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Factor Analysis of Soil and Attic-dust to Separate Mining and Metallurgy Influence, Meza Valley, Slovenia[1]

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Based on the factor analysis of chemical elements determined in topsoil (0–5 cm) and attic-dust, two natural and two man-made (anthropogenic) geochemical associations were discovered in the Meza valley, an old mining and metallurgic area. The natural geochemical association (Al-Ce-Co-K-La-Li-Nb-Rb-Sc-Th-Ti-V) is influenced mainly by weathering of metamorphic rocks, while the anthropogenic association (Ca-Mg) was determined in an area of carbonate rock outcrops. The man-made associations are a result of lead production (Ag-As-Cd-Mo-Pb-S-Sb-Sn-Zn) and iron production (Co-Cr-Mo-Ni-W).

KEY WORDS: pollution; trace elements; factor analysis; Meza valley; Slovenia.

INTRODUCTION

The objective of geochemical investigations conducted in the Meza valley was to demonstrate the applicability of attic-dust and topsoil as sampling materials. Factor analysis was applied to investigate the separation between natural distributions of chemical elements and historic anthropogenic anomalies, especially the spatial distribution of heavy elements. In previous geochemical studies (Sajn, 1999, 2003) the properties of attic-dust as a sampling medium for the territory of Slovenia (regional-scale) were established. The applicability of attic-dust and topsoil for tracing the mercury halo in the Idrija area (Gosar and Sajn, 2003) and pollution of heavy metals in the Celje area (Sajn, 2005) was successfully proven.

The study area lies in the northern part of Slovenia, close to the Austrian border (Fig. 1). The Meza river valley cuts in its upper part through the Eastern Karavanke Mts., and in its lower part through the Alpine mountains of medium

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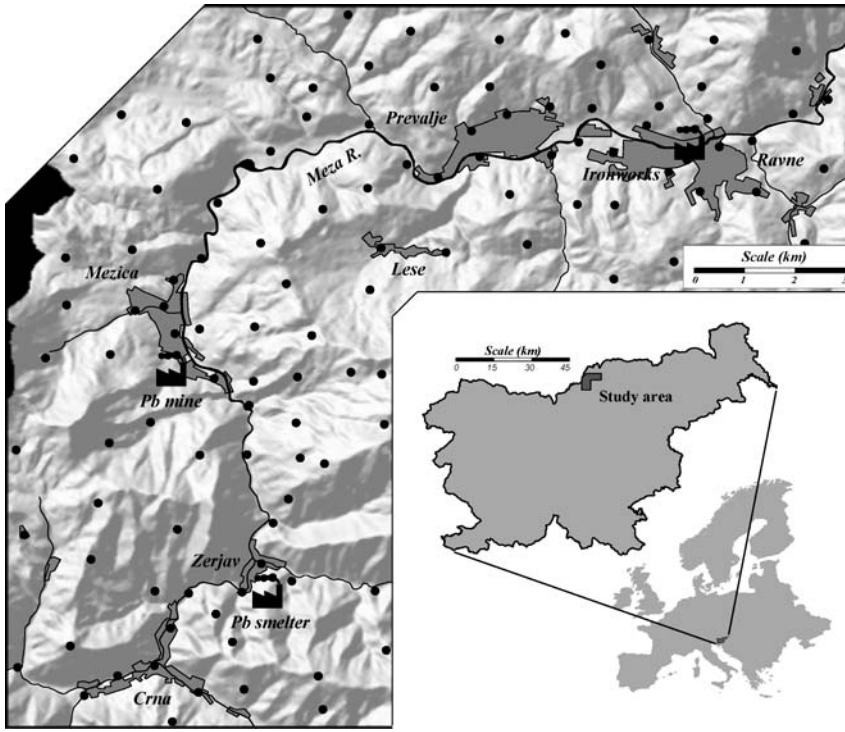

Figure 1. Research area with sampling locations.

altitude. In its upper part, the narrow valley is widened in two places, where two settlements, Crna and Mezica, have grown. In its lower parts, the settlements Prevalje and Ravne are placed. The upper part of the valley cuts mostly through Triassic limestone and dolomite. The lower part of the valley cuts through metamorphic rocks (Mioc and others, 1983).

