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Influence of ironworks on distribution of chemical elements in Bosnia and Herzegovina and Slovenia

Vpliv železarn na porazdelitev kemičnih prvin v Bosni in Hercegovini ter Sloveniji

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Abstract

The objective of this work is the study of the distribution of chemical elements in attic dust and topsoil for the identification of anthropogenic and geogenic element sources in an old metallurgic area in Bosnia and Herzegovina and Slovenia (Slo – BiH bilateral project "Heavy metals in environment as consequences of mining and smelting in the past"). Samples of attic dust and topsoil were collected in localities in BiH (Zenica, Vareš and Ilijaš) and Slovenia (Jesenice, Štore and Ravne).

Analysis for 42 chemical elements was performed. Based on a comparison of statistical parameters, spatial distribution of particular elements and results of cluster analysis one natural and two anthropogenic geochemical associations were identified. The natural geochemical association (Al-K-La-Sc-Th-Ti) is influenced mainly by lithology. The anthropogenic association (Co-Cr-Mo-Ni-V-W) is the result of iron metallurgy in the past. The second anthropogenic association (Ag-As-Cd-Fe-Hg-Mn-Pb-Sb-Sn-Zn) is the result of high level of sulphide phase in iron ore (Vareš) and zinc and sulphuric acid production in the Celje area.

Povzetek

Namen pričujočih raziskav je študij porazdelitve kemičnih prvin v podstrešnem prahu in tleh za ugotavljanje in ločevanje naravnih in antropogeno povzročenih porazdelitev kemičnih prvin na območjih intenzivnega železarstva v Bosni in Hercegovini ter v Sloveniji (Slo-BiH bilateralni projekt "Težke kovine v okolju kot posledica rudarjenja in topilništva v preteklosti"). V ta namen smo zbrali vzorce podstrešnega prahu in tal na petnajstih lokacijah v Bosni in Hercegovni (Zenica, Vareš in Ilijaš) ter v Sloveniji (Jesenice, Štore in Ravne).

Vzorčni material je bil analiziran na 42 kemične prvine. Na osnovi primerjave statističnih parametrov, porazdelitve posameznih prvin in rezultatov clusterske analize smo izločili eno naravno ter dve anropogeno povzročeni geokemični asociaciji. Porazdelitev Al-K-La-Sc-Th-Ti je predvsem posledica vpliva litološke podlage. Antropogeno povzročena asociacija (Co-Cr-Mo-Ni-V-W) je nastala zaradi delovanja železarstva v preteklosti. Naslednja antropogeno povzročena asociacija (Ag-As-Cd-Fe-Hg-Mn-Pb-Sb-Sn-Zn) je rezultat visokega deleža sulfidne faze v železovi rudi (Vareš) ali pa pridelave cinka in žveplove kisline na območju Celja.

Introduction

The objective of this work is the study of the distribution of chemical elements in attic dust and topsoil for the identification of anthropogenic (man-made) and geogenic (natural) element sources in an old metallurgic area in Bosnia and Herzegovina and Slovenia (Slo – BiH bilateral project "Heavy metals in environment as consequences of mining and smelting in the past"). Samples of attic dust and topsoil were collected in localities in BiH (Zenica, Vareš and Ilijaš) and Slovenia (Jesenice, Štore and Ravne).

In previous geochemical studies (Šajn, 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 & Šajn, 2001; Gosar & Šajn, 2003) and pollution of heavy metals in Celje (Šajn, 2005), Mežica (Šajn et al., 2000; Šajn, 2002) and Jesenice area (Šajn et al., 1998) was successfully proven.

The basic idea of the project is the hypothesis that relations between geogenic and anthropogenic chemical elements in sampling media, especially in attic dust, are preserved in wider regional scale regardless of architectonic particularity of attics in the region and lithology. We believe that this research has proven it.

Geographical and geological description of study areas Localities in Slovenia (Fig. 1)

Celje (Štore)

The town of Celje is situated in the central part of Slovenia. In the area of the Celje - Štore urban zone live about 55,000 inhabitants (Antončič, 2001). The industry is concentrated in the eastern part of the Celje town. The Zinc smelter Celje, started its operation in 1873 and is still in operation today. It has been estimated 580,000 tons of zinc were produced between the years 1875 and 1970 (Žibret, 2002).

