Mercury enrichments in soils influenced by Idrija mercury mine, Slovenia

Živo srebro v tleh na širšem vplivnem območju rudnika v Idriji, Slovenija

Mateja Gosar[1,]* Tamara Teršič[1]

[1]Geological Survey of Slovenia, Dimičeva 14, SI-1000 Ljubljana, Slovenia

*Corresponding author. E-mail: mateja.gosar@geo-zs.si

Received: September 14, 2012 **Accepted:** September 19, 2012

Abstract: Presented investigations confirmed that soils in the wider Idrija surroundings are highly enriched with mercury. The most important sources of mercury in soils for wider Idrija area were atmospheric emissions from the roasting plant. Hg gasses and dust particles have spread far into the Idrija environs. Mercury is therefore present in soils at localities far from the outcrops of ore-rich rocks. Some other small but extremely contaminated areas were identified in the woods of the Idrija environs, where ore roasting was performed in the 16th and 17th century. In the Idrija urban area there are mutual mercury impacts on the environment from the atmosphere and the soil parent material. Mercury-rich parent material in the city of Idrija is the bedrock of Pront-area, where ore-bearing rocks containing native mercury and cinnabar crop out. Additionally, mercury is present in soils developed on ore and roasting wastes dumped along the banks of the Idrijca River in the city area. In the lower Idrijca Valley the floodplain soils are contaminated with Hg because most roasted ore residues were dumped into the Idrijca riverbed and washed away because of the torrential nature of the Idrijca River and some of this mercury enriched material was deposited on the floodplains.

Izvleček: Predstavljene raziskave potrjujejo, da so tla v širši okolici Idrije močno obremenjena z živim srebrom. Najpomembnejši vir živega srebra so bile med predelovanjem rude atmosferske emisije. Pri žganju rude je nastajalo veliko prašnih delcev in plinov, ki so obremenjevali širšo okolico pražarne rude in povzročili nastanek izjemno velike

Review paper

avreole živega srebra. Ugotovljena so bila tudi številna majhna, toda izjemno onesnažena mesta v gozdovih v okolici Idrije, kjer so v 16. in 17. stoletju žgali rudo v lončenih žgalnih posodah. Ugotavljamo, da so bila žgalniška območja pomemben vir onesnaženja okoliških ekosistemov z živim srebrom. V urbanem okolju Idrije so delovali na okolje vzajemni vplivi zračnega nanosa in talne podlage. Vir živega srebra na območju Pronta, kjer izdanjajo kamnine, ki vsebujejo samorodno živo srebro in cinabarit, je kamninska podlaga. Nadalje so v mestnem jedru tla razvita na deponijah prežgane rude vzdolž brežin reke Idrijce. Ker so med največjo proizvodnjo večino žgalniških ostankov vsipavali v strugo Idrijce in je bil ta material zaradi hudourniške narave reke prenesen v nižje predele, pa so vsebnosti živega srebra povišane tudi na poplavnih ravnicah v spodnjem toku Idrijce.

Ključne besede: soil, mercury, mining, Idrija, pollution
Key words: tla, živo srebro, rudarstvo, Idrija, onesnaženje

INTRODUCTION

Contamination of the Earth's ecosystems by potentially toxic metals is a global problem. It will probably grow with our planet's increasing population and their requirements for natural resources (SIEGEL, 2002). There are several sources of metals in the environment, both natural and manmade. The natural sources of metals in environment lie with the rocks and processes by which they formed and which affected them after lithification. High values of metals are found, for example, in mineralized areas and in areas where the dominant bedrock is rich in metals as, for example, in black shale. The presence of elevated levels of organic matter in an anoxic environment at the time of sediment deposition was responsible for concentrating anomalous amounts of metals. Volcanic emissions and forest fires are natural springs of some metals in the atmosphere (gases, aerosols, particulates) and after they precipitate they become part of the near-surface ecosystems. There are many anthropogenic sources in the environment: coal combustion residues, mining, metal-smelting industries, car emissions, military actions (PIRC & BUDKOVIČ, 1996; GREIČIUTE et al., 2007; IDZELIS et al., 2006) and primary input sources in agro-ecosystems (fertilizers, liming materials, sewage sludges, pesticides, irrigation water) (ADRIANO, 1986).

The mining and metal industry can be an important source of trace elements in the environment from (a) the mining and milling operations with problems of grinding, concentrating and transporting ores, and disposal of tails along with mine and mill waste water and (b) the smelter-refinery process with problems of concentrate, haulage, storage, sintering, atmospheric discharges and blowing dust (Adriano, 1986; Dudka & Adriano, 1997; Jordan, 2009). The proportion of trace elements releases into environment depends on ores being processed. Mining itself affects relatively small areas. It is the tailings and waste rock deposits close to the mining area that are the source of the metals (Hoskin et al., 2000). The impacts of atmospheric discharges (gaseous and particulate matter emissions) from smelters can be detected within several kilometres from the point of release. 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 (Kesler, 1994).

