ABANDONED METAL MINING IMPACTS – CASE STUDY PODLJUBELJ Hg MINE

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ABSTRACT

In the surroundings of abandoned mining and smelting locations environmental problems such as elevated metal concentrations in soils/sediments, dispersion of toxic metals in soil and water and ecological damage are observed. Physical remobilisation of abandoned tailings, waste piles, channel beds and heavy metal-contaminated floodplains (formed during historic mining activity) provide large amounts of metal contaminants to rivers. Because mining necessarily involves disturbing of previously stable formations, and may involve exposing large quantities of material to weathering processes, the environmental effects of mining activities can continue long after operations have ceased.

To asses environmental impacts of past mining and roasting activities in Podljubelj, concentrations of total mercury in soils and stream sediments were determined in the surroundings of abandoned Hg mine. It was established that on an area of about 9 hectares Hg contents in soil exceed the Slovenian critical value for soil (10 mg/kg). Total mercury concentrations in soil samples vary between 0.17 and 719 mg/kg, with the mean of 3.0 mg/kg. Mercury contents in stream sediments range from 0.065 to 1.4 mg/kg, with the mean of 0.64 mg/kg. The highest determined value in soils was found at the area around the former roasting furnace, where the ore was processed. Elevated contents of Hg were also found on the mine waste dump (108 mg/kg). Mercury contents in soils generally decrease with depth in soil profile and with the distance from the mine and roasting furnace. Mercury also appears in higher concentrations along the road that runs through the valley, which is due to the use of Hg bearing ore residues in road construction.

Key words: mining impacts, mining waste, mercury, soil, stream sediments, Podljubelj.

INTRODUCTION

Metals are one of the foundations for the development of our present society. In addition, many metals are essential for life functions (Salomons, 1995). Since ancient times mining has had a large impact on society. Wars have been fought to acquire minerals. Slavery has been built around mining sites because a lot of labour force was needed for mining. Colonialism in many parts of the world was in part due to the need of Europe to acquire the metals to feed the factories of the industrial revolution.

Today, we are aware of the fact that mining and processing of metal ores can be important causes of environmental degradation. Depending on the efficiency of the recycling of

metals, metals initially released by mining activities end up after a number of years in the various compartments of the surface layer of the Earth. When they have been released through the atmosphere or into waters, they end up as diffuse pollutants in soils and sediments. Some of the metals are discarded with wastes and end up in waste disposal sites (Salomons, 1995).

Mining and beneficiation processes generate four categories of **large-volume waste** (Salomons & Förstner, 1988):

- mine waste (overburden, barren rocks)
- tailings
- dump heap leach
- mine water.

Mines produce large amounts of waste because the ore is only a small fraction of the total volume of the mined material (Dudka & Adriano, 1997). Surface mining generates more waste than underground mining. In surface mining, the amount of waste ranges from 2 to 10 times the total volume of crude ore. Tailings are produced from ore beneficiation. The crushed ores are concentrated to release ore particles (value) from the matrix of less valuable rock. Dump leaching, heap leaching and in situ leaching are the processes used to extract metals from low-grade ore. Dump leach piles often cover hundreds of square meters, which become waste after the process is finished. Heap leaching operations are much smaller than dump leach operations and last over a period of months rather than years. The mine water is water that infiltrates into a mine and must be removed to facilitate mining (USEPA, 1985 in Gosar, 2004).

In many areas worldwide present and historical mining and smelting activities are causing a variety of environmental problems such as elevated metal concentrations in soils/sediments, dispersion of toxic metals in soil and water and ecological damage caused by extensive metal pollution (Salomons, 1995; Gosar et al., 1997; Durn et al., 1999; Šajn et al., 2000; Astrom & Nylund, 2000; Vreča et al., 2001; Šajn, 2002; Horvat et al., 2003). Physical remobilisation of abandoned tailings, waste piles, channel beds and heavy metal-contaminated floodplains (formed during historic mining activity) provide large amounts of metal contaminants to rivers (Gosar et al., 1997; Biester et al., 2000; Hudson-Edwards, 2003). Because mining necessarily involves disturbing of previously stable formations, and may involve exposing large quantities of material to weathering processes, the environmental effects of mining activities can continue long after operations have ceased.

The aim of the investigation reported here was to evaluate the reflection of past mining activities in the increased Hg contents in soils and sediments and to establish areal distribution of Hg in applied sampling materials in the narrow and wider area of the abandoned Podljubelj Hg mine.