The first documents that mention mining in the Meza valley were written in 1668 (Mohoric, 1978). At Zerjav there is a zinc smelter that was built in 1746. In all the 300 years of existence of the Mezica mine, 19,000,000 t of Pb ore was mined from it and 1,000,000 t of Pb was produced in the Zerjav smelter (Souvent, 1994a). After the year 1835, ironworking developed at Prevalje and later at Ravne (Mohoric, 1954).

The Meza valley is strongly polluted with heavy metals as a result of mining and smelting in addition to its geological characteristics. The major pollutants are lead and zinc, which were being extracted in the upper part of the valley for more than 300 years (Sajn, Gosar, and Bidovec, 2000; Vreca, Pirc, and Sajn, 2001). An

ironworks located in the lower part of the valley also contributed to the pollution of the area during a 150-year operating period (Souvent, 1994b).

MATERIALS AND METHODS

On the basis of the results of previous studies, an area of approx. 100 km^2 extending from Crna to Ravne (Fig. 1) was selected for study. The entire area was divided into cells using a sampling grid with a density of 1 sample per km^2. Within the densely-populated urban zone, the sampling density was increased by collecting additional samples at the cell center, between four sites on the regular grid. Randomness of the sample selection from the population was assured by random selection of the starting point of the grid (Pirc, 1993).

In total, 114 sample sites were determined: 6 sites are situated on Quaternary deposit, 7 on Miocene sandstone and marl, 45 on Triassic limestone and dolomite, 4 on Permian shale and sandstone, and 52 on lower Paleozoic metamorphic and igneous rocks.

Close to each sample site an old house with intact attic carpentry was chosen. Most of the selected houses were at least 100 years old. To avoid collecting particles of tiles, wood and other construction materials, the attic-dust samples were brushed from parts of wooden constructions that were not in immediate contact with roof tiles or floors (Sajn, 1999). Garden soil was sampled from the surface to the depth of 5 cm close to the house in which attic-dust was collected. Within the town, urban soil, such as soil in gardens and grass-plot was sampled. One sample represents the composite material collected at the central sample point itself and at six points within a radius of 50 m around it.

Preparation of Samples and Analysis

All samples were air-dried. The <0.125 mm size fraction of attic-dust was prepared for chemical analyses by sieving (Sajn, 1999). Soil samples were gently crushed, then the <2 mm fraction was pulverized (Darnley and others, 1995). Analyses for 41 chemical elements (Al, Ca, Fe, K, Mg, Na, P, S, Ti, Ag, As, Au, Ba, Be, Bi, Cd, Ce Co, Cr, Cu, Hf, La, Li, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Sc, Sn, Sr, Ta, Th, U, V, W, Y, Zn and Zr) was performed by inductively coupled plasma mass spectrometry (ICP-MS) after (total) four-acid digestion (mixture of $HClO_4$, HNO_3, HCl and HF at 200°C). Hg was determined with cold vapor atomic absorption spectrometry CV-AAS after aqua regia digestion (mixture HCl, HNO_3 and water at 95°C).

Selected samples were replicated for the estimation of precision. Geologic standard materials GXR-2, GXR-5 and GXR-6 (Govindaraju, 1989) were used to

Table 1. Basic Statistics of Selected Chemical Elements in Topsoil ($n = 114$) and Attic-dust ($n = 114$) in the Meza Valley

