53	2.3
Sr	µg L <sup>-1</sup>	46	98	190	360	110	180	320
V	µg L <sup>-1</sup>	0.25	1.3	0.37	1.4	0.13	0.029	13

Element	ME	Z1	Z2	Z3	Z4	K	Z	L
As	µg L <sup>-1</sup>	/	0.13	1.65	1.08	0.77	/	4.0
Cd	µg L <sup>-1</sup>	/	/	/	/	4.8	/	0.07
Co	µg L <sup>-1</sup>	/	/	/	/	0.49	/	2.1
Cu	µg L <sup>-1</sup>	/	/	/	/	/	/	31.1
Ni	µg L <sup>-1</sup>	/	/	/	/	0.9	50.8	5.3
Pb	µg L <sup>-1</sup>	/	/	/	0.60	21.3	/	7.6
Rb	µg L <sup>-1</sup>	/	/	2.51	1.48	0.9	/	7.2
Ti	µg L <sup>-1</sup>	/	/	/	/	/	/	587
Y	µg L <sup>-1</sup>	/	0.37	/	0.17	0.18	/	1.52
Zn	µg L <sup>-1</sup>	/	/	/	/	664	/	19.8

Z1-zone 1; Z2-zone 2; Z3-zone 3; Z4-zone 4; N-number of samples in each zone; the Kamenichka river course (K); the Zletovska river course (Z); the Lakavica river course (L)

Table 2. Matrix of factor loadings – factor analysis (FA) of elements' concentration in surface water

Element	F1	F2	F3	Com
Ca	<b>0.94</b>	-0.16	0.06	91.8
K	<b>0.74</b>	0.31	-0.23	70.2
Mg	<b>0.93</b>	-0.16	-0.22	93.4
Na	<b>0.90</b>	0.04	-0.25	86.9
Ba	<b>0.88</b>	-0.02	0.03	76.9
Li	<b>0.93</b>	0.17	-0.12	90.0
Mn	<b>0.63</b>	0.49	0.41	80.5
Sr	<b>0.92</b>	0.01	0.23	89.7
V	<b>0.70</b>	-0.04	-0.18	52.3
Al	-0.27	<b>0.76</b>	0.05	65.7
Fe	0.17	<b>0.89</b>	-0.15	84.8
Sb	-0.17	-0.08	<b>0.90</b>	85.2
Variability (%)	58.7	15.1	10.7	
Eigenvalue	6.65	1.78	1.24	80.6

F1- values of Factor 1 loadings; F2 – values of Factor 2 loadings; F3- values of Factor 3 loadings; Com- communality (%)

Table 1 presents an overview of the values of the medians of the analyzed elements, by the individual zones in the basin of the river Bregalnica. According to the Official Gazette of the R.M., No. 18 [1], the elements concentrations do not exceed the maximum allowed concentrations in accordance with the relevant classification.

Based on the performed multivariate processing of the values of the analyzed elements' contents, three dominant factors were singled out: F1 (Ca-K-Mg-Na-Ba-Li-Mn-Sr-V), F2 (Al-Fe), F3 (Sb). The dominant factor loadings were obtained in the Kamenichka, Zletovska and Lakavica rivers course.

