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Geochemical Soil Survey at Jesenice area, Slovenia

Geokemične raziskave tal na območju Jesenic

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Abstract

The purpose of geochemical investigations in the Jesenice area was to establish contents and distribution of chemical elements in soils, and to separate the natural from the man-produced geochemical distributions.

Shown and commented are distributions of 21 elements (Al, Ca, Fe, K, Mg, Ti, Ba, Cd, Cr, Cu, Hg, La, Mn, Nb, Ni, Pb, Sc, Th, V, Zn and Zr). Based on comparison of distributions of these elements in soils and urban sediments (household and attic dust) of Slovenia two natural geochemical associations were distinguished in the Jesenice area (Al-Fe-K-Ti-Ba-La-Nb-Sc-Th-V-Zr and soil pH-Ca-Mg), and two associations that were influenced by several centuries of mining and iron making (Cd-Cu-Hg-Mn-Pb-Zn and Fe-Cr-Ni).

Povzetek

Namen geokemičnih raziskav na območju Jesenic je bil ugotoviti vsebnosti in prostorske porazdelitve kemičnih prvin v tleh ter ločiti naravne geokemične porazdelitve prvin od antropogeno povzročenih.

Prikazali in komentirali smo porazdelitve 21 kemičnih prvin (Al, Ca, Fe, K, Mg, Ti, Ba, Cd, Cr, Cu, Hg, La, Mn, Nb, Ni, Pb, Sc, Th, V, Zn in Zr). Na osnovi primerjave vsebnosti teh prvin v tleh in urbanih sedimentih (stanovanjski in podstrešni prah) Slovenije smo na območju Jesenic ločili dve naravni geokemični združbi (Al-Fe-K-Ti-Ba-La-Nb-Sc-Th-V-Zr in talni pH-Ca-Mg) in dve združbi, ki predstavljata porazdelitev, na katero je vplivala večstoletna železarska dejavnost (Cd-Cu-Hg-Mn-Pb-Zn in Fe-Cr-Ni).

Introduction

Iron making in the Jesenice area is traditional. The development of mines and furnaces started end of 14th century as testified by the Ortenburg mining regulations. In the second half of the 18th century a number of the properties were bought by Valentin Ruard who started to extend and restore the mining prospects. A number of prospects were owned also by gross merchant Zois. End of 18th century the Zois family ran into financial difficulties owing to obsolete technology and foreign competition. For these reasons in 1869 the Carniolan industrial society was founded. Two bloom areas fused into one that was the largest industrial enterprise in the Duchy of Carniola. From the bloom areas at the banks of the Sava river new modern ironworks was developed, and the settlement grew into an industrial town that assisted the development to many other activities (http://www.jesenice.si/jeobc.html; Resman, 1990).

In the Jesenice area a number of investigations of pollution associated chiefly to emissions of the steelworks were performed. Not known was, however, the "heritage"of several centuries of pollution own to ironmaking, and its impact on the geochemical properties of the landscape. In 1994 we started in the frame of a Alps-Adria project the systematic investigation of soils by sampling them according to pedologic horizons, and analysing a large number of chemical elements in them.

General

Geography and Geology

The Jesenice area is situated in the northwest part of Slovenia (Fig. 1). North of the town is the N-E trending Karavanke mountain range, in the west the Julian Alps and in the south the wooded high plateau of Mežakla. In the valley that passes in the southeast into the Ljubljana basin flows the river Sava. The area is mountainous and it belongs physiographically to the Southern Alps, and its southeastern part is flat. The administrative, political and economic centre is the town of Jesenice, a typical industrial town with ironmaking tradition, inhabited by a population of about 20,000 (http://www.jesenice.si/jeobc.html; Resman, 1990).

The territory is situated at the contact of three geotectonic units: the south Karavanke, the Ljubljana basin and the Julian Alps (Buser & Cajhen, 1980; Buser, 1980; Jurkovšek, 1986a and b). The south Karavanke are separated by the NW-SE trending Sava fault from the Julian Alps and the Ljubljana basin. In the structure of the southern Karavanke the Košuta nappe and the Southern Karavanke nappe can be distinguished. The central ridge of Karavanke is built by the Košuta nappe that consists predominantly of carbonate rocks of Lower to Upper Triassic age. The southern Karavanke nappe, in the area between the Košuta nappe and the Sava fault, consists mostly of Paleozoic clastic and carbonate rocks. The Radovljica-Bled subsided basin in the southeast is filled by Quaternary deposits in the extreme part of the Ljubljana basin. In the southeast, the Mežakla plateau consists of Lower to Upper Triassic carbonate rocks (Buser & Cajhen, 1980; Jurkovšek, 1986b).

The area is cut by faults of predominantly dinaric (NW-SE) direction. Dominant among them is the Sava fault. The course of the Sava valley is conditioned by it. Long dinaric faults were formed in the Upper Pliocene, and the Ljubljana basin

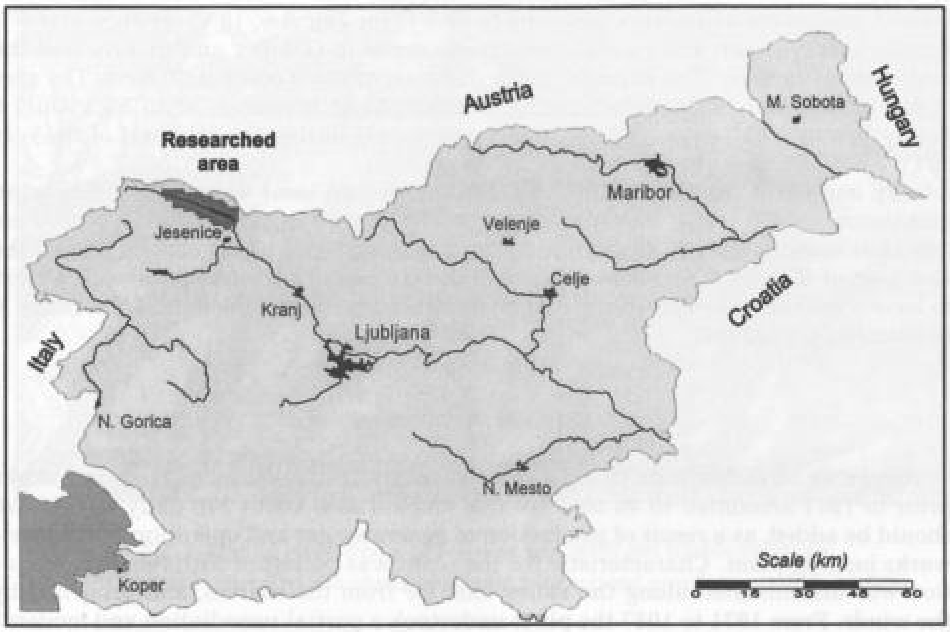


Fig. 1. Researched area

Sl. 1. Lega raziskanega območja

started to sink along them at the start of Pleistocene. The formed basin was filled by large amounts of mainly carbonate fluvial material (Buser & Cajhen, 1980; Jurkovšek, 1986b).

The final touch to the physiography was given by the glacial age. In spite of heavy glacial impact, the valley remained relatively narrow. Characteristic of glaciations are remains of lateral moraines at Mala Mežakla, and front and lateral moraines at Blejska Dobrava. After retreat of the glacier at Mojstrana a smaller dam lake was formed.