The construction of the ironworks Štore started in 1856. The Štore ironworks was a relatively large operation from the beginning. Production and processing were in expansion until 1991, after that the production dropped radically.

In the geological sense, the studied area represents a young tectonic basin. It is filled with Quaternary deposits of the Savinja, Voglajna and Hudinja rivers. In the northern part are Pleistocene clays, quartz gravel and sand. Tuff and marine clay of the Oligocene age underlie these deposits. In the southeast part also Miocene sand, sandstone, marly limestone and lithothamnian limestone are exposed, as a part of the Celje syncline. The oldest rocks (shale, limestone, keratophyre and keratophyre tuff of the Ladinian age, and Upper Triassic massive limestone) crop out in the southern part (Buser, 1977).

Jesenice

The Jesenice area is situated in the northwest part of Slovenia (Fig. 1). The administrative, political and economic centre is the town of Jesenice, a typical industrial town with iron making tradition, inhabited by a population of about 20,000. Iron making in the Jesenice area is traditional. The deve-

Figure 1. Locations of observed ironworks in Bosnia and Herzegovina and Slovenia

Slika 1. Lokacije železarn v Bosni in Hercegovini ter Sloveniji lopment of mines and furnaces started end of 14th century as testified by the Ortenburg mining regulations (http://www.jesenice.si/jeobc.html).

After WWII Jesenice became the center of black metallurgy in Slovenia. Introduction of electrical steel processing marked the era of manufacturing steel of higher quality and in greater quantities. At its peak in 1970s, the ironworks employed more than 8,000 people (http://psychcentral.com/psypsych/jesenice).

The territory is situated at the contact of three geotectonic units: the south Karavanke, the Ljubljana basin and the Julian Alps. 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, 1986).

Ravne

The research 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 parts, the settlements Prevalje and Ravne are placed.

After the year 1835, ironworking had developed at Prevalje and later at Ravne (Mohorič, 1954). The Meža valley is strongly polluted with heavy metals due to mining and smelting. The major pollutants are lead and zinc, which were being extracted in the upper part of the Meža valley for more than 300 years (Šajn et al., 2000; Vreča et al., 2001). Ironwork located in the lower part of the valley also contributed to the pollution of the area during a 150-year operating period (Souvent, 1994).

The upper part of the valley cuts mostly through Triassic limestone and dolomite. The lower part of the valley cuts through metamorphic rocks (Mioč et al., 1983).

Localities in Bosnia and Herzegovina (Fig 1.)

Zenica

Zenica is an industrial city of 130,000, distanced 70 kilometers north from the capital Sarajevo, by the valley of the river Bosna (http://bs.wikipedia.org/wiki/zenica).

Construction of the iron and steelworks in Zenica started in 1892, but already in 1899, the iron and steel works produced about 3700 tons of rolled products. In 1940, the iron and steel works produced 1/3 of the total production of steel and rolled production of Yugoslavia. By putting a new facilities into operation and expansion of production continued in 1986 and reached record of 1,720,000 tons of pig iron and 1,906,000 tons of crude steel. In April 1992, production was stopped but in 1998 emerged a new company called “BH STEEL Company” (http://www.bhsteel.com.ba/istorija.htm).

The city of Zenica is situated in valley that is covered by alluvium of the Bosna River, partly on alluvial terrace sediments. On the West side of the Bosna River, Miocene and Oligocene rocks outcrop and comprise clays, sandstones, conglomerates and marls thought to represent post-orogenic shelf sediments of Pannonian Sea. On the East side of the Bosna River are Upper Cretaceous massive limestones and limestone breccias and on top is flysch (Živanović et al., 1975).

Vareš

This small city is situated in a valley of the river Stavnja with 20,000 inhabitants. In region of Vareš, iron ore mined and smelted from Antique period. With arrival Austrians to Bosnia, Vareš admire revival in economy aspect. Iron work of Vareš is established in 1891, and operated until 1991. Before last war, Vareš had been forcefully industrial centre, but from that time, mining and metallic activities are stopped (http://bs.wikipedia.org/wiki/vares; http://zeljezara-vares.com/onama.html).

The oldest rocks are Triassic age sandstone and sandy shale and massive, thick-bedded limestone. There is a part with Anisian limestones and dolomites, bearing hematite and siderite. The abandoned mine in Vareš was the biggest Fe mine in Bosnia and Herzegovina. The mine zone is represented by carbonates and iron oxide minerals. Moreover, Pb and Zn deposits are reported within the same sequence. In the Vareš area, Pb-Zn mineralization is connected with the Fe deposit. (Olujić et al., 1978).

