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Environmental Impacts of the Abandoned Mercury Mine in Podljubelj (Slovenia)

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Introduction

The Podljubelj mercury mine is situated in the NW part of Slovenia, in a narrow Alpine valley next to the border between Slovenia and Austria (Figure 1). Geographically, the area belongs to the Southern Alps (Karavanke) and has an agitated morphology. The ore deposit is of hydrothermal vein type, developed as a consequence of Ladinian volcanism (DROVENIK et al., 1980). The ore appears in Anisian limestone, mostly as cinnabar in the form of small veins. The mine was first exploited as early as in 1557, and was finally abandoned in 1902. Total production of the mine was 110.000 tons of ore (360 tons of Hg). A smelter located close to the mine had been in operation since 1855. The waste material from the mine and the smelter was dumped in close vicinity of the mine. Total quantity of the waste has been estimated to 170.000 tons. Most of the material was used for the construction of the Ljubljana–Celovec (Klagenfurt) road which runs through the valley.

Materials and methods

63 samples of topsoil (0–5 cm) and 23 samples of subsoil (20–30 cm) were taken in six traverses in the wider area and within a research grid of 100 x 100 m in the narrow area of the mine and smelter (88 ha). 11 samples of stream sediments in a wider area of the mine were also collected. 7 samples were taken from the Mošenik creek, which flows through the valley in the direction N–S and the remaining 4 samples from Mošenik's tributaries. Each soil and sediment sample consisted of 5 sub-samples. The soil samples were gently crushed, then the fraction smaller than 2 mm was pulverized. In sediment samples we separated different fractions with dry sieving. Fraction smaller than 0,125 mm was analyzed. Analysis for 41 chemical elements 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 by means of cold vapor atomic absorption spectrometry CV-AAS after aqua regia digestion (mixture HCl, HNO_3 and water at 95°C). The reliability of analytical procedures was considered adequate for using the determined elemental contents in further statistical analyses. The universal kriging with linear variogram interpolation method (DAVIS, 1986) was applied to construct the maps of spatial distribution of particular elements in soil. For interpolation we considered 41 soil samples (0–5 cm) from the narrow area of the former mine and smelter.

Results

The Hg average in soil determined from analyzed samples amounts to 3.04 mg/kg with individual contents ranging between 0.17 and 719 mg/kg. In topsoil Hg concentrations vary from minimum 0.35 to maximum 244 mg/kg with the median of 3.67 mg/kg. The subsoil median is 1.39 mg/kg and individual values between 0.174 and 71.7 mg/kg. The highest determined value (719 mg/kg) was found at the area of former smelter. The concentrations of mercury in soils generally decrease with depth in soil profile and with the distance from the mine. The average enrichment factor in topsoil with respect to subsoil is 3.3. Average contents of Hg in topsoil exceeded the estimated average for soil in Slovenia, which is 0,065 mg/kg (ŠAJN, 2003), more than 56-times, in subsoil the estimated average was exceeded about 21-times. The areal distribution of mercury in soil (Fig. 1) shows that the mercury halo is limited to the immediate surroundings of the smelter, while away from it the contents rapidly decrease. On an area of about 9 hectares the Hg contents in soil exceed the Slovenian critical value for soil (10 mg/kg).

Examination of areal distributions reveals distinct distribution patterns also for Ca, Cd and P, as well as for additional 21 elements. Distributions of the latter may be divided in two groups that reflect the natural elemental distributions in dependence of geochemical composition of the local geology. Group 1 comprises the elements Zr, Th, Hf, K, Ce, La, Na, Rb, W, Ta, Nb, Al and Ba. Their combined distribution exhibits the highest values in the lowest parts of the studied area. The values decrease with altitude above the sea level. High group 1 element values are associated with the B horizon of brown soils on limestones and dolomites. Group 2 comprises the elements Sc, Cr, Ni, Co, Fe, Li, Ti and V. Their combined distribution is characterized by high values in hilly areas, there where the contents of group 1 ele-