On the highest steep slopes lithosols occur. Rendzinas are frequent on limestones and dolomites, carbonate talus and glacial drift. In favourable conditions rendzinas pass into eutric cambisols or calcareous cambisols on limestones and dolomites. On silicate (siliceous) clastic rocks largely rankers develop, and to a smaller extent, also dystric cambisols.

Climatic Characteristics

The Jesenice area is characterized by a predominance of continental properties of Middle European climate owing to the distance from the sea and the high mountainous barriers in-between. The rainfall regime is of submediterranean type. Appreciable differences in altitudes result into four climatic belts: the submountainous, mountainous, subalpine and alpine climatic belts (Šipec, 1990).

The essential characteristics of climate are cold winters and fresh summers. The mean temperature at Jesenice amounts to -2.5°C for January, 18°C for July, and 8°C for the average year. The rainfall maximums occur in October and in July, and the minimum in January. The average yearly duration of snow cover is 30 days. The area is not considerably subject to forming of atmospheric inversion, or to fogs. Only a yearly average of 10 days are foggy, occurring mainly during the cold part of the year (Šipec, 1990).

Very important for distributing of pollution are two local winds, the valley wind and the mountain wind. The first blows mostly during nights when the cooled air descends towards the Ljubljana basin. The mountain wind blows usually during the first part of the day. It forms by heating of the air, and is directed up the valley. Next to local winds also the cyclonic air circulation transversely to the axis of the valley is present (Šipec, 1990).

Estimate of Pollution

According to earlier data (Šipec, 1990) the daily dust emission from ironworks prior to 1971 amounted to 48 tons. To this amount also about 270 daily tons of ash should be added, as a result of production of generator gas and operation of the steelworks heating plant. Characteristic for the plant was pollution with red dust. Pollution was disseminated along the valley axis far from the sources, and propelled by the winds. From 1971 to 1987 the plant undertook a partial remediation and modernization. The energy concept of steelworks was changed, the furnaces reconstructed, and dust collectors and cleaning devices installed. At that time also regular monitoring of pollution was started. Then followed modernization of Steelworks 1 that further reduced the dust emissions. After 1987 follows the final sanitation with abandoning of furnaces and Siemens-Martin ovens, and with the start of Steelworks 2 (Osojnik et al., 1988, 1990).

It was estimated that the emission from Steelworks 1, Steelworks 2 and the plants for regeneration of hydrochloric acid emit daily approximately 2 t dust and 950 kg SO_2 (Šipec, 1990). Traffic and communal emissions contribute during heating season about 7 t SO_2 daily. Iron works are indubitably the principal factor of environmental degradation, followed by dense traffic in the valley, and by households in the town. The contribution of iron works is gradually diminishing.

Materials and Methods

Sampling

Soil sampling in the Jesenice area was performed at a 1,4 x 1,4 km grid (Figs. 1 and 2). In 44 localities pedologic profiles were dug, and in total 122 samples of soil horizons collected. Sampled were principally soils on carbonate rocks (30 localities), followed by sandstone (6 localities) and Quaternary fluvial deposits (8 localities). Soil types (Škorić, 1977) comprised rendzinas in 16 cases, calcareous cambisols in 16 cases, dystric cambisols in 5 cases, ranker in 2, and agricultural soil, fluvisol, luvisol and eutric cambisol in each one case.

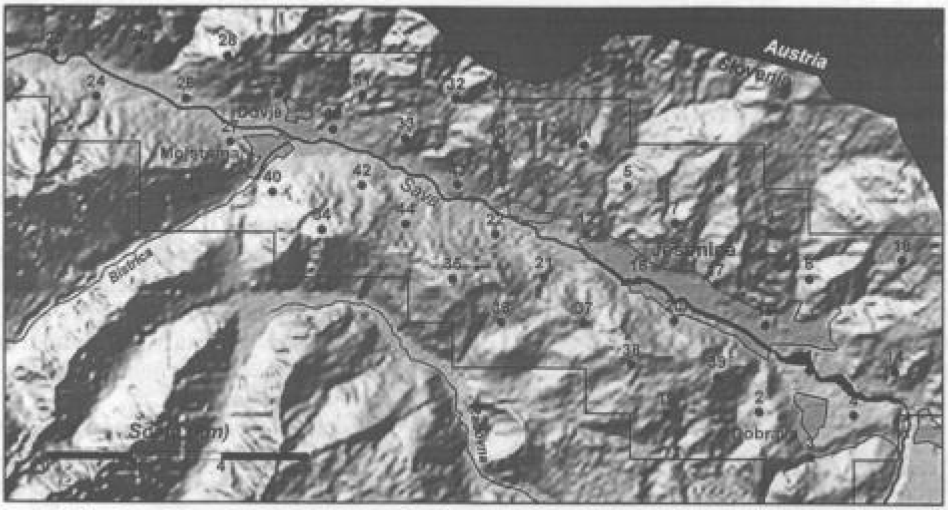


Fig. 2. Digital relief model of Jesenice area with soil profile locations
Sl. 2. Digitalni model reliefa območja Jesenic z lokacijami vzorčenja v talnih profilih

Preparation of Samples and Analysis

Preparing of samples for chemical analysis was done along the lines given by Pirc et. al. (1991) that is similar to recommendation s of the UNESCO IGCP 259 project (Darnley et al., 1994). The sampled material was first air dried for 15 days, and then 48 hours in a fan oven at 40°C. The dry soil was gently crushed in a ceramic mortar. The material was then passed through a stainless steel sieve with 2 mm openings and quartered, and then crushed and milled to the analytical grain size of 0,063 mm.

Analysis in the ACME laboratories in Vancouver, Canada, was performed by plasma emission spectrometry (ICP) after a total 4 acid digestion. The 0,5 g sample was dissolved at 200 °C in 10 ml mixture of $HClO_4$, HNO_3, HCl and HF. In total, 35 elements were determined by ICP (Al, Ca, Fe, K, Mg, Na, P, Ti, Ag, As, Au, Ba, Be, Bi, Cd, Co, Cr, Cu, La, Mn, Mo, Nb, Ni, Pb, Sb, Sc, Sn, Sr, Th, U, V, W, Y, Zn and Zr). Hg was determined after aqua regia digestion with atomic absorption spectrometry (AAS) according to the cool evaporation procedure (ACME, 1994).

Potential acidity was determined by the procedure in which 10 g of sieved soil sample is left for 24 hours in 25 ml 0,1 N $CaCl_2$, mixed, left for 24 hours, mixed again and pH measured (Rhoades, 1982; Hodnik, 1988).

A number of randomly selected samples was replicated for estimation of precision. Geologic standard materials GXR-6, SJS-1 and SRM-2711 (Abbey, 1983; Epstein, 1990) were used for estimating accuracy. All soil samples, replicates and geologic standards were submitted to laboratory in a random succession. This procedure assured unbiased treatment of samples and random distribution of possible drift of analytical conditions across all samples.

Sensitivity, Accuracy and Precision on Analysis

The sensitivity in the sense of the lower limit of detection was adequate for 28 out of 36 analysed chemical elements. The elements Ag, Au, Be, Bi, Mo, Sb, Sn and U, however, were removed from further statistical analysis (Miesch, 1976), since their contents in the majority of analysed samples appeared to be below the lower detection limit of the analytical method. Excluded were also determinations of W and Co because of the evidence on contamination of samples from grinding equipment made out of W-Co steel, as established in former studies (Šajn, 1995).

