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Influence of Mining and Metallurgy on the Chemical Composition of Soil and Attic Dust in the Meža Valley (Slovenia)

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Introduction

The objective of geochemical investigations conducted in the Meža valley was to introduce attic dust as sampling material in the process of separation between natural distributions of chemical elements and historic anthropogenic anomalies, especially spatial distribution of heavy elements.
The Meža river valley cuts in its upper part through the Eastern Karavanke Mountains, and in its lower part through the Alpine mountains of medium height. In its upper part, the narrow valley is widened in two places, where two settlements, Črna and Mežica, have grown. In its lower part, settlements Prevelje 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.
The Meža valley is strongly polluted with heavy metals due to mining and smelting, as well as its geogenic characteristics. The major pollutants are lead and zinc, which were being extracted in the upper part of the valley for more than 300 years. An ironworks located in the lower part of the valley also contributed to the pollution of the area during a 150-year operating period.

Materials and Methods

On the basis of the results of previous studies, we defined a 100 km^2 research area extending from ?rna to Ravne. The entire research area was covered with a mesh of a density of 1 sample per km^2. In densely populated urban areas the mesh density was increased. A group of 115 sample points were defined. At each point, a sample of soils and a sample of attic dust are taken.
Attic dust samples are brushed from the parts of wooden roof construction that were not in contact with roof tiles or floor. Soil samples were taken from a depth of up to 5 cm. Soils in gardens and green spaces along roads were sampled in towns, while pasture soils were sampled outside the populated areas.
All samples were air-dried. The size fractions of attic dust smaller than 0.125 mm are prepared for a chemical analysis by sieving. Soil samples are gently crushed then the fraction smaller than 2 mm was pulverized. 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 regia digestion (mixture HCl, HNO_3 and water at 95°C).

Results and Discussion

The major geochemical association consists of Al, Ba, Ce, Co, K, La, Li, Na, Nb, Rb, Sc, Th, Ti and V. High concentrations of those elements are characteristic for lower part of the Mežica valley, while lower values are significant for the attic dust. Their distribution results from natural processes, such as weathering of metamorphic and magmatic rocks. Contents of the above mentioned chemical elements in the sampling material oscillate, with some exceptions, within the Slovenian average.
High concentrations of the geochemical association Ca and Mg are characteristic for the carbonate rock areas in the upper part of the Meža valley. Concentrations of Ca and Mg (with the exception of the area around Ravne na Koroškem) exceed the Slovenian average for about four times.
Geochemical anomaly resulting from the production of lead shows high contents of Ag, As, Cd, Cu, Hg, Mo, Pb, S, Sb, Sn and Zn. Content of elements in the chemical association change according to the type of sampling material and .distance from the source of contamination. Contents in the soils of the lower Meža valley oscillate within the Slovenian average, while in the soils around Mežica, Žerjav and »rna they exceed the Slovenian average about four times. Anthropogenic source of the mentioned chemical elements is especially obvious in the case of attic dust. Contents of those chemical elements exceed the Slovenian average a few tenth times. The form of a pollution halo

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depends strongly on morphology, height above sea level and local winds. Highest contents of the mentioned chemical elements were found in the soils and especially attic dust in the areas around Žerjav and Črna. The main source of the geochemical anomaly was smelting of lead ore from the middle of the 17th century to the 1990-ies.
Geochemical association which was formed as a result of production of iron includes Co, Cr, Cu, Fe, Mn, Mo, Ni and W. The contents of those elements in soils are not higher than the Slovenian average, while the contents in attic dust exceed the Slovenian average for about four times. The area of heightened contents of Co, Cr, Cu, Fe, Mn, Mo, Ni, W includes the entire lower part of the Meža valley, and especially the areas around Prevalje and Ravne. The source of high contents of those chemical elements is, according to the shape of the halo, past and present metallurgic activity.