SEVENTH FRAMEWORK PROGRAMME

RESTCA

GeoZS

Reinforcing S&T Capacities of Two Emerging Research Centers for Natural and Industrial Pollutant Materials in Serbia and Slovenia (RESTCA - TERCE - NIPMSS)

Applied Environmental Geochemistry - Anthropogenic impact on the human environment in the SE Europe

October, 6-9, 2009

PROCEEDINGS BOOK

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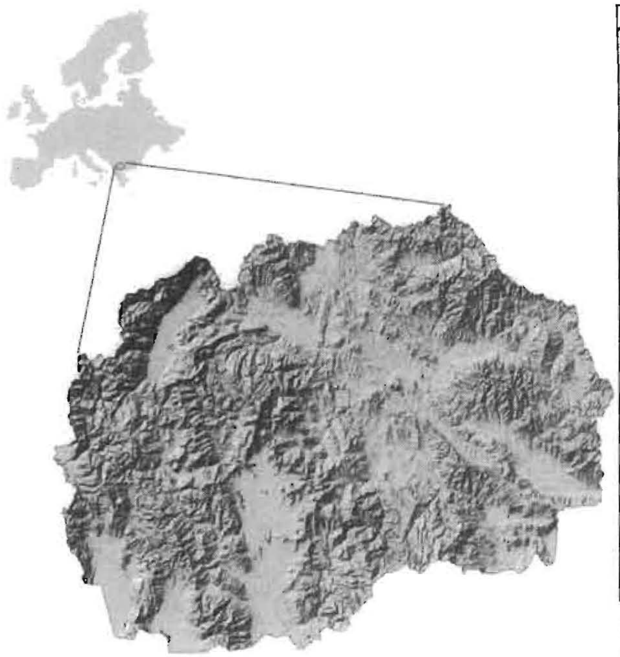


Fig. 1: Location of the study area

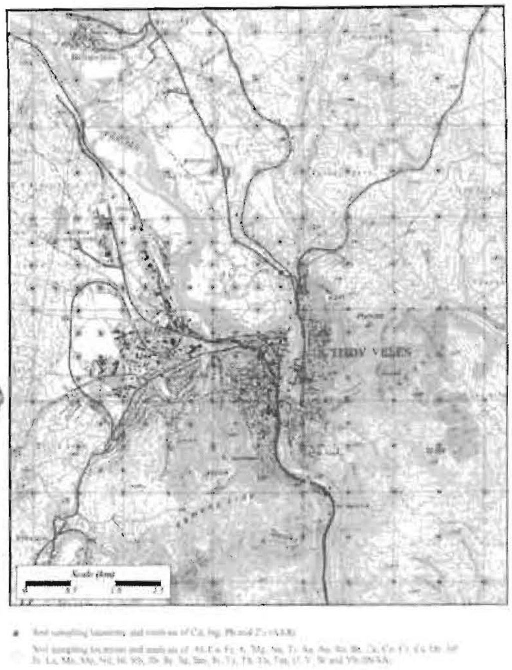


Fig. 2: Geographic map of the Veles area with soil sampling locations

Sampling, sample preparation and analysis

A total of 201 samples of topsoil were collected over the area of 35.8 km^2 (Fig. 2) according to the European guidelines for soil pollution studies (Salminen et al., 2005). The surroundings were sampled in a 1×1 km; the town in a 500×500 m; and the polluted areas in a 250×250 m grid. Soil was sampled from the topsoils (0–5 cm), the possible organic horizon excluded. The soil samples were air dried indoor at room temperature, then gently crushed, cleaned and sifted through a plastic sieve with 2 mm. The shifted mass was quartered and milled in agate mill to an analytical grain size below 0.125 mm.

Two complementary analytical techniques were used: atomic absorption spectrometry (AAS) performed at the Institute of Chemistry in Skopje, Macedonia, and the epithermal neutron activation analysis (ENAA) at the IBR–2 reactor, FLNP Joint Institute for Nuclear Research in Dubna, Moscow, Russia.