Accuracy of analytical method for the remaining 26 elements was estimated by calculation of relative systematic error between the determined and recommended values of geological standards. Most analysed elements show in the range of the actual soil samples very low deviations. The means of elements in analysed standards generally differ for less than 15% of the recommended values. Larger negative deviations showed Mg, P, Cd, La, Pb and Th, and larger positive deviations Cr.

Precision of determinations was controlled by relative differences between pairs of analytical determinations of the same samples (Blejec, 1976). Precision was considered good, since of the 26 considered elements only Cd, Th and Zr showed less accurate results.

The reliability of analytical procedures, as shown by the mentioned control of sensitivity, accuracy and precision, was considered adequate for using the determined elemental contents in further statistical analyses.

Results of Study

In statistical analysis all 122 samples of soil horizons were used. For estimation of the association between chemical elements multivariate statistical analyses of cluster and R mode factor analysis were used (Le Maitre, 1982, Košmelj, 1983, Davis, 1986, Rodionov et al., 1987). For the measure of similarity between variables the product-moment correlation coefficient (r) was applied. In the final multivariate analyses only 21 elements were retained. The elements Na, P, As, Sr and Y were excluded because of the lack of significant associations with other chemical elements. These elements formed independent clusters, or they resulted into low communalities in factor analysis.

For illustration of results of the cluster analysis the dendrogram based on relative association D/Dmax in percent were used (Fig. 3), and of the factor analysis the matrix of higher rotated factor loadings (Tab. 2).

The geographic distribution of elemental composition of topsoil and of the lower soil horizons is illustrated by maps of scores of extracted factors (Figs. 4a to 7b) and maps of contents of Cd (Figs. 9a and 9b), Pb (Figs. 10a and 10b) and Zn (Figs. 11a and 11b). In the process of construction of geochemical maps the interpolation method of universal kriging with linear variogram was applied (Perišić, 1983; Davis, 1986). In interpolation of elemental contents 44 samples of topsoil and 78 samples of lower soil horizons were taken in consideration. The basic cell for interpolation was of the size of 200 x 200 m.

For class limits the percentile values of distribution of the interpolated values were taken. Seven classes with the values of the following percentiles were selected: 0-10, 10-25, 25-40, 40-60, 60-75, 75-90, 90-100. The classes around the average are broader, and the classes at both extremes narrower.

Tab. 1. Averages of content of elements in different sample materials (average values of Al, Ca, Fe, K, Mg, Na, P and Ti are in %, Hg in mg/t, remaining elements in g/t)

Tab. 1. Povprečja vsebnosti prvin v različnih vzorčnih sredstvih (povprečne vrednosti Al, Ca, Fe, K, Mg, Na, P in Ti so v %, Hg v mg/t, preostalih prvin pa v g/t.)

	Clarke	Slo	Jes-ZT	Jes-ST	Jes-SP	Jes-PP
Al	7.10	6.92	7.01	4.10	1.60	2.50
Ca	1.50	0.78	1.21	1.04	8.10	9.10
Fe	4.00	3.80	4.04	2.86	2.20	13.0
K	1.40	1.40	1.10	0.54	0.69	0.55
Mg	0.50	0.83	1.30	0.46	2.50	2.40
Na	0.50	0.47	0.33	0.20	0.77	0.29
P	0.08	0.06	0.04	0.07	0.10	0.05
Ti	0.50	0.36	0.26	0.18	0.10	0.09
As	6	4	18	16	-	-
Ba	500	360	253	179	706	57
Cd	0.4	0.5	0.8	2.1	2.8	6.2
Cr	70	88	60	52	299	193
Cu	30	23	16	26	131	154
Hg	60	160	263	795	385	950
La	40	30	25	18	29	10
Mn	1000	904	594	770	1413	4139
Nb	10	6	11	7	5	4
Ni	50	47	34	27	96	82
Pb	35	34	44	292	256	1437
Sc	7	13	13	8	2	5
Sr	250	82	111	68	99	154
Th	9	11	9	5	2	3
V	90	113	80	57	30	91
Y	40	15	13	10	5	13
Zn	90	103	108	293	1386	2592
Zr	400	45	47	32	16	18

Clarke - Clarke in soil; Svetovno poprečje vsebnosti prvin v tleh (Bowen,1979)
Slo - Slovenian average of elements in soil; Slovensko povprečje vsebnosti prvin v tleh; n = 817 (Andjelov, 1994); Hg, n = 119 (Pirc, 1993)
Jes-ZT - Average of elements in top soil in Jesenice area; Povprečje vsebnosti prvin v zgornjem talnem horizontu na območju Jesenic; n = 44
Jes-ST - Average of elements in bottom soil in Jesenice area; Povprečje vsebnosti prvin v spodnjih talnih horizontih na območju Jesenic; n = 78
Jes-SP - Average of elements in household dust in Jesenice area; Povprečje vsebnosti prvin v stanovanjskem prahu na območju Jesenic; n = 3 (Šajn, 1998)
Jes-PP - Average of elements in attic dust in Jesenice area; Povprečje vsebnosti prvin v podstrešnem prahu na območju Jesenic; n = 3 (Šajn, 1998)

Tab. 2. Characteristic values of rotated factor loadings; n = 122
Tab. 2. Dominantne vrednosti rotiranih faktorskih obremenitev; n = 122

	F1	F2	F3	F4	Kom
Al	0.98				99
Sc	0.95				94
Ti	0.95				93
Th	0.93				90
V	0.90				84
La	0.87				79
Zr	0.79				66
Ba	0.76				60
K	0.72				55
Nb	0.71				54
Zn		0.97			97
Cu		0.92			88
Pb		0.92			88
Hg		0.90			85
Cd		0.88			81
Mn		0.77			62
Cr			0.95		94
Fe			0.93		90
Ni			0.92		88
Ca				0.95	94
Mg				0.94	91
pH				0.83	72
Var	**34**	**23**	**13**	**12**	**82**

F1 ... F4 - Factor Loadings; Faktorske obremenitve
Kom - Communality in %; Komunalnost v %
Var - Variance in %; Varianca v %

Discussion

With the factor analysis the initial 22 considered variables were reduced to 4 factors, synthetic variables that represent the geochemical associations of chemical elements. The four factors explain more than 80% of variability within data (Tab. 2). The geochemical associations suggested by results of factor analysis are confirmed also by the outcomes of the cluster analysis (Fig. 3).

The geochemical distributions in soils of the Jesenice area are compared with the means for Slovenian soils (Andjelov, 1994), the means for urban sediments from three localities in the Jesenice area (Šajn, 1998) and with world averages for soils