				Topsoil (0–5 cm)				Attic-dust			
	MD	A	P	Min–Max	Me	X, Xg	C	Min–Max	Me	X, Xg	C
Al	0.01	–	2.4	1.1–11	6.6	6.3	5.9–6.7	1.0–5.6	2.6	2.5	2.3–2.7
Ca	0.01	2.0	4.0	0.17–16	2.9	2.5	2.0–3.1	1.3–12	6.3	6.4	5.9–6.9
K	0.01	5.9	2.9	0.12–3.8	1.8	1.7	1.5–1.8	0.46–2.7	1.1	1.1	1.0–1.2
Mg	0.01	2.3	2.9	0.41–8.6	1.6	1.9	1.6–2.2	0.23–5.0	1.5	1.4	1.3–1.6
S	0.02	7.4	3.4	0.020–0.35	0.080	0.076	0.069–0.083	0.31–8.0	3.7	3.8	3.5–4.1
Ti	0.001	8.1	3.5	0.054–1.2	0.28	0.27	0.24–0.29	0.058–0.28	0.12	0.12	0.11–0.13
Ag	0.1	–	4.3	<0.10–13	0.10	0.18	0.15–0.21	0.20–23	0.95	0.97	0.84–1.1
As	2	6.9	1.8	7.0–390	17	17	16–19	6.0–370	31	32	29–36
Cd	0.2	2.4	8.2	0.40–71	2.0	2.5	2.0–2.0	2.1–280	9.8	12	9.9–14
Ce	1	25	6.0	11–90	60	57	54–60	11–52	29	29	27–31
Co	1	4.0	5.4	2.0–32	15	15	14–16	4.0–52	9.0	9.7	8.8–11
Cr	1	4.7	3.2	23–830	95	89	81–99	37–4700	110	150	125–190
La	1	19	5.8	5.0–56	34	32	30–34	6.0–34	16	17	15–18
Li	1	11	3.5	6.0–240	46	43	39–48	7.0–76	21	19	18–21
Mo	0.5	5.0	3.9	0.70–290	2.8	3.3	2.8–4.0	2.4–290	13	15	13–19
Nb	0.2	30	3.3	1.9–22	8.1	7.6	7.0–8.2	1.9–9.7	4.0	4.0	3.8–4.3
Ni	1	11	3.7	7.0–170	43	38	35–42	15–830	50	59	50–70
Pb	3	11	2.2	56–27000	300	350	280–440	220–25000	1800	2400	1900–2900
Rb	1	28	3.3	10–180	110	100	97–110	28–110	54	54	51–57
Sb	1	19	3.4	1.0–1300	3.0	3.3	2.7–3.9	4.0–1700	21	26	21–31
Sc	1	6.5	3.1	2.0–23	12	12	11–13	2.0–10	5.0	5.0	4.7–5.4
Sn	0.5	9.5	8.5	1.7–190	5.6	6.2	5.5–7.0	6.0–510	29	34	29–40
Th	1	9.4	7.0	1.0–15	10	9.1	8.6–9.7	2.0–7.0	4.0	3.8	3.5–4.0
V	1	8.5	2.8	21–240	110	110	100–110	19–260	60	59	53–65
W	1	52	7.1	<1.0–61	1.0	1.7	1.5–2.0	1.0–270	6.0	6.8	5.3–8.9
Zn	2	8.2	1.9	110–4200	320	450	380–520	300–10000	1200	1300	1100–1500

Average values of Al, K, Mg, S and Ti are in %, remaining elements in mg/kg; data rounded; MD: detection limits; A: accuracy (%); P: precision (%); Min; minimum; Max: maximum; Me: median; X, Xg: arithmetic mean resp. geometric mean; C: 95%-confidence intervals of the mean.

Table 2. Characteristic Values of Rotated Factor Loadings of Selected Chemical Elements ($n = 228$)

	F1	F2	F3	F4	Com
Ce	0.93				94.7
La	0.92				90.9
Sc	0.91				94.3
Th	0.90				94.5
Al	0.89				95.8
Ti	0.88				88.7
Li	0.87				86.9
Nb	0.86				82.3
V	0.86				83.3
Rb	0.81				89.6
Co	0.68		0.58		84.5
K	0.64			0.61	80.9
As		0.89			81.4
Sb		0.88			94.8
Pb		0.87			94.5
Cd		0.87			94.6
Zn		0.81			85.6
Ag		0.76			85.8
Sn		0.71			82.2
S	−0.58	0.61			82.7
Cr			0.94		91.9
Ni			0.88		87.2
W			0.87		83.5
Mo		0.60	0.63		87.9
Ca				−0.75	86.0
Mg				−0.92	91.5
Var	39.1	25.6	14.5	9.2	88.4

F1–F4: factor loadings; Com: communality in %; Var: variance in %.

estimate the accuracy. All samples ($n = 224$), replicates ($n = 10$) and geologic standards ($n = 9$) were submitted to the laboratory in a random order. This procedure assured an unbiased treatment of samples and a random distribution of possible drifts of analytical conditions for all samples.