Results and discussion

Data processing

Data analysis and construction of maps were performed using the Statistica (ver. 6.1), AutoDesk Map (ver. 2008) and Surfer (ver. 8.09) software. Methods of parametric and nonparametric statistics were used for the data (Snedecor and Cochran, 1967; Davis, 1986). The descriptive statistics data of the analyzed chemical elements and the average of elements are shown in Table 1. The degree of association of the chemical elements in soil was assessed with the linear coefficient of correlation *r* (Le Maitre, 1982) between their contents. For better illustration, the matrix of the correlation coefficient is divided into three parts, according to the results of multivariate analysis (Table 2). The multivariate R-mode factor analysis (Snedecor and Cochran, 1967; Davis, 1986) was used to reveal the associations of the chemical elements. In the factor analysis, 159 samples and 30 chemical analyses were considered. From the multivariate analysis 12 elements (Au, Br, Ca, Dy, Mg, Mn, Mo, Na, Nd, Se, Sr, W) were excluded from further analysis, because of low share of communality or tendency to form independent factors. The factor analysis distribution is decreased on three synthetic variables (F1 to F3), including 73% of variability of treated elements (Table 2). Universal kriging with linear variogram interpolation method (Davis, 1986) was used to construct maps of areal distribution of particular elements. The basic grid cell size for interpolation was 5×5 m.

Table 1: Descriptive statistics of measurements. Values of Al, Ca, Fe, K, Mg, Na and Ti are in %, Au in μg/kg, remaining elements in mg/kg (data rounded to two digits)

	n	Dis	Md	X	s	A	E	Min - Max	P_{10} - P_{90}
Al	159	N	6.2	6.2	1.2	0.08	0.57	2.6 - 10	4.7 - 7.9
Ca	159	Log	4.1	3.9	2.3	-0.08	1.06	0.5 - 94	1.2 - 10
Fe	159	Log	2.8	2.8	1.5	-0.43	-0.02	0.8 - 6.2	1.6 - 4.6
K	159	Log	2.2	2.2	1.5	0.04	1.11	0.6 - 7.1	1.3 - 3.3
Mg	159	Log	0.36	0.51	2.3	0.22	-1.53	0.1 - 2.8	0.20 - 1.5
Na	159	N	1.0	1.0	0.40	0.25	-0.02	0.2 - 2.3	0.52 - 1.5
Ti	159	Log	0.36	0.36	1.4	-0.42	1.15	0.1 - 0.82	0.24 - 0.56
As	159	Log	9.2	9.8	2.1	0.74	2.19	1.3 - 110	4.1 - 22
Au	159	Log	11	11	3.1	0.88	2.64	0.7 - 1000	2.9 - 42
Ba	159	Log	460	460	1.4	-0.48	1.91	130 - 1600	300 - 700
Br	159	Log	3.9	3.7	2.1	-0.01	2.59	0.4 - 100	1.4 - 8.4
Cd	201	Log	6.4	7.7	3.5	0.60	0.38	0.3 - 600	1.9 - 44
Ce	159	Log	65	65	1.4	-0.05	0.44	25 - 180	41 - 99
Co	159	Log	13	13	1.6	-0.57	0.87	2.5 - 38	6.7 - 22
Cr	159	Log	160	160	2.1	0.32	1.70	17 - 1800	71 - 330
Cs	159	Log	3.7	3.6	1.5	-0.33	-0.13	1.2 - 7.4	2.1 - 5.7
Cu	201	Log	41	44	2.0	1.78	6.95	11 - 1700	22 - 84
Dy	159	Log	4.5	4.1	2.1	-2.71	12.06	0.1 - 44	2.6 - 7.4
Hf	159	Log	4.4	4.5	1.4	-0.21	0.24	1.4 - 11	2.7 - 7.3
Hg	201	Log	0.28	0.25	3.7	-0.44	1.43	0.010 - 12	0.062 - 0.85
In	159	Log	0.24	0.25	2.8	0.57	1.31	0.012 - 9.2	0.075 - 0.90
La	159	Log	29	29	1.4	0.08	0.51	12 - 78	19 - 44
Mn	159	Log	830	840	1.7	0.92	4.67	160 - 8300	510 - 1400
Mo	159	Log	0.54	0.55	2.1	0.14	1.01	0.064 - 5.0	0.24 - 1.4
Nd	159	Log	24	24	1.6	0.29	1.18	8.1 - 150	13 - 39
Ni	159	Log	54	54	1.9	0.42	1.99	7.3 - 600	24 - 120
Pb	201	Log	210	220	3.4	0.42	0.57	13 - 15000	53 - 1100
Rb	159	N	93	96	29	0.58	1.16	27 - 210	59 - 130
Sb	159	Log	1.9	2.3	2.7	0.73	1.34	0.2 - 110	0.81 - 11
Sc	159	Log	9.6	9.6	1.5	-0.15	-0.25	3.6 - 22	6.0 - 16
Se	159	Log	0.41	0.25	13	-0.20	-0.97	0.0050 - 61	0.0050 - 5.1
Sm	159	Log	5.6	5.5	1.3	-0.25	0.12	2.5 - 11	3.8 - 7.7
Sr	159	Log	230	210	1.5	-0.45	0.42	52 - 690	120 - 350
Ta	159	Log	1.3	1.3	1.4	-0.40	0.82	0.4 - 2.9	0.84 - 1.9
Tb	159	Log	0.79	0.78	1.4	-0.25	-0.22	0.3 - 1.7	0.51 - 1.2
Th	159	Log	10	10	1.5	0.36	1.22	3.3 - 43	6.3 - 17
Tm	159	N	0.51	0.51	0.15	0.04	0.23	0.078 - 1.0	0.31 - 0.72
U	159	Log	2.4	2.4	1.4	-0.13	0.44	0.8 - 5.6	1.5 - 3.6
V	159	N	78	79	27	0.46	0.23	26 - 160	45 - 120
W	159	Log	9.7	9.9	1.6	0.79	3.32	1.8 - 67	6.3 - 18
Yb	159	Log	2	2	1.4	-0.39	0.23	0.8 - 4.0	1.4 - 3.3
Zn	201	Log	210	280	3.2	1.07	1.52	22 - 27000	82 - 1300