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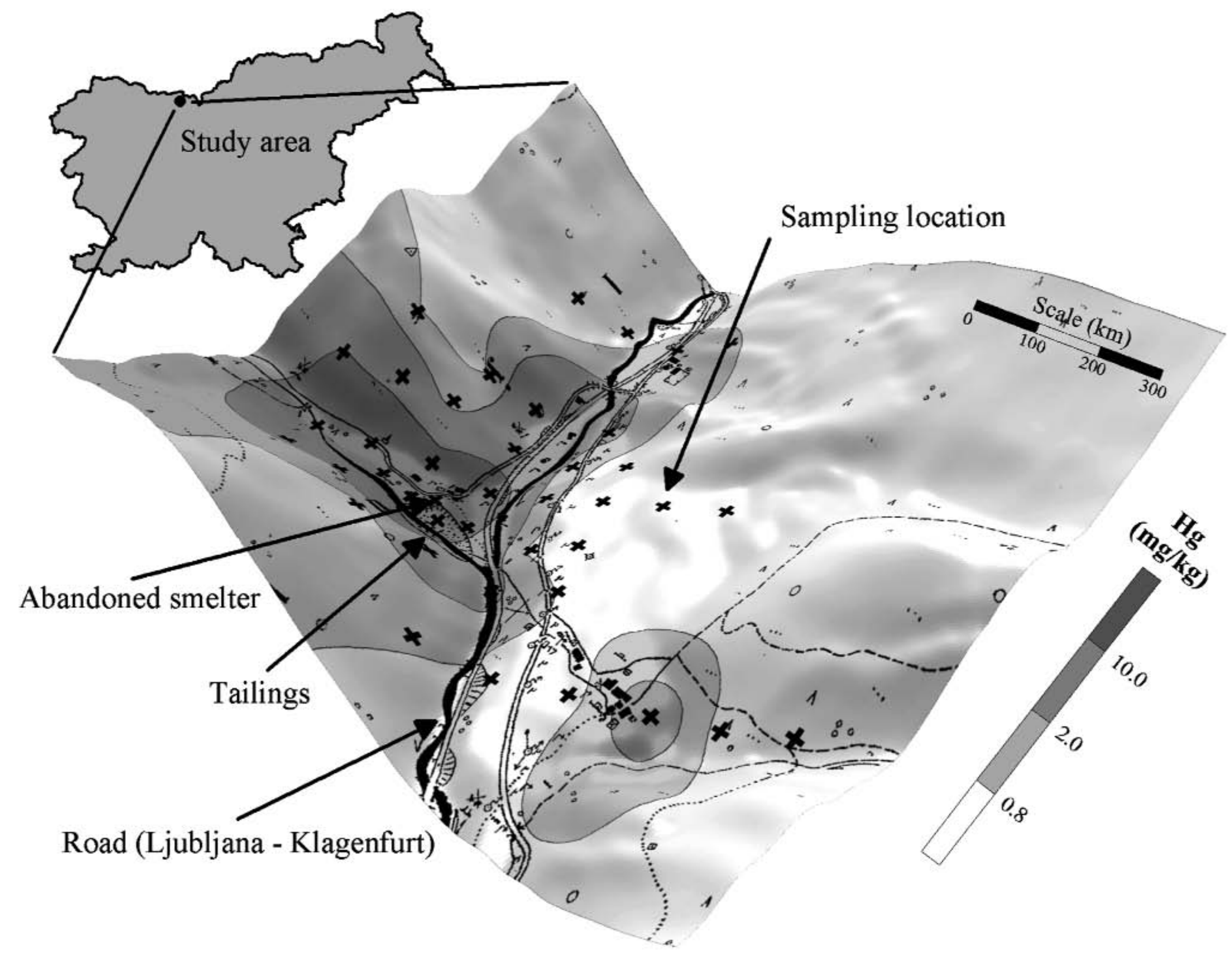

Fig. 1.
Areal distribution of Hg in topsoil.

ments are the lowest. Their contents increase with altitude above the sea level.

The estimated average of mercury in stream sediment is 0.64 mg/kg and values vary from minimum 0.065 to maximum 1.36 mg/kg. The highest Hg value was determined in a sample collected in the Potočnikov graben ravine, where the material from the dump of roasted ore remains is washed to the creek. The highest determined Hg value from the Mošenik creek was in the sample collected just downstream of the confluence of Potočnikov graben. Contents of Hg then consistently decrease downstream (Figure 2).

Discussion

High contents of Hg in soil around the abandoned smelter are a consequence of former atmospheric emissions from smelter and of other losses in the process of ore treatment. In addition, the soils at this site are humic to a high degree, which favours additional fixing of Hg in soil. Also in samples from the waste material dump the Hg concentrations are elevated. The source of mercury is here the soil substrate which consists of remains of roasted ore, low grade unroasted ore and barren rocks. The highest Hg content in soil from the dump (108 mg/kg) is almost 7-times lower than the soil contents at the smelter (719 mg/kg). As the recovery of roasting was only 55 % (MOHORIČ, 1957), roasted ore remains still contain appreciable mercury. Considering the primitive roasting technique at time of smelter operation the prevailing form of Hg in the roasting remains is most probably cinnabar. Soils along the Ljubljana–Celovec (Klagenfurt) road are also enriched with Hg, which is a consequence of the use of mining and smelter waste in the construction of the road. At the margins of the researched area and in the samples of stream sediments the Hg concentrations are low. No appreciable geogenic impact could be determined in any of the sampling locations. The relatively low Hg contents in stream sediment samples can probably be ascribed to the periodical nature of the creek that rapidly washes away the material from higher areas of outcropping mineralized rocks, and from the dumps of the mining waste. In the sampled material the proportion of the clayey-silty fraction, which is normally the main carrier of heavy metals, is very low. Pollution owing to mining is best expressed in the Potočnikov graben ravine and below the confluence of Potočnikov graben into the Mošenik creek, but farther downstream it rapidly dies off.