Ilijaš

Ilijaš is a municipality located about 20 km north east of the city of Sarajevo. As per dates in 2002, in a district of Ilijaš have lived 15,000 inhabitants. Ironwork of Ilijaš begun with production in 1954, and in time developed in giant who spread around 60 ha. Now, production stagnates. Pre war number of employed decreased from 3,500 on approximately 200 (http://bs.wikipedia.org/wiki/ilijas; http://www.geocities.com/suceska 2003/aktilijas.htm).

The ironwork Ilijaš is situated on Quaternary sediments. Rocks in the Ilijaš basin are Miocene and Oligocene ages, same as in the town Zenica (Jovanović et al., 1978).

Materials and methods

Sampling design and materials

Samples were collected from three localities in Bosnia and Herzegovina (Zenica, Vareš and Ilijaš) and in Slovenia (Jesenice, Ravne and Štore) (Fig. 1). In each Slovenian locality we collected three samples and from each Bosnian locality, two samples. In total we sampled fifteen localities, and at each we collected topsoil (0-5 cm) and attic dust.

Close to each sample site location an old house was chosen with intact attic carpentry. 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. 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 the gardens and on grass verges was sampled (Šajn, 2003; 2005).

Preparation of samples and analysis

All samples were air-dried. The size fraction of attic dust smaller than 0.125 mm was prepared for chemical analyses by sieving. Soil samples were gently crushed then the fraction smaller than 2 mm was pulverized (Darnley et al., 1995; Salminen et al., 2005). Analysis 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 region digestion (mixture HCl, HNO_3 and water at 95°C).

All samples, replicates and geologic standards were submitted to the laboratory in a random order. This procedure assured unbiased treatment of samples and random distribution of possible drift of analytical conditions across all samples.

Sensitivity, accuracy and precision of analysis

The sensitivity in the sense of the lower limit of detection was adequate for 36 out of 42 determined chemical elements. The elements Au, Be, Bi, Hf, Ta and W, however, were removed from further statistical analysis, (Miesch, 1976) since their contents in the majority of analyzed samples were below the lower detection limit of the analytical method. Accuracy of the analytical method for the remaining 36 elements was estimated by calculation of the relative systematic error between the determined and recommended values of geological standards. Most elements show, in the range of the actual samples, very low deviations. The means of elements in the standards generally differ by less than 15% of the recommended values.

Results and discussion

In these analyses we excluded some elements because some of them have concentrations below detection limits, but some of them did not show any connection to other elements in multivariate statistical analyses. Consequently 22 elements (Tab. 1) used in the final statistical treatment.

Number of samples for making a cluster analysis is small, but significant enough. Principally, no geochemical variations compare to other previous similar analysis. Based on a comparison of statistical parameters (Tab. 1), results of cluster analysis (Fig. 2) and calculated enrichment ratios (Tab. 2), one natural and two anthropogenic geochemical associations were identified. The natural geochemical association (Al-K-La-Sc-Th-Ti) is influenced mainly by lithology. The first anthropogenic association (Co-Cr-Mo-Ni-V-W) is the result of iron metallurgy in the past. The second anthropogenic association (Ag-As-Cd-Fe-Hg-Mn-Pb-Sb-Sn-Zn) is the result of high level of sulphide phase in iron ore (Vareš) and zinc and sulphuric acid production in the Celje area.

First group: naturally distributed elements

The first group links Al, K, La, Th, Ti and Sc. Characteristics for this geochemical group are high values of correlation coefficients (Tab. 3a) and results of Cluster analyses (Fig. 2) between analyzed chemical elements.

For these elements it is important to note that their average concentrations in topsoil are around 80% concentration in Slovenian soil. Concentration ratios vary between 0.5 and 1.2 (Tab. 2, Fig. 3). Highest concentrations were found in two areas, Ravne and Štore, and are a consequence of weathering of igneous rocks in their environment. The average of these elements in attic dust is 50% (varying between 0.3 and 0.7) concentration in Slovenian soil (Tab. 2, Fig.4). The highest ratio between attic dust and topsoil was found in the Ilijaš area (0.9) and the lowest in the Ravne area (0.4) (Tab. 2, Fig.5).