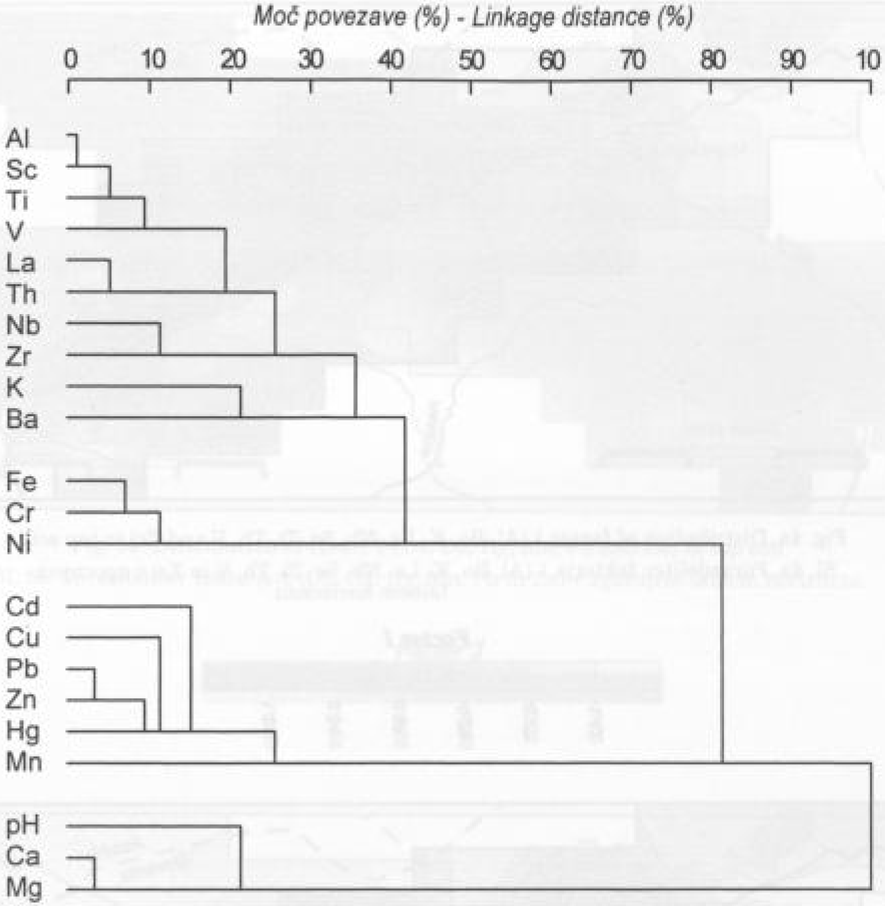


Fig. 3. Dendrogram of cluster analysis; n = 122
Sl. 3. Dendrogram clusterske analize; n = 122

(Bowen, 1979) (Tab. 1). The samples of all listed studies in Slovenia were analysed in the same laboratory by using the same procedures of digestion and analysis. The urban sediments in Šajn's (1998) study are (1) household dust which is closely associated to rooms where inhabitants live, and (2) attic dust that keeps accumulating in attics.

Natural Distribution of Chemical Elements

The natural geochemical distributions are suggested by factors 1 and 4 by which about 45% of total variation within data is accounted for. The factor scores of these factors are the lowest in the topsoil horizons, and they increase in horizons with depth.

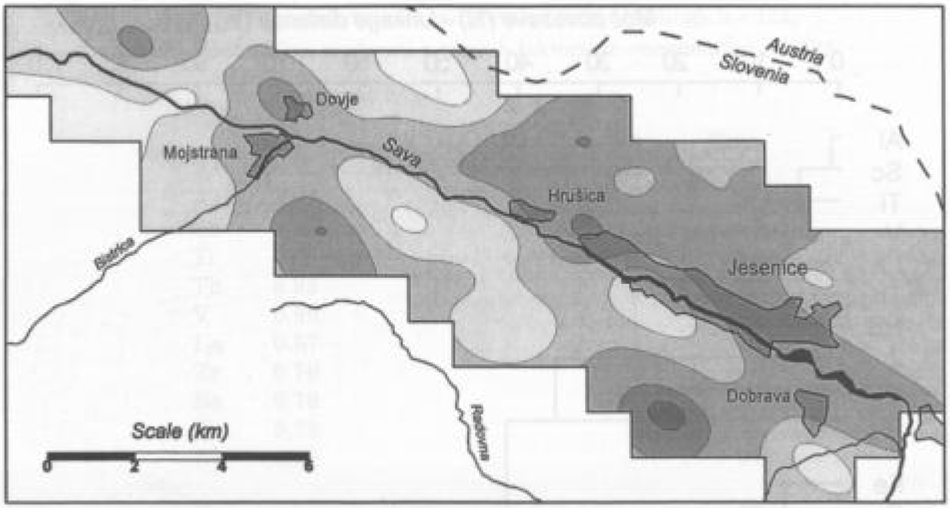
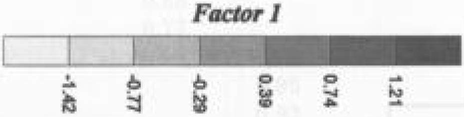


Fig. 4a. Distribution of factor 1 (Al, Ba, K, La, Nb, Sc, Ti, Th, V and Zr) in top soil

Sl. 4a. Porazdelitev faktorja 1 (Al, Ba, K, La, Nb, Sc, Ti, Th, V in Zr) v zgornjem talnem horizontu



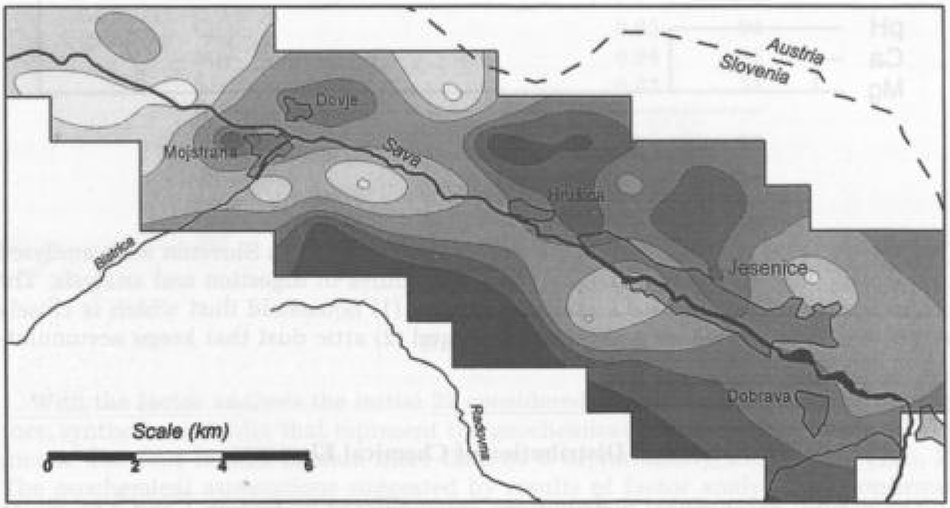


Fig. 4b. Distribution of factor 1 (Al, Ba, K, La, Nb, Sc, Ti, Th, V and Zr) in bottom soil

Sl. 4b. Porazdelitev faktorja 1 (Al, Ba, K, La, Nb, Sc, Ti, Th, V in Zr) v spodnjem talnem horizontu

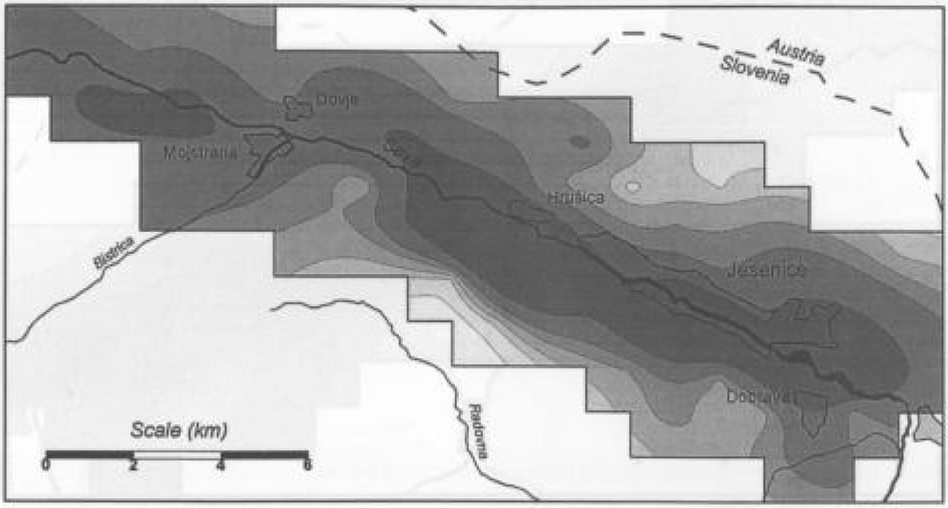
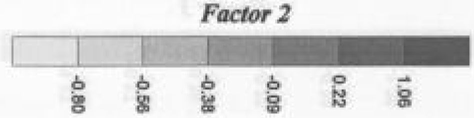