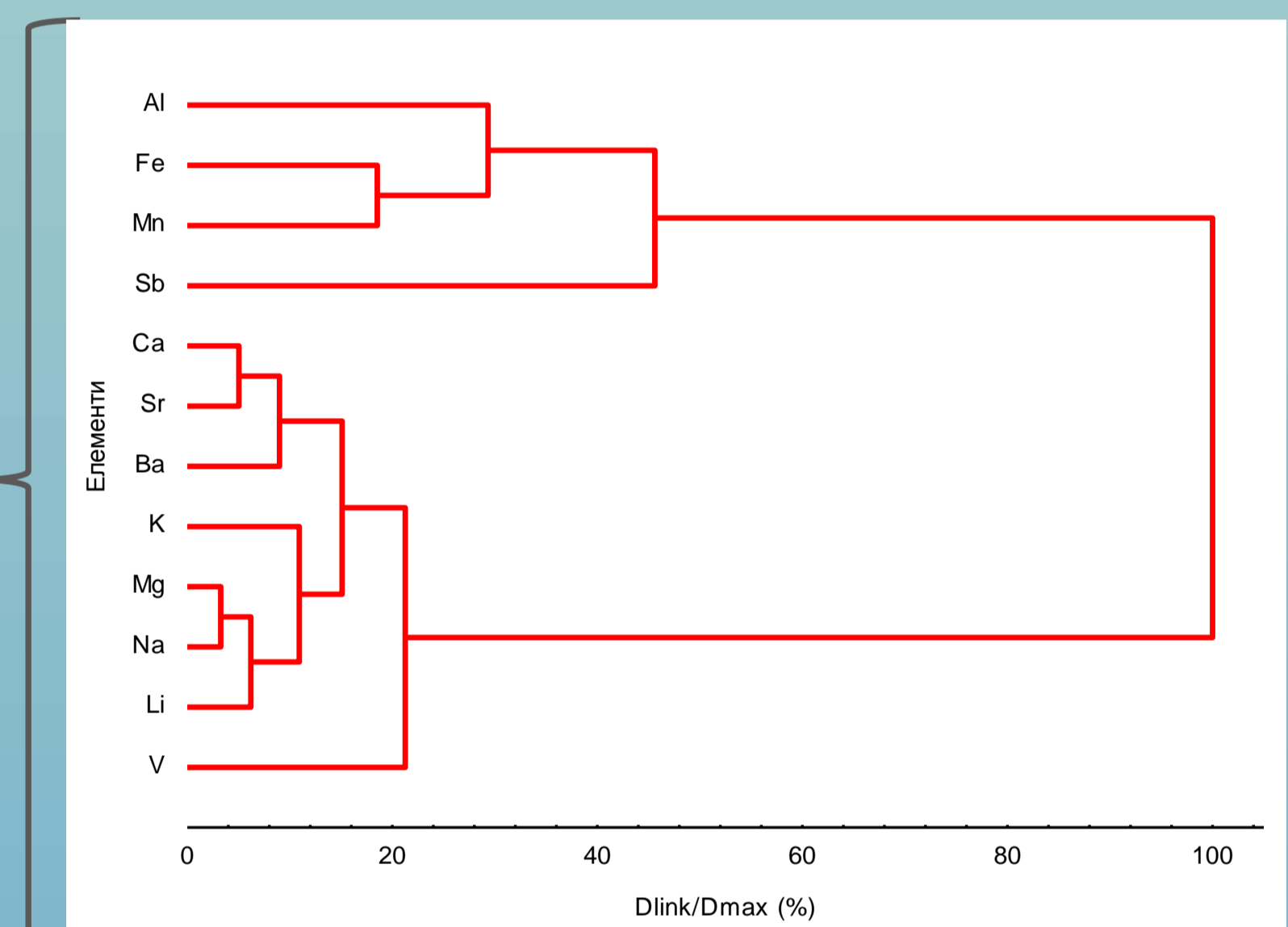


Fig. 2. Dendrogram of interdependence of the elements analyzed in samples of surface water