Table 1. Slovenian averages in topsoil (Šajn, 2003) and average values of 22 selected chemical elements for considered ironworks
(Concentrations of Al, Fe, K and Ti are expressed in %, remaining elements in mg/kg)

Tabela 1. Slovenska povprečja v tleh (Šajn, 2003) ter povprečne vrednosti 22 izbranih kemičnih prvin glede na obravnavano železarno
(Vsebnosti Al, Fe, K in Ti so izražene %, vsebnosti ostalih prvin v mg/kg)

	Topsoil (0-5 cm)							Attic dust					
Element	Slo	Jesenice	Štore	Ravne	Zenica	Vareš	Ilijaš	Jesenice	Štore	Ravne	Zenica	Vareš	Ilijaš
First group of elements													
Al	6.9	5.1	6.0	7.1	4.2	4.0	4.2	2.4	3.0	2.6	3.0	2.3	4.1
K	1.6	1.2	1.8	1.9	1.0	1.0	1.1	0.66	1.0	0.76	0.59	0.79	1.2
La	32	23	35	34	24	22	39	9.0	15	15	12	16	22
Sc	12	10	10	15	9.0	10	6.7	5.3	7.0	5.0	7.0		
Th	11	8.3	10	11	7.3	5.6	7.4	4.7	4.3	3.7	4.7	3.3	7.5
Ti	0.33	0.22	0.30	0.25	0.24	0.27	0.23	0.10	0.29	0.12	0.16	0.12	0.23
Second group of elements													
Co	16	9.0	12	22	16	25	34	14	16	42	19	32	17
Cr	91	242	99	574	161	271	166	445	354	3327	156	194	218
Mo	0.80	7.0	2.5	33	1.8	5.2	5.5	22	26	214	5.4	16	7.6
Ni	50	83	53	130	133	187	114	211	144	604	181	144	92
V	102	79	98	124	80	91	89	76	107	162	89	82	74
W	1.4	2.0	2.3	26	1.5	6.5	4.7	2.7	6.7	186	2.8	24	5.6
Third group of elements													
Ag	0.090	0.58	0.20	0.30	1.0	2.6	0.45	2.1	1.7	8.5	4.0	6.1	0.35
As	14	19	28	20	57	31	91	44	116	28	121	83	44
Cd	0.45	1.9	4.9	2.1	1.5	3.5	1.8	5.8	37	6.2	4.3	9.0	1.6
Fe	3.5	5.3	4.7	5.7	4.5	7.6	11	13	14	13	8.6	19	6.8
Hg	0.070	0.59	0.63	0.22	0.51	1.1	5.4	2.6	1.8	0.29	1.8	3.6	0.99
Mn	1054	2320	976	1292	1284	3704	2674	6089	2418	2792	2598	5173	1310
Pb	42	430	175	500	267	918	166	1651	1368	1223	982	2412	199
Sb	1.1	2.5	2.0	5.7	11	29	8.3	12	15	17	52	85	7.7
Sn	3.1	8.3	5.7	12	6.5	20	12	17	27	39	14	58	14
Zn	124	828	706	1431	441	2434	361	2200	6835	1911	1204	5830	453

Table 2: Average enrichment ratios of group of elements according considered ironworks

Tabela 2: Povprečna obogatitvena razmerja skupin kemičnih prvin glede na obravnavano železarno