The sensitivity in the sense of the lower limit of detection was adequate for 37 of 42 determined chemical elements. The elements Au, Be, Bi, Hf, and Ta were removed from further statistical analysis, since their contents were below the lower detection limit of the analytical method in the majority of analyzed samples. The analytical concentrations of Ag and W which were below the detection limit were replaced by the half of the detection limit (Table 1). The accuracy (A) of the analytical method for the remaining 37 elements was estimated calculating the

Table 3. Averages of Selected Chemical Elements in Sampling Materials Collected in Outcrops of Metamorphic, Igneous and Carbonate Rocks

	Soil (0–5 cm)		Attic-dust	
	Me-Ig	Carb	Me-Ig	Carb
Al	7.5	4.7	3.3	1.8
Ca	1.3	8.5	5.1	7.3
K	2.1	1.1	1.2	0.95
Mg	1.3	3.5	1.2	2.2
S	0.057	0.11	3.7	4.1
Ti	0.32	0.24	0.14	0.098
Ag	0.16	0.21	1.0	1.0
As	17	18	28	40
Cd	1.6	4.4	8.9	18
Ce	67	45	34	22
Co	18	11	13	7.0
Cr	120	67	290	70
La	36	26	19	13
Li	60	33	23	15
Mo	2.9	4.5	23	11
Nb	8.8	7.1	4.9	3.1
Ni	49	28	93	34
Pb	220	660	1700	4000
Rb	120	81	63	43
Sb	2.5	4.8	19	44
Sc	14	8.6	6.1	3.9
Sn	6.5	6.0	35	34
Th	11	6.8	4.2	2.9
V	130	85	73	46
W	2.8	1.1	17	2.2
Zn	390	560	1400	1400

Average values of Al, K, Mg, S and Ti are in %, remaining elements in mg/kg; the influence areas of samples were considered; data rounded; Me-Ig: averages of chemical elements in outcrops of metamorphic and igneous rocks; $n = 52$; Carb: averages of chemical elements in outcrops of carbonate rocks; $n = 45$.

absolute systematic error between the determined (X_a) and recommended values (X_p) of geological standards using the equation:

$$A = \frac{|x_a - x_p|}{x_p} \times 100\ (\%)$$

Most elements differ from the average of the standard samples less than 15%, compared with the recommended values in the sample concentration range

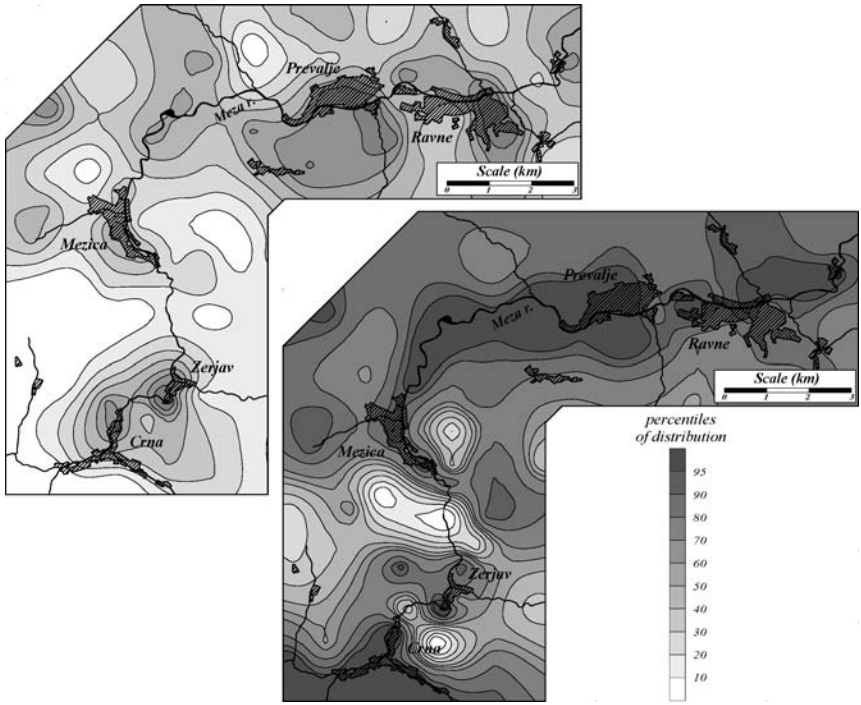

Figure 2. Areal distribution of factor 1 scores (Al, Ce, Co, K, La, Li, Nb, Rb, Sc, Th, Ti, V and -S) in attic-dust (above) and soil (below).