Fig. 5a. Distribution of factor 2 (Cd, Cu, Hg, Mn, Pb and Zn) in top soil
Sl. 5a. Porazdelitev faktorja 2 (Cd, Cu, Hg, Mn, Pb in Zn) v zgornjem talnem horizontu



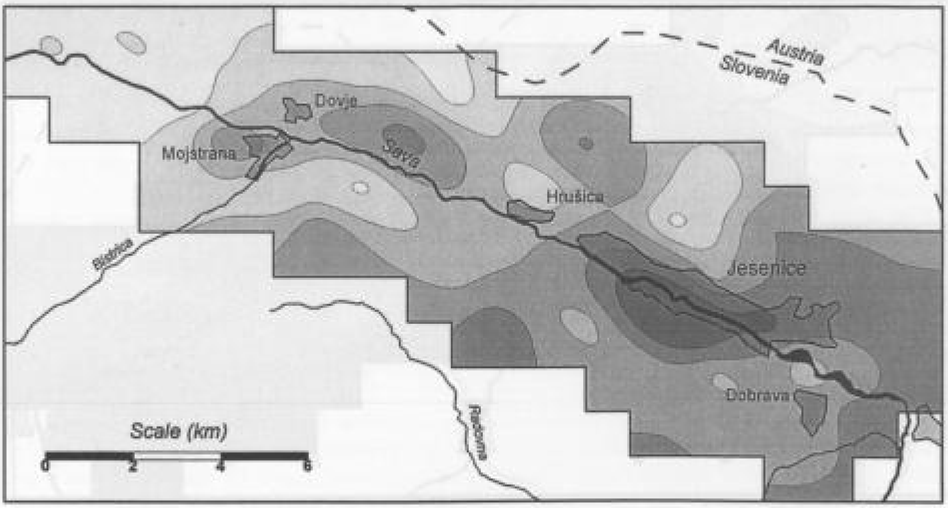


Fig. 5b. Distribution of factor 2 (Cd, Cu, Hg, Mn, Pb and Zn) in bottom soil
Sl. 5b. Porazdelitev faktorja 2 (Cd, Cu, Hg, Mn, Pb in Zn) v spodnjem talnem horizontu

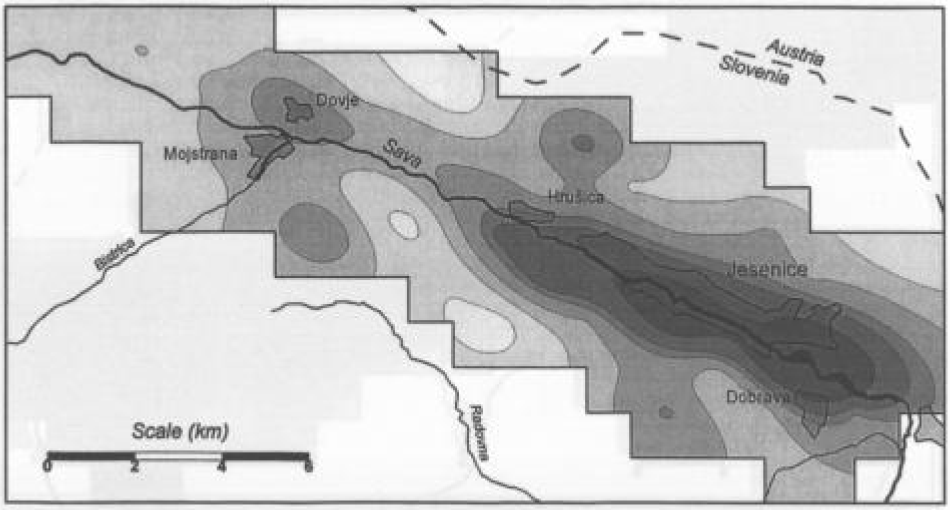
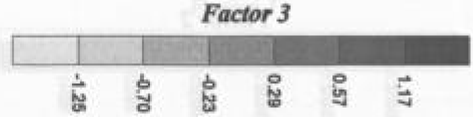


Fig. 6a. Distribution of factor 3 (Cr, Fe and Ni) in top soil
Sl. 6a. Porazdelitev faktorja 3 (Cr, Fe in Ni) v zgornjem talnem horizontu



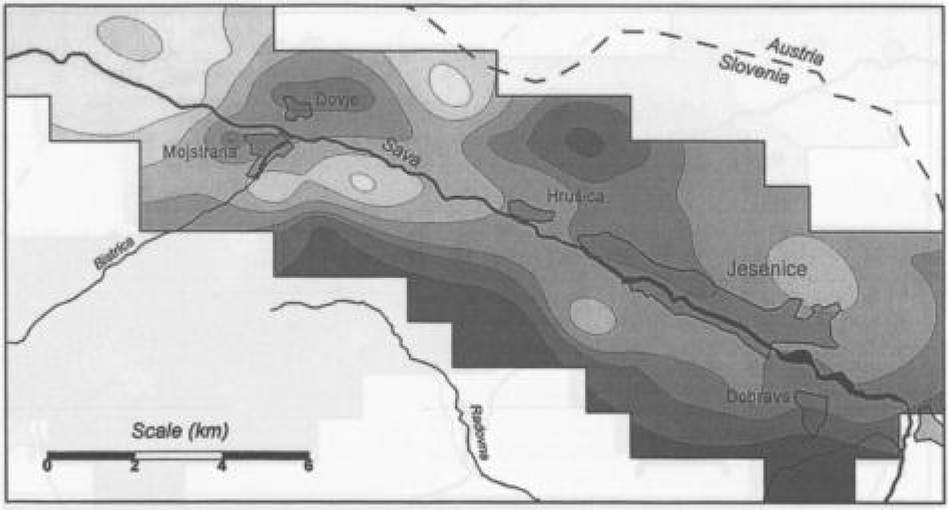


Fig. 6b. Distribution of factor 3 (Cr, Fe and Ni) in bottom soil
Sl. 6b. Porazdelitev faktorja 3 (Cr, Fe in Ni) v spodnjem talnem horizontu