	Group 1		Group 2		Group 3	
Location	$\bar{X}$, $\bar{X}g$	Min - Max	$\bar{X}$, $\bar{X}g$	Min - Max	$\bar{X}$, $\bar{X}g$	Min - Max
Enrichment ratio ($M_{topsoil}/M_{slovenian\ average}$)						
Jesenice	0.75	(0.67 - 0.81)	1.7	(0.56 - 8.7)	3.6	(1.3 - 10)
Štore	0.97	(0.86 - 1.1)	1.3	(0.77 - 3.2)	3.5	(0.93 - 21)
Ravne	1.1	(0.78 - 1.3)	5.3	(1.2 - 42)	3.7	(1.2 - 12)
Zenica	0.70	(0.61 - 0.75)	1.4	(0.78 - 2.7)	3.8	(1.2 - 12)
Vareš	0.67	(0.53 - 0.83)	2.8	(0.89 - 6.5)	9.0	(2.2 - 31)
Ilijaš	0.79	(0.62 - 1.2)	2.4	(0.67 - 6.8)	5.6	(2.5 - 82)
Average	**0.82**	**(0.53 - 1.2)**	**2.2**	**(0.56 - 42)**	**4.6**	**(0.93 - 82)**
Enrichment ratio ($M_{attic\ dust}/M_{slovenian\ average}$)						
Jesenice	0.37	(0.28 - 0.44)	3.0	(0.74 - 28)	11	(3.2 - 41)
Štore	0.56	(0.41 - 0.88)	3.5	(1.0 - 32)	15	(2.3 - 82)
Ravne	0.42	(0.35 - 0.48)	20	(1.6 - 267)	10	(2.0 - 100)
Zenica	0.45	(0.37 - 0.58)	2.1	(0.87 - 6.7)	11	(2.5 - 47)
Vareš	0.40	(0.31 - 0.51)	3.9	(0.80 - 20)	22	(4.9 - 77)
Ilijaš	0.67	(0.58 - 0.73)	2.2	(0.72 - 9.4)	4.1	(1.2 - 15)
Average	**0.48**	**(0.28 - 0.73)**	**4.0**	**(0.72 - 267)**	**11**	**(1.2 - 100)**
Enrichment ratio ($M_{attic\ dust}/M_{topsoil}$)						
Jesenice	0.49	(0.40 - 0.56)	1.8	(0.95 - 3.1)	3.0	(2.0 - 4.9)
Štore	0.58	(0.43 - 0.95)	2.7	(1.1 - 10)	4.3	(0.67 - 9.7)
Ravne	0.40	(0.34 - 0.47)	3.8	(1.3 - 7.2)	2.7	(1.3 - 28)
Zenica	0.65	(0.51 - 0.78)	1.5	(0.97 - 3.1)	2.8	(1.9 - 4.9)
Vareš	0.61	(0.44 - 0.78)	1.4	(0.72 - 3.7)	2.5	(1.4 - 3.2)
Ilijaš	0.88	(0.57 - 1.0)	0.95	(0.49 - 1.4)	0.74	(0.18 - 1.3)
Average	**0.60**	**(0.34 - 1.0)**	**1.8**	**(0.49 - 10)**	**2.7**	**(0.18 - 28)**

$\bar{X}$ - mean (srednja vrednost); **$\bar{X}g$** - geometric mean (geometrična srednja vrednost)
Min – minimum (minimum); **Max** – maximum (maksimum)

Whereas these elements are not included in technological processes of ironworks, we presume that the source of the above elements in topsoil and attic dust is natural, i.e. they originate from soil dust and represent the natural state. Based on these ratios, we can roughly evaluate that the lowest pollution is in the Ilijaš area and the highest in the Ravne area. Similar relationships have been determined during previous research of soil and attic dust in Celje (Šajn, 2005), Jesenice (Šajn, 1998) and Ravne (Šajn, 2002) areas. It is proposed that the distribution of most elements is related to bedrock.

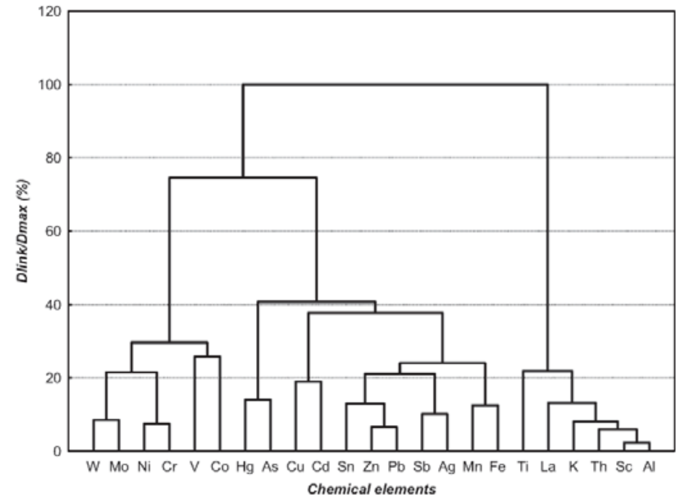

Figure 2. Dendrogram of cluster analysis (15 samples of each attic dust and topsoil; 22 selected elements)

Slika 2. Dendrogram clusterske analize (po 15 vzorcev podstrešnega prahu in tal; 22 izbranih kemičnih prvin)