(Table 1). The precision (P) was tested by the relative differences between pairs of analytical determinations (x_1, x_2) (Table 1) of the same sample using the equation:

$$P = \frac{2|x_1 - x_2|}{(x_1 + x_2)} \times 100\ (\%)$$

The precision was additionally tested by the Thompson–Howarth method (cf. Analytical Methods Committee, 2000). The reliability of analytical procedures was adequate in further statistical analyses.

Data Processing

In statistical analysis, data from 114 samples of each attic-dust and topsoil were used (Table 1). On the basis of the results of normality tests and visual inspection of distribution histograms for all elements in soil and attic-dust the logarithms of elemental contents were considered normally distributed.

Table 4. Averages of the Selected Chemical Elements in Sampling Materials in the Meza Valley

	Soil (0–5 cm)			Attic-dust		
	Slo	Rav	Mez	Slo	Rav	Mez
Al	6.9	7.5	5.1	2.7	3.5	1.9
Ca	0.72	1.0	5.3	7.6	5.2	6.4
K	1.6	2.0	1.2	1.2	1.3	1.0
Mg	0.74	1.1	2.7	1.4	1.2	1.7
S	0.080	0.050	0.10	–	3.4	3.5
Ti	0.33	0.30	0.25	0.16	0.14	0.10
Ag	0.085	0.12	0.14	<0.50	0.86	0.80
As	14	16	16	12	25	34
Cd	0.45	0.96	2.6	1	7.3	15
Ce	61	67	48	–	35	21
Co	16	17	11	6	11	6.7
Cr	91	110	70	54	215	65
La	32	36	26	15	19	12
Li	50	55	37	–	24	14
Mo	0.80	2.2	3.1	1.9	15	9.1
Nb	8.3	7.8	7.2	4.6	4.9	3.1
Ni	50	47	31	27	76	31
Pb	40	140	410	130	1200	3700
Rb	110	120	87	–	65	44
Sb	1.1	2.1	3.1	3.5	15	34
Sc	12	14	9.2	4	6.4	3.9
Sn	3.1	5.6	4.8	9.8	27	32
Th	11	11	7.1	4.7	4.6	2.7
V	100	130	91	63	72	41
W	1.4	1.9	1.0	<5.0	12	2.3
Zn	120	260	400	280	1100	1100

Average values of Al, K, Mg, S and Ti are in %, remaining elements in mg/kg; the influence areas of samples were considered; data rounded; Slo: Slovenian averages of elements; $n = 60$; Rav: averages of chemical elements in Prevalje - Ravne area; $n = 53$; Mez: averages of chemical elements in Mezica - Crna area; $n = 61$; –: not determined.

The multivariate cluster analysis and R-mode factor analysis (Davis, 1986; Reimann, Filzmoser, and Garrett, 2002) were used to reveal the associations of chemical elements in the two sampling media. The factor analysis was performed on variables standardized to zero mean and unit standard deviation (Reimann, Filzmoser, and Garrett, 2002). As a measure of similarity between variables, the product-moment correlation coefficient was applied. For orthogonal rotation the varimax method was used. In the final multivariate factor solution 26 elements were retained (Table 2). The elements Ba, Cu, Fe, Hg, Mn, Na, P, Sr, U, Y and

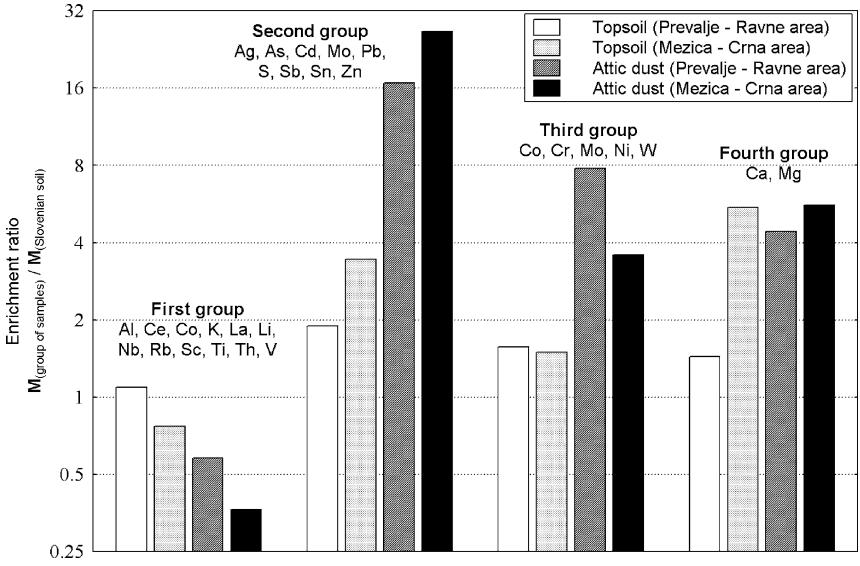

Figure 3. Average enrichment ratios of element groups with regard to sampled material and the location of sampling.