Study area

Podljubelj mercury mine is situated in the NW part of Slovenia, in a narrow alpine valley near the border between Slovenia and Austria (Fig. 1). Geographically, the area belongs to

the Southern Alps (Karavanke) and has an agitated morphology. The ore deposit is located between 700 and 800 m above sea level in a narrow glacial valley. The prevailing soil types in the research area are rendzinas and chromic cambisols. In the close vicinity of the roasting furnace and mine entrances, thin skeleton soils are developed on top of mine waste dump.

The ore deposit is of hydrothermal vein type, developed as a consequence of Ladinian (T_2^2) volcanism (Drovenik et al., 1980). The ore appears in Anisian (T_2^1) limestone, mostly as cinnabar in the form of small veins (Dimkovski, 1972). The mine was first exploited as early as in 1557, and was finally abandoned in 1902. Because of small ore-bodies and low concentrations of Hg in ore (0.38 % to 0.40 %, Dimkovski, 1972), the mine hardly covered the operation expenses. The entire operating period yielded about 110,000 tons of ore, from which 360 tons of Hg was produced. A roasting furnace located close to the mine had been in operation since 1855. The waste material from the mine and the roasting furnace was dumped in close vicinity of the mine. Most of the material was used for the construction of the Ljubljana–Celovec (Klagenfurt) road which runs through the valley.

MATERIALS AND METHODS

26 topsoil samples (0–5 cm) and 23 subsoil samples (20–30 cm) were collected within a research grid of 100 x 100 m in the narrow area of the mine and roasting furnace (88 ha). Further 12 soil samples (0–5 cm) were collected in bigger distance from the mine and four additional soil samples were taken in the area of abandoned ore furnace and waste material dump. Soil samples locations are presented on Figure 1. Eleven stream sediment samples were also collected in the wider area of the mine. Seven samples were taken from the Mošenik creek which flows through the valley in the N–S direction, and the remaining 4 samples from Mošenik's tributaries. Each soil and sediment sample consisted of 5 sub-samples. The soil samples were air-dried and gently crushed in a ceramic mortar and passed through a sieve with 2 mm openings. Fraction smaller than 2 mm was pulverized before chemical analysis. Stream sediment samples were air-dried. The size fraction smaller than 0.125 mm was prepared for chemical analysis by dry sieving.

The samples were analyzed in the ACME laboratories in Vancouver, Canada. Analysis for 41 chemical elements (Ag, Al, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hf, Hg, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Ta, Th, Ti, S, Sb, Sc, Sn, Sr, U, V, W, Y, Zn, Zr) was performed by inductively coupled plasma mass spectrometry (ICP-MS) after the four-acid digestion (mixture of $HClO_4$, HNO_3, HCl and HF at 200ºC). Hg was determined by cold vapor atomic absorption spectrometry (CV-AAS) after aqua regia digestion (mixture HCl, HNO_3 and water at 95ºC). Quality assurance was carried out by shipment of samples, duplicates and geological standards GXR-2, GXR-5 in GXR-6 (Epstein, 1990) to the laboratory in a random succession to distribute evenly any errors due to laboratory performance. Objectivity was assured through the use of neutral laboratory numbers. The reliability of analytical procedures was considered adequate for using the determined elemental contents in further statistical analyses. A more detailed description of material and methods is presented in Teršič et al. (2006).

The universal kriging with linear variogram interpolation method (Davis, 1986) was applied to construct the maps of spatial distribution of particular elements in topsoil.

Also Hf-normalized enrichment factors (EF) of chemical elements in topsoil with respect to subsoil were calculated, and the soil enrichment factors with respect to Slovenian soil averages (0–5 cm; data after Šajn, 2003) (EF_{slo}). The enrichment factor permits to classify the chemical elements in sample materials with regard to their origin – natural or man produced (Fergusson & Kim, 1991). For calculation of enrichment factors (EF) the following equations were used:

$$EF = K_{(topsoil)} / K_{(subsoil)}$$

$$EF_{slo} = K_{(Podljubelj\ area)} / K_{(Slovene\ average)} \qquad K = element\ content / Hf\ content$$