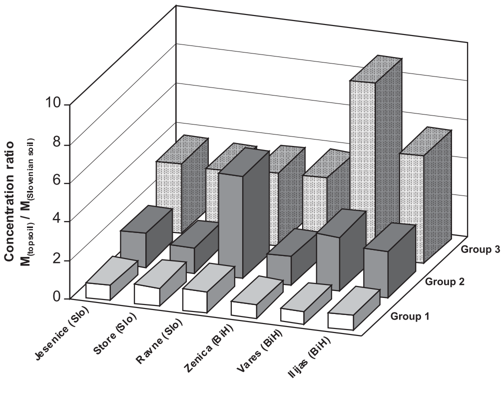

Figure 3. Concentration ratios of groups of elements in topsoil with regard to location of sampling

Slika 3. Koncentracijska razmerja skupin kemičnih prvin v tleh v odvisnosti od lokacije vzorčenja

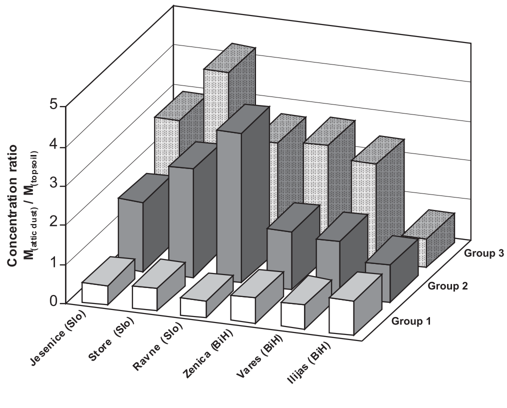

Fig. 5. Concentration ratios (attic dust/topsoil) of groups of elements with regard location of sampling

Slika 5.Koncentracijska razmerja (podstrešni prah/tla) skupin kemičnih prvin v odvisnosti od lokacije vzorčenja

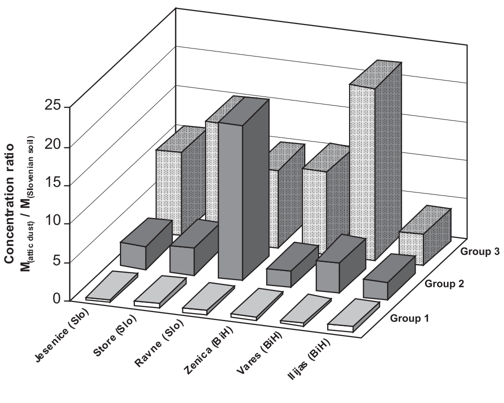

Figure 4. Concentration ratios of groups of elements in attic dust with regard to location of sampling

Slika 4. Koncentracijska razmerja skupin kemičnih prvin v podstrešnem prahu v odvisnosti od lokacije vzorčenja

Second group: anthropogenically introduced siderophile elements

The second group links mainly siderophile elements: Mo, Ni, Co, W, V, and Cr. As with the previous group, high values are observed for correlation coefficients (Tab. 3b), reinforced by results of Cluster analyses (Fig. 2) between analyzed chemical elements.

For these elements it is significant that their average concentration ratio in topsoil exceeds the average for Slovenian soil by a factor of around 2.2. Concentration ratios vary between 0.6 and 42 (Tab. 2, Fig. 3). The highest concentration is again in the Ravne area. The average of these elements in attic dust exceeds by a factor of 4 average for Slovenian soil (variation is between 0.7 and 267). Again, the highest concentration is in the Ravne area (Tab. 2, Fig. 4). As in first group, the highest ratio between attic dust and topsoil is found in the Ravne area (3.8) and lowest in the Ilijaš area (0.95) (Tab. 2, Fig. 5).

From this, it is possible to conclude that the consequences of mining are most pronounced in Ravne and least pronounced in Ilijaš. However, ironwork in Ilijaš has a shorter history than in the other five localities. Similar relationships have been determined during previous research of soil and attic dust in the areas Celje (Šajn, 2005), Jesenice (Šajn et al., 1998) and Ravne (Šajn, 2002).