Zr were excluded because of lack of significant associations with other chemical elements or because of their low communalities.

The universal kriging with linear variogram interpolation method (Davis, 1986) was applied to construct the maps of the spatial distribution of particular elements and factor scores in soil and attic-dust. The basic grid cell size for interpolation was 100 m × 100 m.

RESULTS AND DISCUSSION

The major geochemical association is indicated by the strongest factor 1 (Table 3) which associates with high contents of Al, Ce, Co, K, La, Li, Nb, Rb, Sc, Th, Ti, V and low S. High concentrations of those elements are characteristic for the lower part of the Meza valley, while lower values are significant for attic-dust (Fig. 2). Their distribution results from natural processes, such as weathering of metamorphic and igneous rocks (Table 3). Contents of the above-mentioned chemical elements in the sampling materials oscillate, with some exceptions, within the Slovenian averages. The average concentrations in attic-dust are only at one half of those in the soils (Table 4, Fig. 3).

High concentrations of the geochemical association Ca and Mg (Table 2 – factor 4) are characteristic for the carbonate rock areas (Table 3) in the upper part

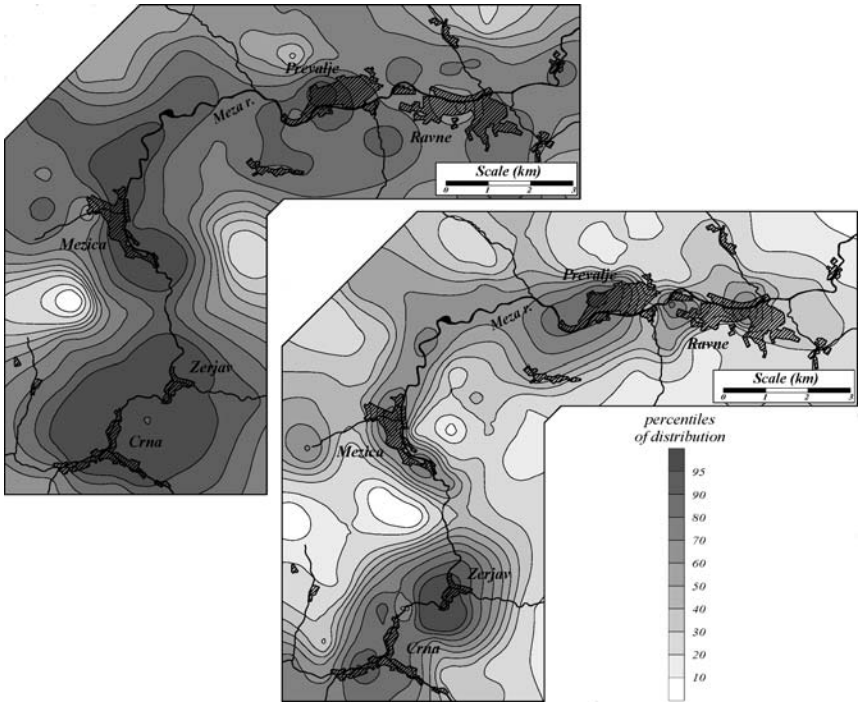

Figure 4. Areal distribution of factor 2 scores (Ag, As, Cd, Mo, Pb, S, Sb, Sn and Zn) in attic-dust (above) and soil (below).

of the Meza valley. Concentrations of Ca and Mg (with the exception of the area around Ravne) exceed the Slovenian average by about five times (Table 4, Fig. 3).