n – number of observation; *Dis.* – distribution (N – normal, Log – lognormal); *Md* – median; *X* – arithmetical or geometrical mean; *s* – arithmetical or geometrical standard deviation; *A* – skewness; *E* – kurtosis; *Min* – minimum; *Max* – maximum; P_{10} – 10 percentile; P_{90} – 90 percentile.

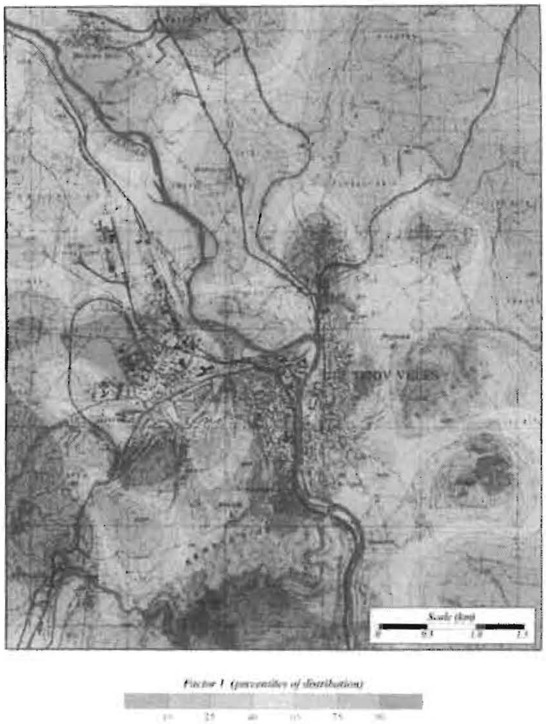
Table 4: Matrix of dominant rotated factor loadings (n = 159, 30 selected elements)