Table 3a. Correlation coefficients (r) between geogenic elements (n=30; $P_{0.05,\ 28}$=0.361)

Tabela 3a. Korelacijski koeficienti (r) med geogenimi kemičnimi prvinami (n=30; $P_{0.05,\ 28}$=0.361)

	Al	K	Ti	La	Sc	Th
Al	1.00					
K	0.90	1.00				
Ti	0.75	0.68	1.00			
La	0.78	0.79	0.61	1.00		
Sc	0.96	0.86	0.74	0.76	1.00	
Th	0.95	0.85	0.66	0.77	0.89	1.00

Third group: anthropogenically introduced chalcophile elements

This group links Ag, As, Cd, Pb, Zn, Sb, Sn, Hg, and two siderophile elements Fe and Mn. In this group, as with the two previous groups, we observe a strong relationship between correlation coefficients (Tab. 3c) and results of Cluster analyses (Fig. 2) between analyzed chemical elements.

The highest enrichments are in topsoil, in attic dust and in ratios attic dust/topsoil. In topsoil, the average concentration is 4.6 times higher than in average Slovenian soil (highest concentration is in Vareš and lowest in Štore) (Tab. 2, Fig.3). The average of these elements in attic dust exceeds by a factor of 11 the average for Slovenian soil (varying from 1.2 to 100). The highest concentration of these elements (22) is found in the Vareš area, and basically represents the maximum for this group (Tab. 2, Fig.4). The highest ratio between attic dust and topsoil is found in the Štore area and, as with the two previous groups, the lowest in the Ilijaš area (Tab. 2, Fig.5).

The high content of the aforesaid group of elements in the Vareš area is consequence of the appearance of Pb-Zn. Metallurgical processes considerably increased the content of sulphide elements in all sampled materials and caused serious environmental pollution. A few kilometers west of the Štore is the town of Celje (Šajn, 2005), where there was an old Zn smelter (over 100 years old), that contributed to a high concentration of chalcophile elements.

Table 3b. Correlation coefficients (r) between anthropogenically introduced siderophile elements (n=30; $P_{0.05,\ 28}$=0.361)

Tabela 3c. Korelacijski koeficienti (r) med antropogeno vnesenimi siderofilnimi kemičnimi prvinami (n=30; $P_{0.05,\ 28}$=0.361)

	Co	Cr	Mo	Ni	V	W
Co	1.00					
Cr	0.56	1.00				
Mo	0.48	0.84	1.00			
Ni	0.70	0.86	0.68	1.00		
V	0.53	0.68	0.46	0.58	1.00	
W	0.68	0.74	0.85	0.61	0.49	1.00

Conclusion

Based on these analyses, we can compare pollution levels in each of these six ironworks. We have found that in the cities Zenica and Vareš there exist high concentrations of chalcophile and siderophile elements. Because of this it is very important to continue with further research on these two localities. In the Ilijaš area, by contrast, the pollution level is very low and, for now, further research will be discontinued.

In the Vareš area there is a very high concentration of chalcophile elements, which originate from ore deposits. This ironwork had a major influence on soil, stream sediments and stream terraces of the River Stavnja. My future work will focus more on this area.

It is also very important to continue with research in the city of Zenica, because this

Table 3c. Correlation coefficients (r) between anthropogenically introduced chalcophile elements (n=30; $P_{0.05,\ 28}$=0.361)

Tabela 3c. Korelacijski koeficienti (r) med antropogeno vnesenimi halkofilnimi kemičnimi prvinami (n=30; $P_{0.05,\ 28}$=0.361)

	Fe	Ag	As	Cd	Mn	Pb	Sb	Sn	Zn	Hg
Fe	1.00									
Ag	0.67	1.00								
As	0.62	0.53	1.00							
Cd	0.65	0.47	0.46	1.00						
Mn	0.77	0.72	0.41	0.42	1.00					
Pb	0.75	0.80	0.39	0.71	0.75	1.00				
Sb	0.67	0.82	0.62	0.43	0.58	0.74	1.00			
Sn	0.73	0.69	0.39	0.61	0.56	0.78	0.78	1.00		
Zn	0.68	0.62	0.35	0.86	0.60	0.88	0.62	0.77	1.00	
Hg	0.66	0.45	0.75	0.34	0.64	0.40	0.48	0.31	0.34	1.00

ironwork is the largest in the Balkans, and there is a prominent metallurgical tradition.

Based on the results, we can expect high pollution both siderophile and chalcophile elements. This two, in Zenica and Vareš and several other industrial giants are situated in the valley of the River Bosna. It would be very important to check the content of these elements in its stream sediments, as well as alluvial plains where there are intensive agricultural activities. This may have a huge influence on human health and groundwater.

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