A geochemical anomaly caused by the lead mining and smelting is shown by factor 2 (Table 2). It associates heavy metals of anthropogenic origin (Ag, As, Cd, Mo, Pb, S, Sb, Sn and Zn). Contents in the topsoil of the lower Meza valley oscillate within the Slovenian range, while in the topsoil around Mezica, Zerjav and Crna they are about four times above the Slovenian average. Anthropogenic source of the mentioned chemical elements is especially obvious in the case of attic-dust. Contents of those chemical elements in the Mezica-Crna area exceed the Slovenian average for soil by 26 times (Table 4, Fig. 3). The form of a pollution halo depends strongly on morphology, altitude and (probably) local winds. The highest contents of the chemical elements mentioned were found in the soils and especially attic-dust in the areas around the Pb smelter Zerjav (Fig. 4). The maximum contents of the strongest pollutants are 282 mg/kg Cd, 2.5% Pb and 1.0% Zn in attic-dust, and 71 mg/kg Cd, 2.7% Pb and 0.42% Zn in topsoil. The

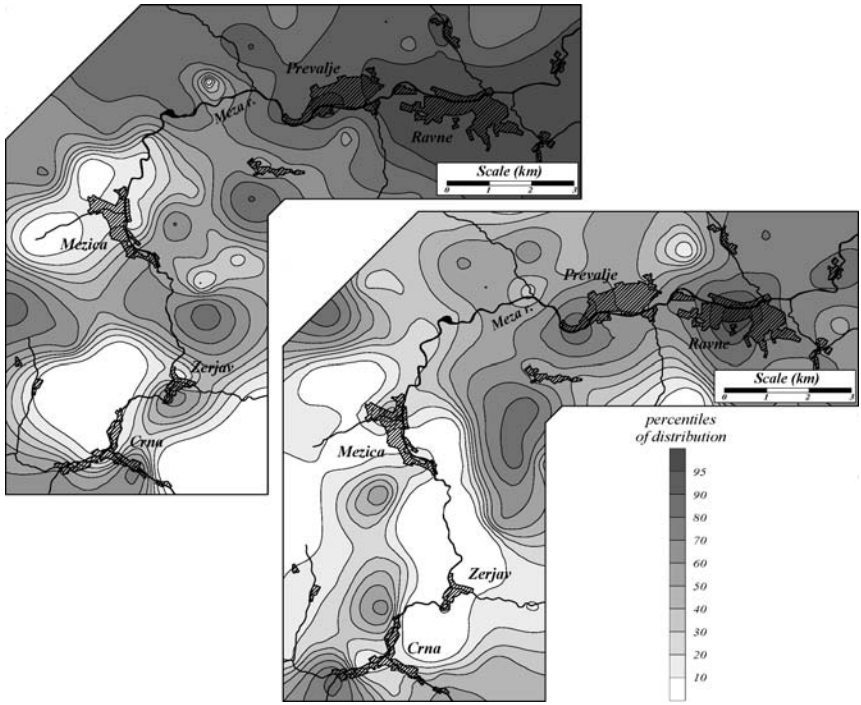

Figure 5. Areal distribution of factor 3 scores (Co, Cr, Mo, Ni and W) in attic-dust (above) and soil (below).

main source of the geochemical anomaly was smelting of lead ore from the middle of the 17th century to the 1990s.

A geochemical anomaly resulting from iron metallurgy is represented by factor 3, which associates with Co, Cr, Mo, Ni and W (Table 2). The contents of those elements in soils are not higher than the Slovenian average, while the contents in attic-dust exceed the Slovenian average by about four times (Table 4, Fig. 3). The area of the highest contents of these elements includes the entire lower part of the Meza valley, and especially the areas around Prevalje and Ravne (Fig. 5) as a result of past and present metallurgic activity.

CONCLUSION

This study shows that natural element sources can be distinguished from the anthropogenic ones by comparing the geochemical properties of attic-dust and topsoil with the use of factor analysis.

With respect to geogenic dispersion resulting from an underlying lithological setting (Al-Ce-Co-K-La-Li-Nb-Rb-Sc-Th-Ti-V), the soil has proven to be a better sampling medium than attic-dust. The spatial distribution patterns of chemical elements in topsoil are clearly seen, in contrast to the distribution in attic-dust. In the case of the spatial distribution patterns resulting from intense anthropogenic influences (Ag-As-Cd-Mo-Pb-S-Sb-Sn-Zn), the anomalous patterns are shown with more contrast in attic-dust. The advantage of attic-dust over topsoil is evident in the case of less clear anthropogenic anomalous patterns, such as that produced by iron metallurgy (Co-Cr-Mo-Ni-W): a clear anthropogenic halo appears in attic-dust in contrast to soil.

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