	F1	F2	F3	Comm
Rb	0.90	-0.15	0.04	83
Ta	0.90	0.02	0.08	81
Th	0.88	-0.22	0.06	82
Ce	0.88	0.18	-0.01	80
La	0.83	0.03	0.09	70
Yb	0.78	0.48	-0.06	85
U	0.78	0.04	0.15	63
Tm	0.78	0.21	-0.06	65
Sm	0.77	0.38	0.13	76
Hf	0.73	0.27	-0.02	61
Al	0.72	0.16	0.07	55
K	0.70	-0.23	0.03	54
Tb	0.69	0.59	0.04	82
Ba	0.66	-0.21	-0.04	49
Cs	0.64	0.58	0.09	76
Fe	0.17	0.94	0.13	94
Sc	0.31	0.92	0.04	95
Co	-0.03	0.91	0.20	86
V	0.12	0.85	0.11	74
Ti	0.14	0.77	0.14	63
Ni	-0.24	0.72	0.28	66
Cr	-0.48	0.59	0.01	58
Zn	0.06	0.07	0.94	89
Cd	0.07	-0.07	0.92	86
Pb	0.18	0.01	0.89	81
Sb	0.12	0.23	0.88	85
In	-0.04	-0.00	0.82	67
Cu	0.09	0.24	0.76	64
Hg	-0.07	0.23	0.64	47
As	-0.08	0.48	0.61	61
Var	32	22	17	73

F1, F2, F3 – Factor loadings; Com – Communality (%); Var – Variance (%)

Natural distribution of chemical elements

Two geogenic and one anthropogenic geochemical association were established on the basis of: visually indicated similarity of geographic distribution of elemental patterns in the topsoil; the comparisons of the descriptive statistics (Table 1), the correlation coefficient matrices and the results of factor analyses (Table 2). The first group consists of Al, Ba, Ce, Cs, Hf, K, La, Rb, Sm, Ta, Tb, Th, Tm, U and Yb (Table 2). These elements are little affected by the anthropogenic activities. High values of the correlation coefficients between the chemical elements are characteristic for the group. The strongest Factor 1 explains 32% of the total variability within the data. The ca 17 % enrichment in the topsoil of the study area with respect to the European average in topsoil (Salminen et al, 2005) is characteristic for all these elements. The occurrence of these elements comes from mainly natural phenomena, such as rock weathering and chemical processes in soil. In addition, the distribution of Factor 1 scores in the topsoil (Table 2, Fig. 3) strongly depends on the lithogenesis. The areal distribution of Factor 1 scores is given in Fig. 3.



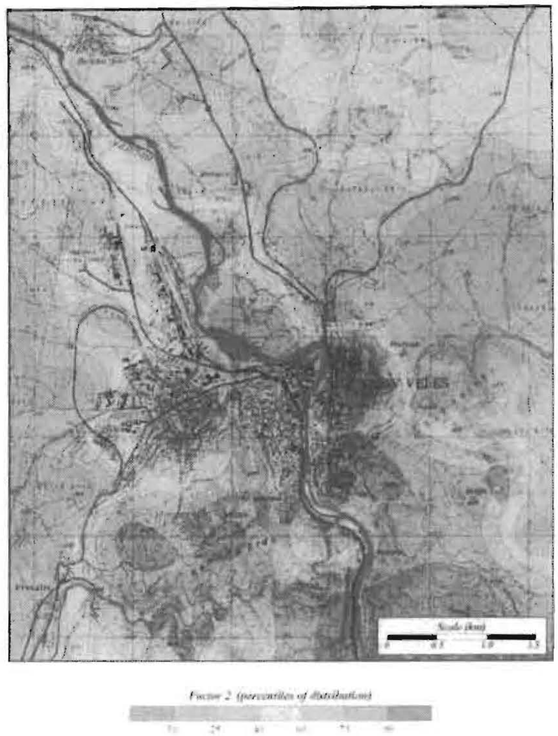


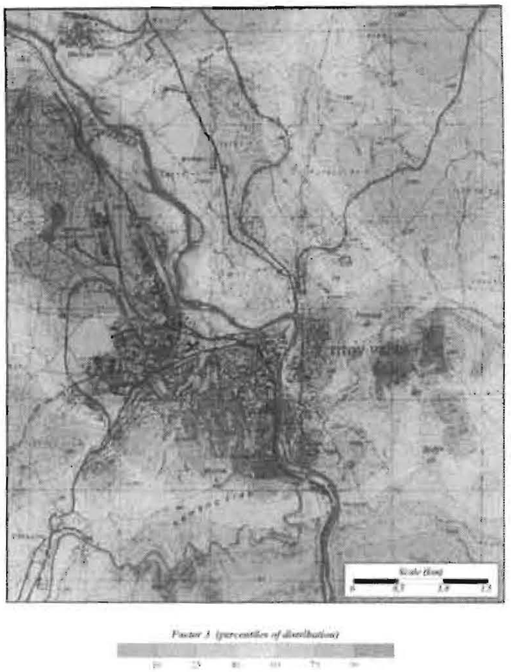
Fig. 3: Spatial distribution of factor 1 scores (Al, Ba, Ce, Cs, Hf, K, La, Rb, Sm, Ta, Tb, Th, Tm, U and Yb) in the topsoil