RESULTS AND DISCUSSION

Soil

The Hg average in soil determined from analyzed samples amounts to 3.0 mg/kg with individual contents ranging between 0.17 and 719 mg/kg. Hg concentrations in topsoil vary from minimum 0.35 to maximum 244 mg/kg with the median of 3.7 mg/kg. In subsoil values are between 0.17 and 72 mg/kg with the median 1.4 mg/kg. The highest determined value, 719 mg/kg Hg, was found at the area of former roasting furnace where the ore was roasted for about fifty years, and the immediate surroundings were under strong influence of smoke emissions 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. Hg concentrations are elevated also in samples from the waste material dump. Here the source of mercury is 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 content at the roasting furnace. In other samples from the dump the contents are considerably lower (28 mg/kg and 11 mg/kg). Soils on heap dump are poorly developed soils on waste material. The content of organic matter is very low. In places they are overgrown by scarce tufts of grass, and in places barren, without vegetation. The content of larger pieces of unweathered material, composed of fragments of roasted and low-grade unroasted ore, is high. Differences of Hg contents on dump evidently depend upon the type of material sampled (barren rocks, low-grade ore, roasted ore). Low grade unroasted ore and barren rocks most probably contain very low mercury, mostly in the form of cinnabar. Large parts of the material on dump are remains of roasted ore. As the recovery of roasting was low (55 % according to Mohorič, 1957), the roasted ore remains still contain appreciable amount of mercury. Considering the primitive roasting technique at time of the smelter operation the prevailing form of Hg in the roasting remains is most probably cinnabar.

The areal distribution of mercury in soil shows that the mercury halo is limited to the immediate surroundings of the roasting furnace, while away from it the contents rapidly decrease (Fig. 1). On an area of about 9 hectares the Hg contents in soil exceed the Slovenian critical value for soil (10 mg/kg; Uradni list RS 68/96). The anomaly of critical values is of small extent and it presents a health hazard only for the community living in the immediate environs of the roasting furnace ruins.

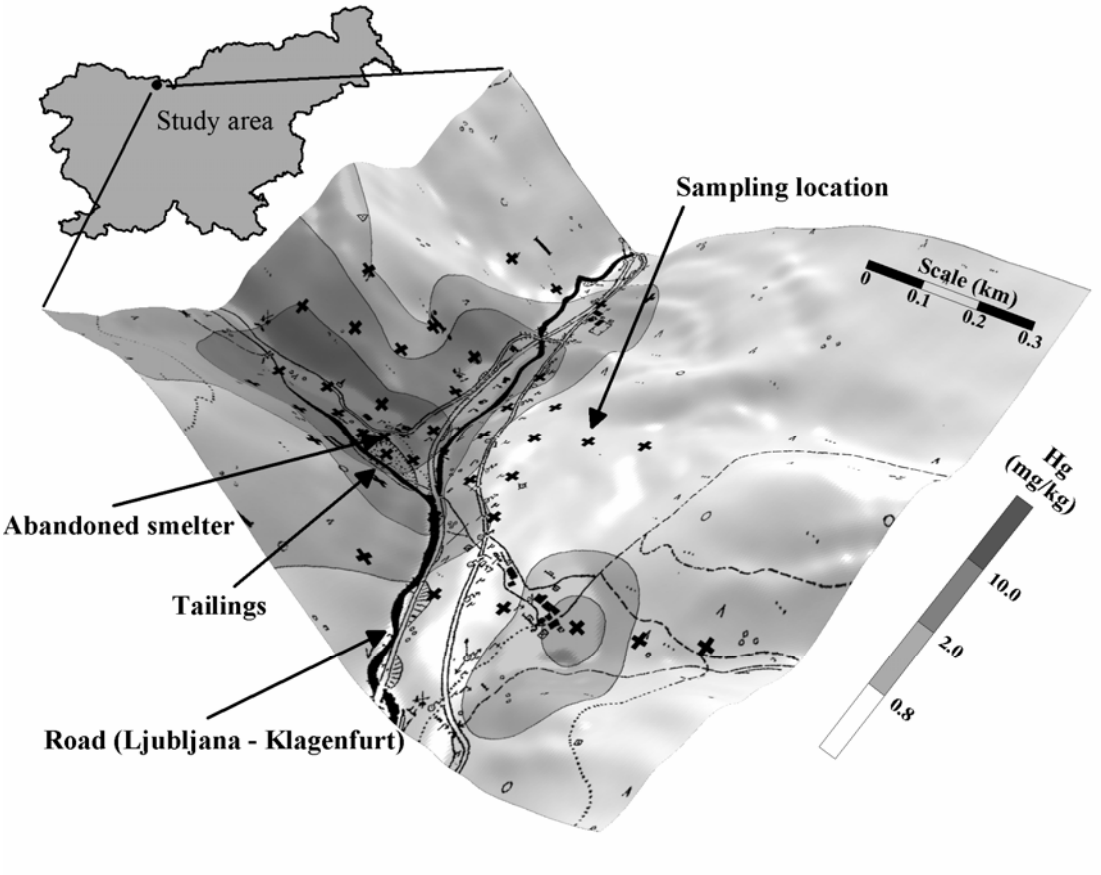

Figure 1.: Areal distribution of Hg in topsoil.