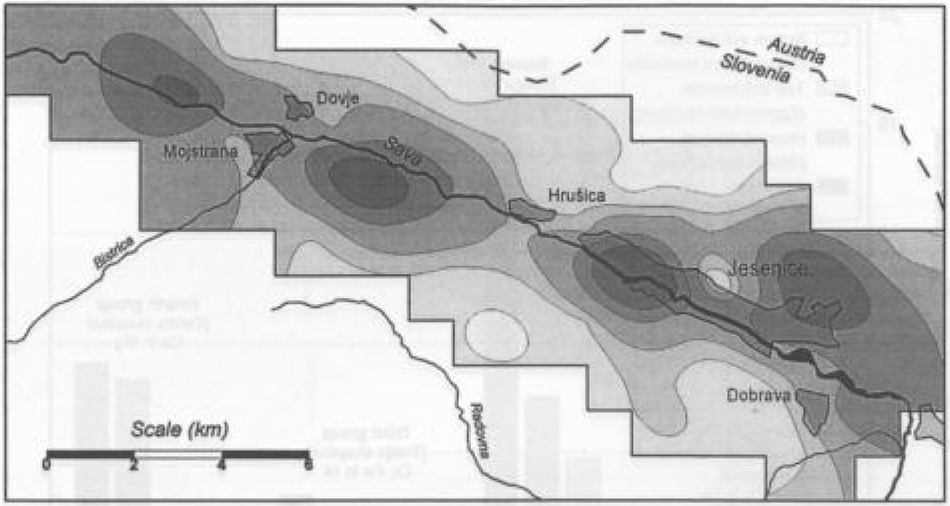


Fig. 7a. Distribution of factor 4 (Ca, Mg and pH) in top soil

Sl. 7a. Porazdelitev faktorja 4 (Ca, Mg in pH) v zgornjem talnem horizontu

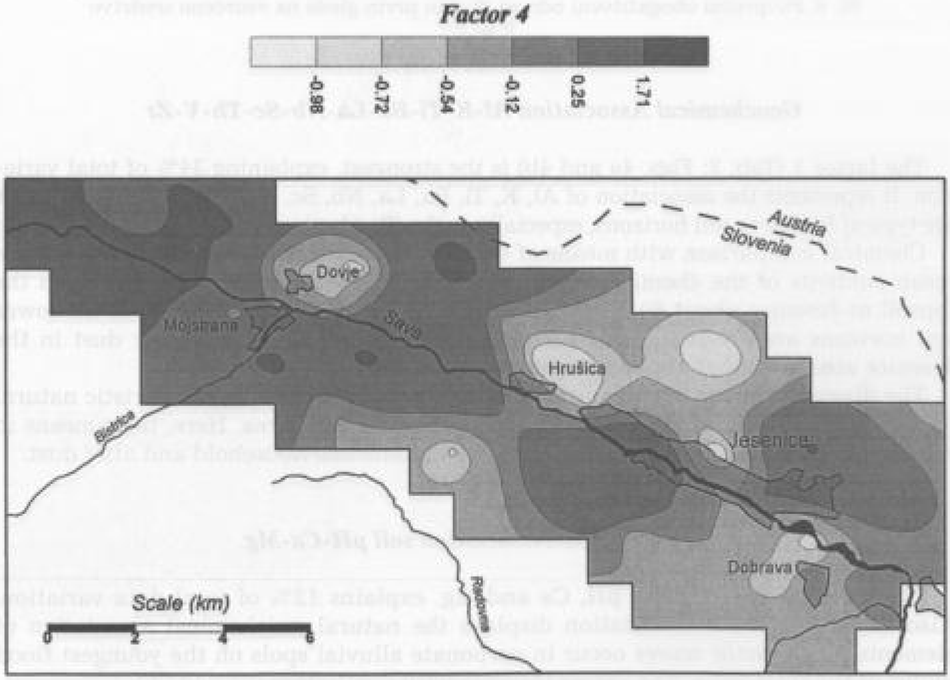


Fig. 7b. Distribution of factor 4 (Ca, Mg and pH) in bottom soil

Sl. 7b. Porazdelitev faktorja 4 (Ca, Mg in pH) v spodnjem talnem horizontu

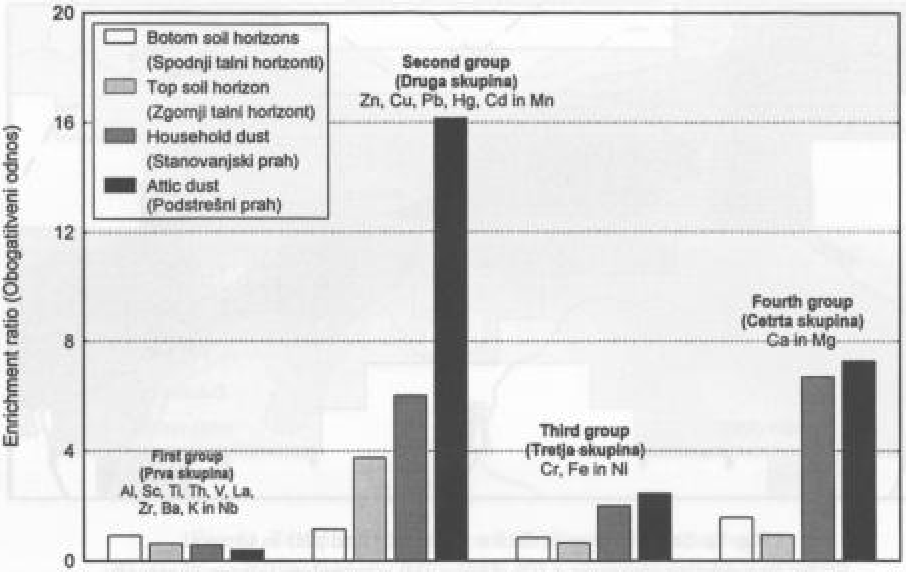


Fig. 8. Average enrichment ratios of element group with regard sampled material

Sl. 8. Povprečni obogatitveni odnosi skupin prvin glede na vzorčeno sredstvo

Geochemical Association Al-K-Ti-Ba-La-Nb-Sc-Th-V-Zr

The factor 1 (Tab. 2; Figs. 4a and 4b) is the strongest, explaining 34% of total variation. It represents the association of Al, K, Ti, Ba, La, Nb, Sc, Th, V and Zr. High values are typical for lower soil horizons, especially in the (B_{rz}) horizon of calcareous cambisols.

Chemical comparison with means of soils in Slovenia (Tab.1; Fig. 8) shows that the mean contents of the chemical elements associated with the first factor are in the topsoil at Jesenice about 60% of soils in Slovenia, while their contents in the lower soil horizons are about the same. The contents in household and attic dust in the Jesenice area are about 40% of the estimated means for Slovenia.

The discussed group of chemical elements represents a most characteristic natural pattern of behaviour of chemical elements in the Jesenice area. Here, their means in soils are appreciably higher than in the urban sediments, household and attic dust.

Geochemical Association soil pH-Ca-Mg

The factor 4, loaded with pH, Ca and Mg, explains 12% of total data variation. Also this geochemical association displays the natural geochemical association of elements. High factor scores occur in carbonate alluvial spols on the youngest flood plains of the river Sava. The values increase with depth (Figs. 7a and 7b).