Fig. 4: Spatial distribution of factor 2 scores (Co, Cr, Fe, Ni, Sc, Ti and V) in the topsoil

The elements from the second group (Co, Cr, Fe, Ni, Sc, Ti and V) are also slightly affected by anthropogenic activities, just like the first group (Fig. 4). Relatively high values of the correlation coefficients between the elements are characteristic for this group. The existence of the group is confirmed by the results of factor analysis (Table 4). Factor 2 contains high values of Co, Cr, Fe, Ni, Sc, Ti and V, explaining ca 22% of total variability within the data. Similarly to the example of distribution of Factor 1 scores, the spatial distribution of Factor 2 scores (Co, Cr, Fe, Ni, Sc, Ti and V) in the topsoil (Table 2, Fig. 4) strongly depends on the lithogenesis. The areal distribution of the Factor scores distribution is shown in Fig. 4.

Anthropogenetic distribution of chemical elements

The elements in the group comprises As, Cd, Cu, Hg, In, Pb, Sb, and Zn were introduced into the environment through the anthropogenic activities. Their correlation coefficients are relatively high and the group's existence is also confirmed by the results of factor analysis (Table 2). The geochemical association is indicated by Factor 3 (Fig. 5). It explains 19% of the total variability. The enrichment of the elements in the topsoil, compared to the European topsoil (Salminen et al, 2005) is typical for this elemental assemblage, from 2.2-times for Sb to 27-times for Cd. High contents, as well as enrichments of the mentioned elements are noticeable close to the Zn smelter in Veles and in the urban zone (Figs. 5, 6). The spatial distribution patterns of individual elements do not differ much. In the topsoil a clear anomaly occurs around the Zn smelter in Veles and the urban area. The shape of the dispersion halo has been strongly influenced by the local winds and the shape of the Veles basin. The spatial distribution of Factor 3 scores is shown in Fig. 5.



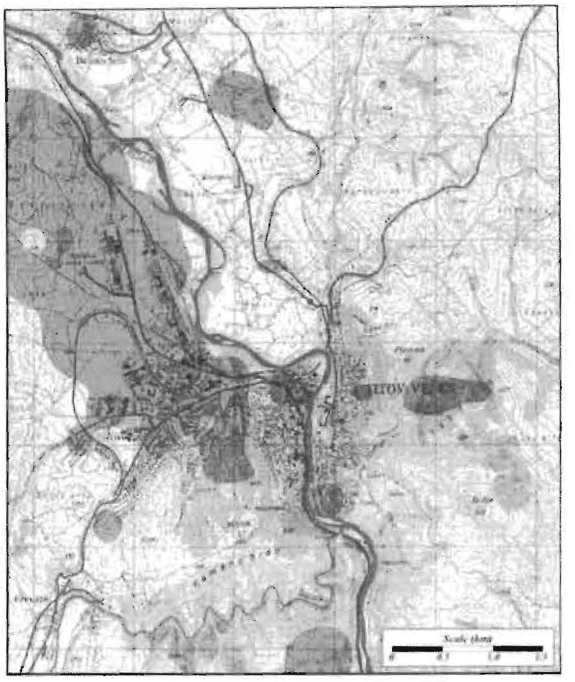


Fig. 5: Spatial distribution of factor 3 scores (As, Cd, Cu, Hg, In, Pb, Sb and Zn)

Fig. 6: Critically polluted topsoil in the Veles area

On the based on the intervention values of Dutch standards a high pollution area with heavy metals was determined (http://www.contaminatedland.co.uk), Fig. 6. The enrichment of the elements in the topsoil, compared to the European topsoil (Salminen et al., 2005) ranges from 2.2-times for Sb to 27-times for Cd. The content of As, Cd, Cu, Hg, Pb and Zn exceeds the critical value in 6.8 km^2.

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