In most of the collected samples the Hg content is higher in topsoil than in subsoil. This indicates that increased Hg contents in soils are predominantly caused by anthropogenic pollution from mining and ore processing. At no sample site the determined Hg concentrations indicate any appreciable geogenic influence. The average enrichment factor in topsoil with respect to subsoil is the highest for Hg (3.3) followed by Cd (3.2), Pb (2.7), Ca (2.4) and P (1.9). These elements were largely anthropogenically introduced. The lowest enrichment factors (1.0 and less) were calculated for the elements K, Sr, Zr, Co, Ta, Nb, Ti, Rb, Ce and Fe.

The average enrichment factor in studied soils with regard to the established Slovenian soil averages (Šajn, 2003) is the highest for Hg, amounting to 19 for topsoil and 13 for subsoil. Enrichment factors of other determined elements do not exceed 3.0. In topsoil Hg is followed by the elements Mo (2.9), Sr (2.3), Cd (2.07), Ca (1.7), U (1.5), Pb (1.3) and Sb

(1.1), and in subsoil by Mo (2.6), Sr (2.1), U (1.3) and Zr (1.1). The enrichment factors for all other determined elements are lower than unity (Fig. 2). These values of enrichment factors with respect to Slovenian averages do not indicate appreciable anthropogenic influences except for Hg which is highly enriched owing to mining activities.

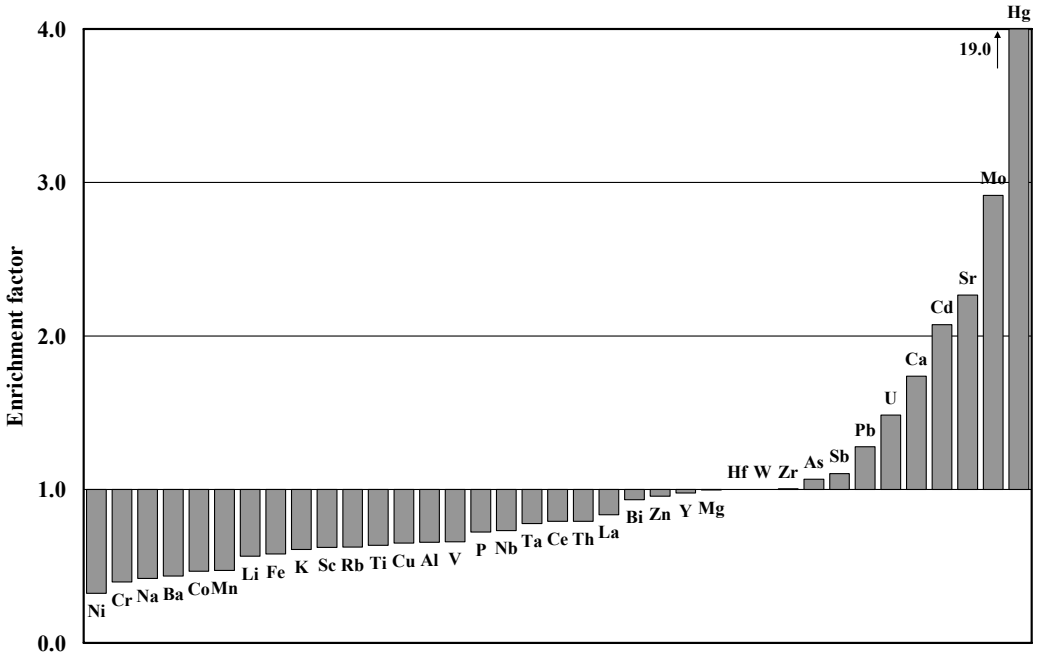

Figure 2.: Average enrichment factors of elements in topsoil with regard to Slovenian averages of elements in soil (values are normalized on Hf).

Sediments

The estimated average of mercury in stream sediment is 0.64 mg/kg and values vary from 0.065 to 1.4 mg/kg. The highest Hg value was determined in a sample collected in the ravine of Potočnikov graben, where the material from the dump of roasted ore remains is washed to the creek. During operation of the mine a part of the dumped material was discharged most probably directly into 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. Mercury contents in sediment samples of Mošenik creek are presented in Figure 3.