Ca and Mg are typical elements of the carbonate rocks. In comparison with the soil means for Slovenia (Tab. 1; Fig. 8), for Jesenice somewhat lower values were established in topsoils, and up to 50% higher values in the lower soil horizons. The high

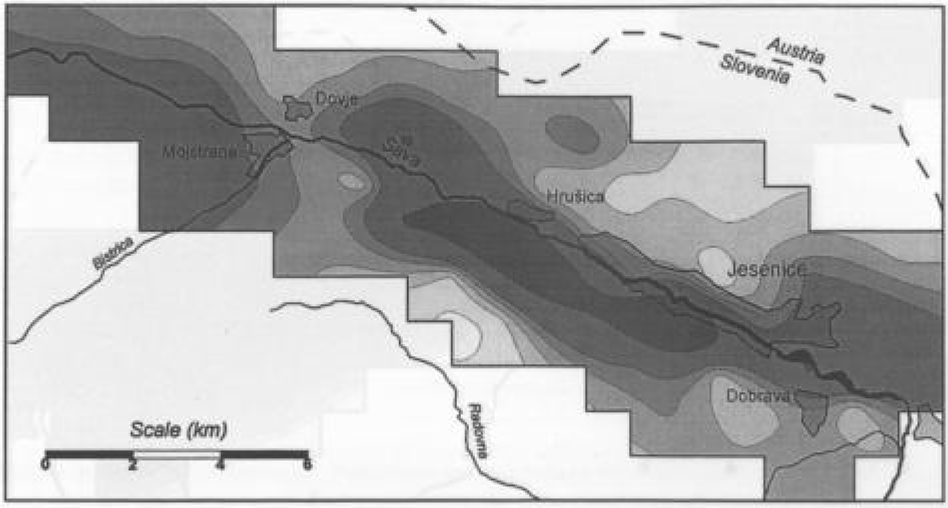
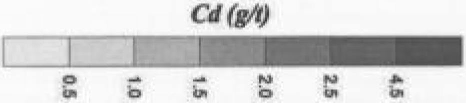


Fig. 9a. Distribution of cadmium in top soil
Sl. 9a. Porazdelitev kadmija v zgornjem talnem horizontu



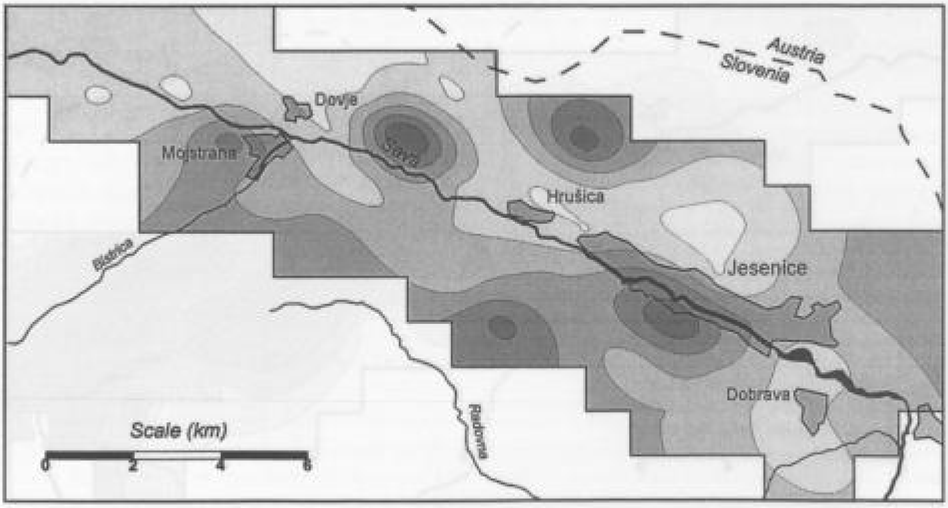


Fig. 9b. Distribution of cadmium in bottom soil
Sl. 9b. Porazdelitev kadmija v spodnjem talnem horizontu

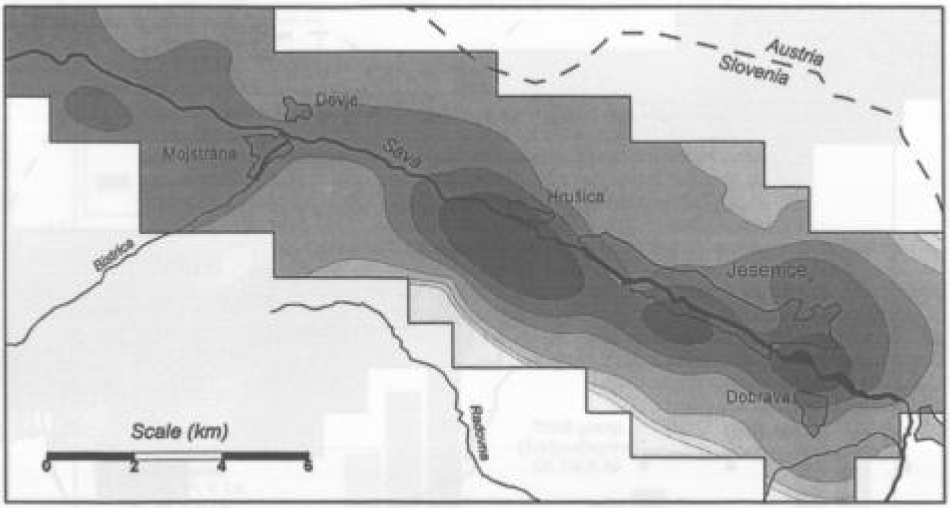
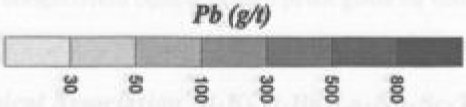


Fig. 10a. Distribution of lead in top soil
Sl. 10a. Porazdelitev svinca v zgornjem talnem horizontu



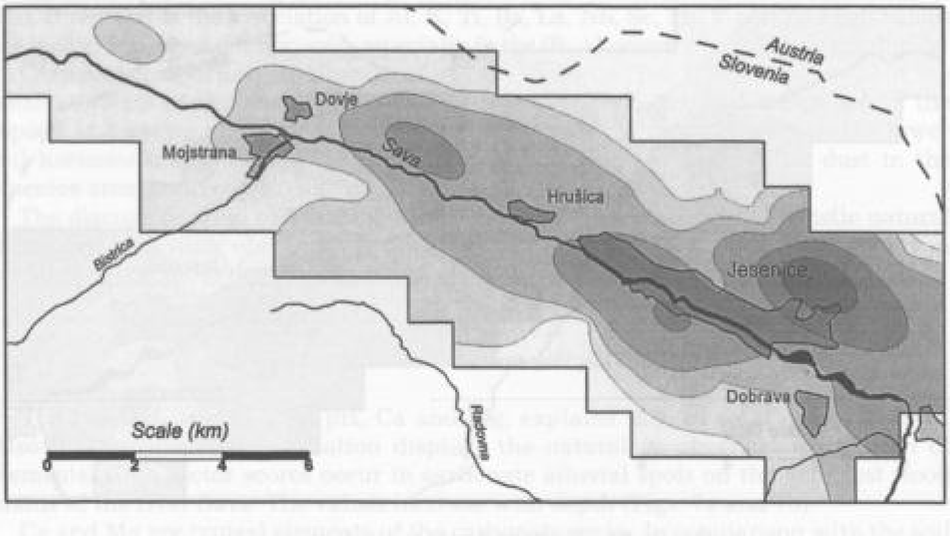


Fig. 10b. Distribution of lead in bottom soil
Sl. 10b. Porazdelitev svinca v spodnjem talnem horizontu

