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Influence of Mining and Smelting on Chemical Composition of Soil around the Abandoned Pb Mine Sitarjevec and the Pb Smelter Litija

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Introduction

In the municipality of Litija, an abandoned mine Sitarjevec and a few smaller mines are situated scattered in the hills of the river Sava and form a productive mining field, about 10 km^2 wide. Mining in this region began in the Roman period, which is proven by archaeological artefacts. From the middle ages to 1965, with a small interruption, Pb, Zn, Hg, Ag ore and mineral barite had been produced in this region. We assumed that mining and processing of those metals had noticeable influence on the environment. The aim of the presented study was to calculate the rate of progressing soil pollution with heavy metals as a consequence of mining and smelting.

Materials and Methods

The study area (30 km^2) is covered by a soil sampling grid 500 by 500 m (120 sampling locations). In each point, samples of topsoil (0-5 cm) and deeper soil horizon (20–30 cm) were collected. The methods of sampling, sample preparation and analyses of the results were consistent with the recommendation of the IGCP and FOREGS geochemical mapping project. 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) were performed by means of inductively coupled plasma mass spectrometry (ICP-MS) after four-acid digestion. Hg was determined with cold vapour atomic absorption spectrometry CV-AAS after aqua regia digestion.

Results and Discussion

Two geogenic and two anthropogenic geochemical associations were established on the basis of: visually indicated similarity of geographic distribution of elemental patterns and with comparisons of basic and multivariate statistics (cluster and factor analyses).

The main geogenic association connects Ce, Cr, Fe, Hf, Nb, La, Th, Ti, Ta, U, V, W and Zr. Significant for geogenic geochemical associations are higher concentrations of elements in the dipper horizon of soil (20–30 cm) than in the topsoil (0–5 cm). High contents of those elements are characteristic of soils developed on the old Sava river terraces. The second group links Al, Ba, K, Li, Rb, and Sc. High concentrations of those elements is characteristic of carbonate claystones, while low concentrations is characteristic of carbonate sandstones.

For anthropogenic geochemical associations, higher concentration of elements in the topsoil (0–5 cm) then in the deeper soil horizon (20–30 cm) is significant. The geochemical association (As, Mo, Hg, Pb, Sb and Sn) is typical for past mining and smelting activities. The highest content of those metals is significant for the areas around the Pb mine Sitarjevec and former Pb smelter Litija. Low concentrations are characteristic for alluvial sediments of the river Sava. The second association links typical elements (Ca, Mg, Sr) for alluvial sediments of the river Sava and heavy metals (Cd, Co, Cu, Ni, Mn and Zn), which appear mainly as a consequence of ferrous metallurgy in the Jesenice area in the upper part of the Sava valley.

Our study was focused on toxic elements (Pb, Zn, Cu, As, Cd, Mo, Ni, Co, Cr and Hg), some of which are present in soil with the concentrations well above the global soil means. Pb, As and Hg, with topsoil medians of 120 mg/kg, 14 mg/kg and 0.35 mg/kg, respectively, exceeded the means for Slovenian soils. According to the Slovenian law and the New Dutchlist is the critical or action value of the analyzed elements exceeding in an area of 1.6 km^2. Pb pollution is the most significant.

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