Contents of determined elements in stream sediments of the studied area are generally lower of the estimated elemental averages in soil and stream sediments of Slovenia. Somewhat enhanced are only the values for Hg, Ca and Mg. Enhanced Ca and Mg are caused by geology of the area which consists prevailingly of carbonate rocks. The enhanced Hg contents in stream sediments of the studied area are the consequence of a higher natural background as well as of the anthropogenic influence. Pollution owing to mining is best expressed in the Potočnik graben ravine and below the confluence of Potočnik graben into the Mošenik creek, but farther downstream it rapidly dies off. In four collected samples the limit immission value for Hg in soil (0.8 mg/kg) is exceeded, but they are all below the

warning value of 2 mg/kg (Uradni list RS 68/96). 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 mining waste dumps. In the sampled material the proportion of the clayey-silty fraction, which is normally the main carrier of heavy metals, is very low.

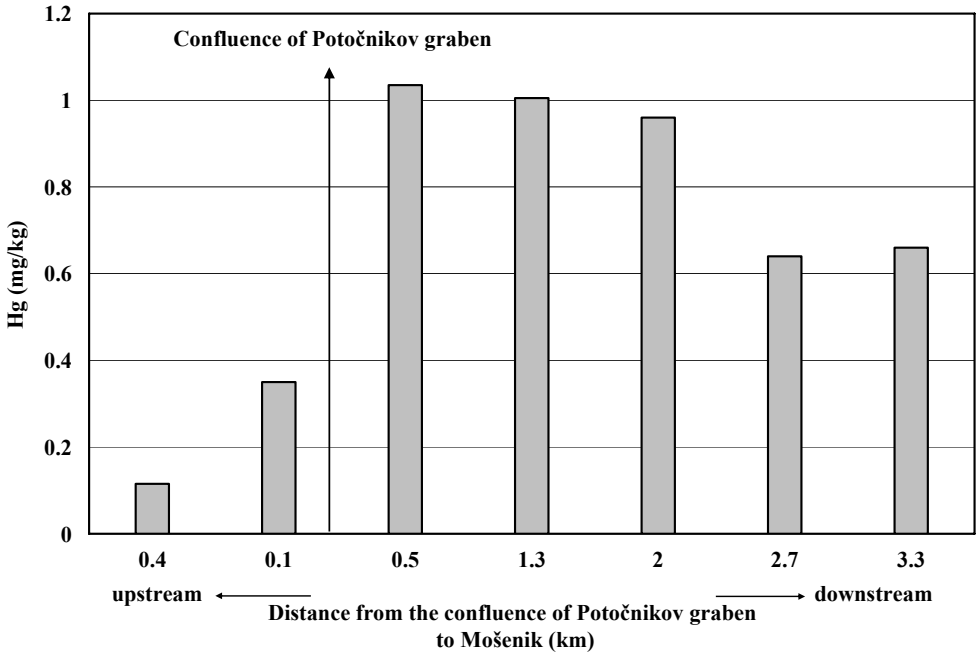

Figure 3: Mercury contents in sediments of Mošenik.

CONCLUSION

The environmental impact of mining and ore processing around Podljubelj mercury mine is spatially limited. The Hg contents are very high in the close vicinity of the past mining area and decrease with depth in soil profile and with the distance from the source of pollution. High contents of Hg in soil around the residues of abandoned roasting furnace are a consequence of former atmospheric emissions and technological losses. They are sustained by high proportion of organic matter in soils. Elevated contents of Hg were also found in soil on the mine waste dump. The highest determined Hg content in this area (108 mg/kg) is almost 7 times lower than the Hg content at the roasting furnace (719 mg/kg). As the recovery of the roasting process was only 55 % (Mohorič, 1957), the roasted ore waste still contains much Hg, mostly in the form of cinnabar. Soils along the Ljubljana–Celovec (Klagenfurt) road are also enriched in Hg, which is a consequence of the use of mining and roasted ore waste in the road construction. Elevated Hg contents in soil of the research area are mostly the consequence of anthropogenic activities. The average Hg enrichment factor in topsoil is 3.3 with respect to subsoil and 19 with regard to Slovenian soil averages. No appreciable geogenic impact could be determined in any of the sampling locations. At the margins of the researched area and in the stream sediments samples the Hg concentrations are low. The low Hg concentrations in stream sediment samples are the result of rapid

washing off of the material from mining waste dumps and from higher areas of outcropping mineralized rocks down the Potočnikov graben and Mošenik creeks.

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

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