The impact of mining and processing of Hg on the environment is spatially limited. The contents of Hg are very high in the close vicinity of the mine and decrease with depth in soil profile and with distance from the source of pollution.

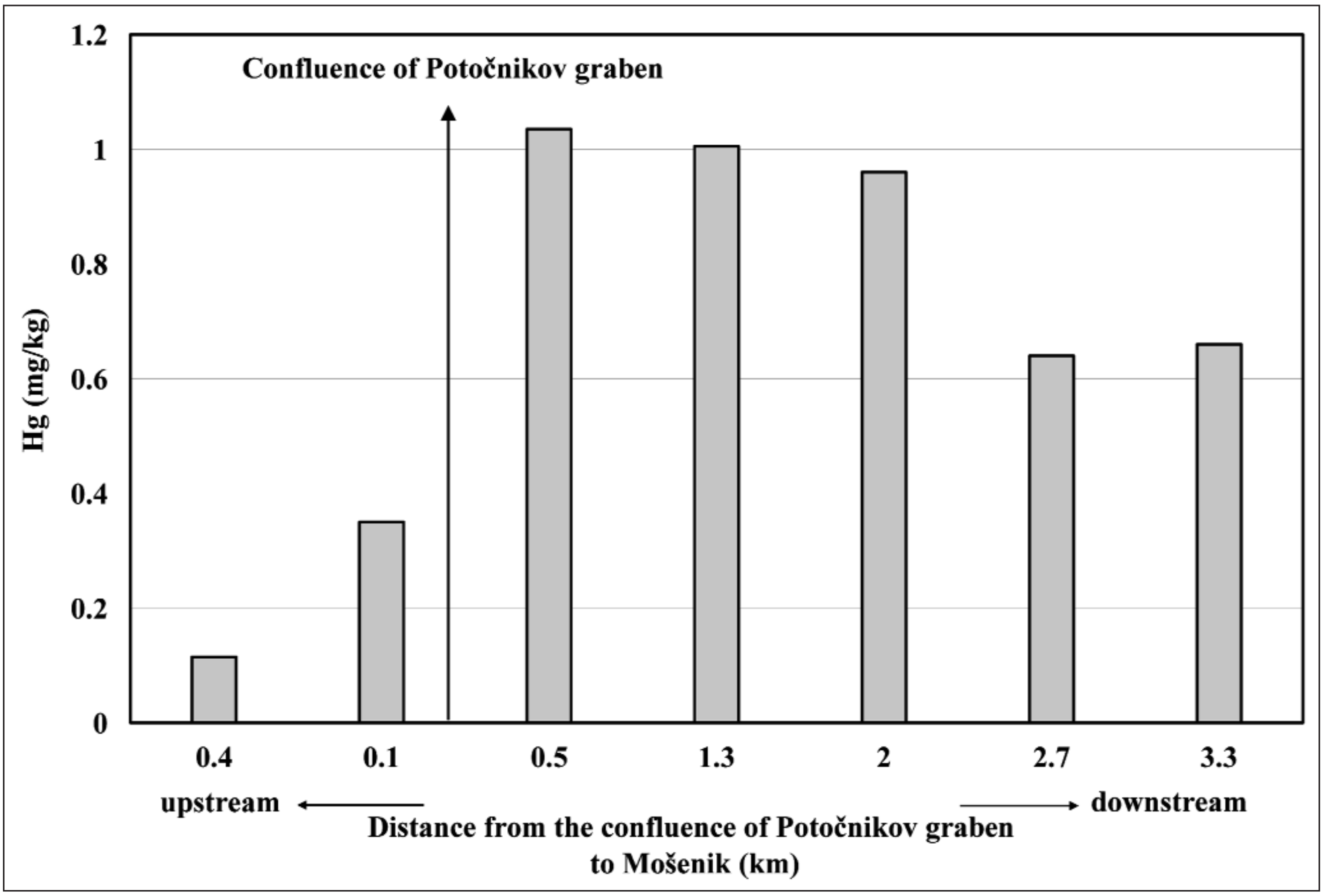

Fig. 2.
Mercury contents in sediments of Mošenik.

The wider area of the mine is not densely populated; therefore, high contents of Hg are not critical. Anomalous critical values of Hg are a potential threat only to population living in the close vicinity of the abandoned smelter.

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