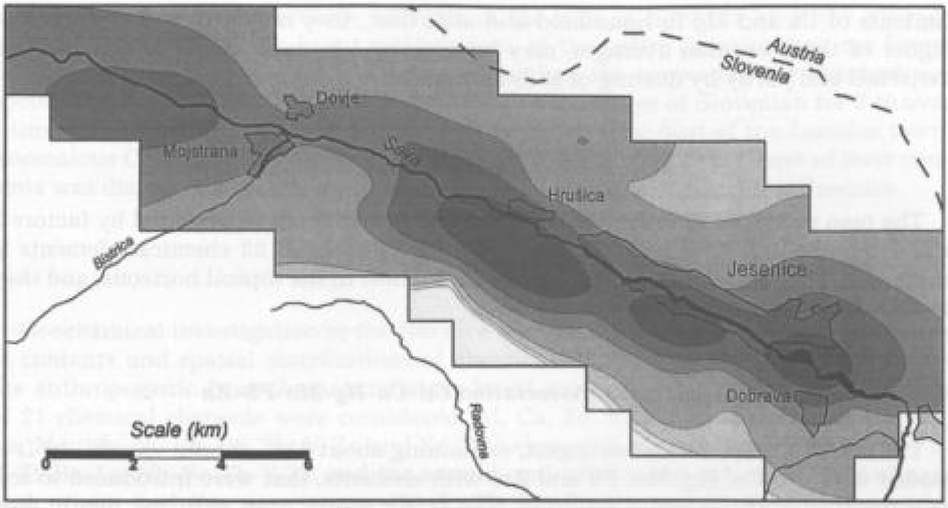
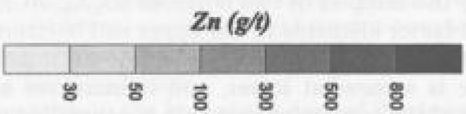


Fig. 11a. Distribution of zinc in top soil

Sl. 11a. Porazdelitev cinka v zgornjem talnem horizontu



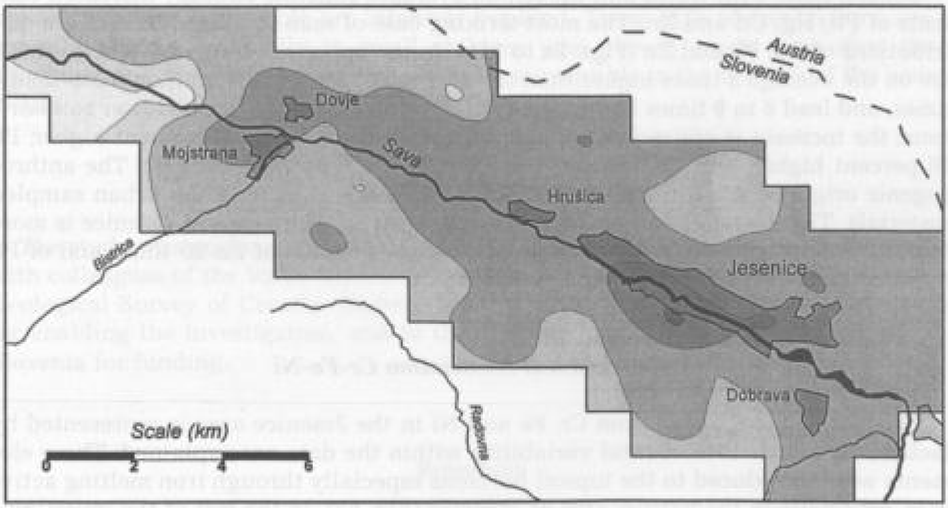


Fig. 11b. Distribution of zinc in bottom soil

Sl. 11b. Porazdelitev cinka v spodnjem talnem horizontu contents of Ca and Mg in household and attic dust, they may be more than 8 times higher of the Slovenian averages, may be explained by weathering of construction materials and partly by dusting of soils and roads.

Man-made Elemental Distributions

The man produced distributions of chemical elements are represented by factors 2 and 3 by whom 36% of total variability of the considered 22 chemical elements is explained. The scores of these factors are the highest in the topsoil horizons, and they tend to diminish with depth.

Geochemical Association Cd-Cu-Hg-Mn-Pb-Zn

The factor 2 is the second strongest, explaining about 23% of total variability. It is loaded with Cd, Cu, Hg, Mn, Pb and Zn, with elements, that were introduced to soil as a result of anthropogenic activities. The factor scores drop with soil depth: they are several times higher in the topsoil horizons than in the lower soil horizons (Figs. 5a and 5b). These differences are more contrasting on highly polluted localities with lower soil horizons of brown soils. The differences are less expressed in rendzinas in which most often only the samples of two horizons (O_hA_h, AC), were collected.

The impact of the 2 factor elements in the upper soil horizon extends in a 2 to 4 km wide belt along the entire length of the Sava valley. At Mojstrana, where the valley widens, the influence is somewhat lower, and it increases again when it narrows westwards. The shape of the contamination halo is controlled much by the mentioned two local winds.

Comparisons with world and Slovenian averages suggests strongly increased contents of Pb, Hg, Cd and Zn. The most striking case of man produced impact are distributions of Cd, Pb and Zn (Figs. 9a to 11b). In the upper soil horizons, zinc contents are on the average 3 times higher than the average of Slovenia, cadmium more than 4 times, and lead 8 to 9 times higher than the Slovenian average. In the lower soil horizons, the increase is appreciable smaller, Cd is on the average 60 percent higher, Pb 30 percent higher, and Zn is about the same as the Slovenian average. The anthropogenic origin of most of Cd, Pb and Zn is especially drastic in the urban sampled materials. The average contents of Cd in attic dust in the houses at Jesenice is more than 12 times higher than the average of soils in Slovenia, of Zn 25 times and of Pb for more than 42 times higher (Tab. 1; Fig. 8).

Geochemical Association Cr-Fe-Ni

The geochemical association Cr, Fe and Ni in the Jesenice area is represented by factor 3 by which 13% of total variability within the data are explained. These elements were introduced to the topsoil horizons especially through iron melting activities, especially in the narrow area of Jesenice (Fig. 6a). In the rest of the investigated territory, the major part of contents of these metals is of geogenic origin; they tend to accumulate especially in the (B_{rz}) horizon of the calcareous cambisols (Figs. 6a and 6b).

In comparison to the average contents in the soils of Slovenia area, the average contents in topsoil and in lower soil horizons of the entire Jesenice area are lower. However, in the halo of about 10 km^2 surrounding the ironworks the averages are about 40 % higher. High contents that surpass the averages of Slovenian for 2 to over 3 times are found in household and even more in the attic dust of the Jesenice town. Anomalous Cr, Fe and Ni in urban materials are another proof that most of their contents was dispersed into the environment by the metallurgic industry at Jesenice.

Conclusions

Geochemical investigation in the Jesenice area permitted to establish the estimates of contents and spatial distributions of chemical elements in soils, and to separate the anthropogenic from the naturally produced geochemical patterns. Distributions of 21 chemical elements were considered: Al, Ca, Fe, K, Mg, Ti, Ba, Cd, Cr, Cu, Hg, La, Mn, Nb, Ni, Pb, Sc, Th, V, Zn and Zr. Two elemental associations, the first Al-Fe-K-Ti-Ba-La-Nb-Sc-Th-V-Zr, and the second, soil pH-Ca-Mg, are considered of natural origin, and the associations Cd-Cu-Hg-Mn-Pb-Zn and Cr-Fe-Ni man made, influenced strongly by the iron metallurgy.

The established estimates of chemical elements and of geochemical trends of single elements and of their associations in the soils of Jesenice are a good basis for further research of geochemical distributions in other media, as air, air deposit, stream sediment and plants. These additional studies should permit to establish the natural and anthropogenic cycles of chemical elements in the urban environment, and permit to estimate the hazards for the population.

Alarming is the recognition in the household dust of the Jesenice area of very high values of Cd, Pb and Zn that are more than 20 times higher than in natural loose materials. The urban sediments, and especially the household dust, are the substances to which the people are intensely exposed. These high concentrations are a potential danger especially to small children who absorb much more dust than grownups, and are at the same time also more susceptible to the toxicity of the heavy metals.

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