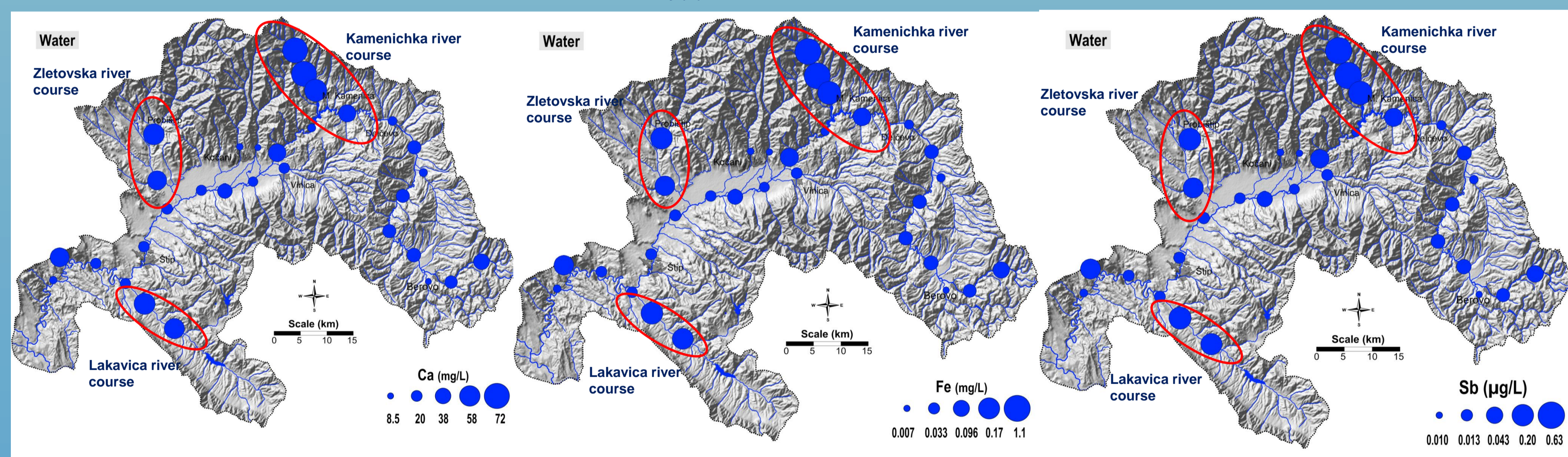


Fig. 3. Spatial distribution of calcium, iron and antimony in the surface river waters in the Bregalnica river basin

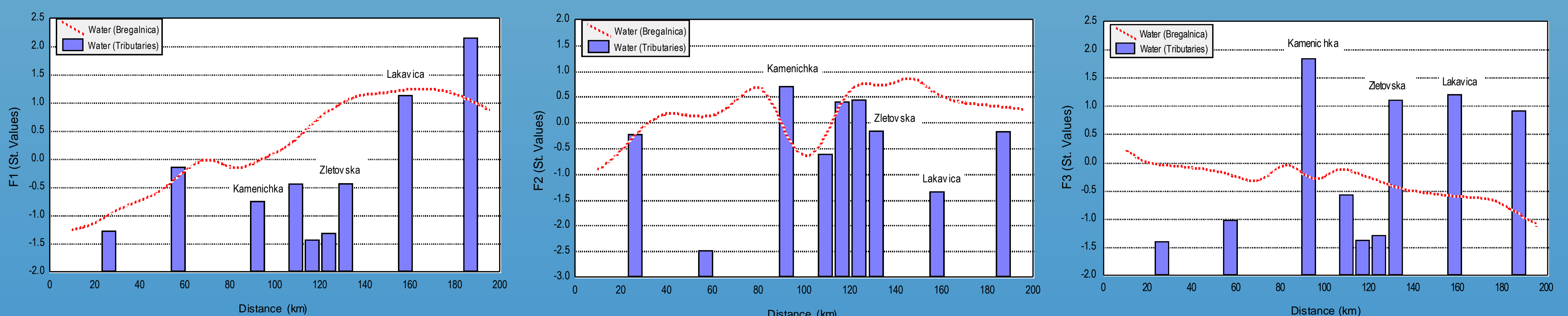


Fig. 4. Distribution of F3 elements along the Bregalnica river course and its tributaries, depending on the distance from the river source (Tributaries: Ratevska river, Ochepalska river, Kamenichka river, Osojnica, Orizarska river, Kochanska river, Zletovska river, Lakavica, Sveti Nikolska river)

## CONCLUSIONS

Elements concentrations do not exceed the maximum allowed concentrations in accordance with the relevant classification (class) for river water quality. However, the Pb concentration in the Kamenichka river course enrich 21.3 µg L<sup>-1</sup> while the Zn concentrations enrich 664 µg L<sup>-1</sup>. The water of the Zletovska river is characterized only with Ni concentration of 50.8 µg L<sup>-1</sup>. The water from Lacavica river is concern with the Cu concentration of 31 µg L<sup>-1</sup> and Ti concentration of 587 µg L<sup>-1</sup>. The dominant geochemical association in the river waters from the Bregalnica river basin are: Ca-K-Mg-Na-Ba-Li-Mn-Sr-V; Al-Fe and single Sb. The F1 distribution increase along the Bregalnica course, with maximum concentration levels in Lakavica and Sveti Nikolska rivers. While the F2 and F3 association the dominant concentration levels are obtained for Kamenichka, Zletovska, Lakavica and Sveti Nikolska rivers.

References  
 [1] Official Gazette of the Republic Macedonia, No. 118, Decree on water classification in R. Macedonia, 1999.