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. Because ore is only a small fraction of the total volume of mined material, ore extraction, beneficiation processes and further processing of ores produce large amounts of waste which can contain metals or chemicals from manufacturing processes (Siegel, 2002). The environmental concern in mining areas is primarily related to mechanical damage of the landscape and acid mine drainage (AMD). The trace element uptake from contaminated soils and direct deposition of contaminants from the atmosphere onto plant surfaces can lead to plant contamination by trace elements. These results in plant toxicity and a potential transfer of contaminating elements along the food chain exist (Dudka & Adraiano, 1997).

In context of long and intensive history of metal mining in Slovenia, it is clear that many older mining operations started at a time when there was little concern for the surrounding environment. The impact of long history of mining and metallurgy was intensively investigated in the last decade. It was established that, in Slovenia, mining and ore processing represent one of the major modes for anthropogenic input of metals into the environment. One of the most important districts influenced by metal mining and ore processing in Slovenia is the area around Idrija mercury mine, where half a millennium of mercury production is reflected in increased mercury contents in all of its environmental segments.

Mercury with its unique physicochemical properties is highly toxic and more

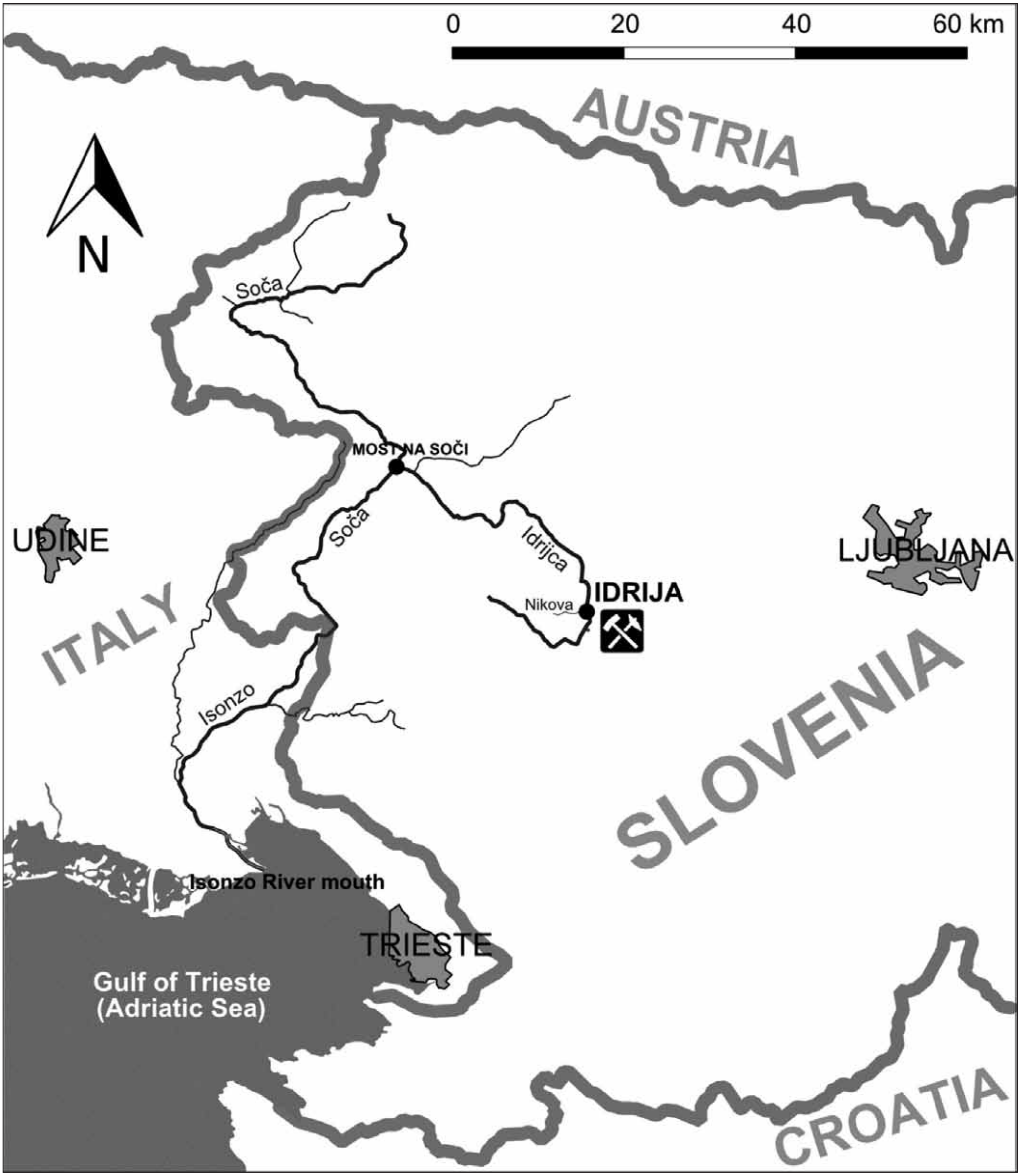

Figure 1. Map of study area

dangerous for living organisms than most other trace elements. It is regarded as a global pollutant. The outbreak of mass poisoning with this metal in the second half of 20th century (Minamata and Niagata in Japan, Iraq) warned the world about the danger of intoxication and mercury came into the focus of environmental investigations all around the world. Interest also arose at Idrija area, and pioneer's investigations on influence of mercury production on the environment were conducted (Byrne & Kosta, 1970; Kosta et al., 1974; Dermelj, 1974; Kavčič, 1974). After that investigations at Idrija area ceased for about 20 years.

In the last two decades numerous extensive and detailed investigations on mercury emissions, distribution, deposition, speciation and pollution in general were performed in Idrija region determining an unprecedented legacy of mercury contamination (Gnamuš, 1992, 2002; Hess, 1993; Palinkaš et al., 1995; Gosar, 1997; Gosar et al., 1997a, 1997b, 2006; Biester et al., 1999, 2000; Horvat et al., 1999, 2003; Dizdarević, 2001; Gnamuš et al., 2000; Gosar & Šajn, 2001, 2003; Gosar & Žibret, 2011; Kocman et al., 2004, 2011a, 2011b; Gosar & Čar, 2006; Hines et al., 2006; Žibret & Gosar, 2006; Gosar, 2008; Kocman & Horvat, 2010; Teršič et al., 2011a; Teršič et al., 2011b; Gosar & Žibret, 2011; Gosar & Teršič, 2012). Idrija and its surroundings are heavily polluted with Hg due to naturally increased mercury contents in mineralized rocks, mining and ore processing. During the operation period of the mine 107 692 t of mercury were produced. Taking into account the losses during mining and inefficient roasting process, the total amount of mercury mined is estimated to be at least 144 725 t (Mlakar, 1974; Miklavčič, 1999; Cigale, 2006). It has been estimated that 37 033 t of mercury were emitted into the environment during the operation period of the mine that ceased production in 1995 (Cigale, 2006).

In this paper environmental geochemistry studies of soils in the area of Idrija (Figure 1) which were performed at the Geological survey of Slovenia together with collaborating partners in the last 20 years are presented. This paper is dedicated to our honoured professor dr. Simon Pirc, who taught us geochemistry and to professor dr. Jože Čar who gave us basic knowledge and the idea of studying old roasting sites in Idrija area.

Materials and methods

The soil samples were air-dried, afterwards gently crushed in a ceramic mortar and passed through a sieve with 2 mm openings. The soil fraction smaller than 2 mm was pulverised before chemical analyses. The powdered soil samples were submitted for chemical analysis to ACME Analytical Laboratories in Vancouver (Canada) accredited under ISO 9001:2000. After aqua-regia digestion (1 hour, 95 °C) mercury was analysed eighter with Cold Vapor Atomic Absorption Spectrometry (CVAAS) (up to year 2008) or with inductively coupled plasma mass spectrometry (ICP-MS). Samples with more than 50 mg/kg Hg were analyzed with ICP emission spectrometry (ICP-ES).

The accuracy and analytical precision of the analytical methods were verified against standard reference materials (standards GXR-2 (Park City, Summit Co., Utah), GXR-5 (Somerset Co., Maine), GXR-6 (Davidson Co., North Carolina) and SJS-1 (San Joaquin Soil)) and duplicate samples in each analytical set. The shipment of samples, duplicates and geological standards to the laboratory was carried out in a random succession to distribute evenly any errors due to laboratory performance. This procedure ensured an unbiased treatment of samples and a random distribution of possible drift of analytical conditions for all samples. Objectivity was assured through the use of neutral laboratory numbers.

Geochemical mapping

Geochemical soil mapping was performed during summer months of the years 2000 and 2001. In the most polluted areas, such as Idrija and Spodnja Idrija, an average of samples 4/km^2 were taken, whereas in more distant areas sampling density was approximately 1/km^2. There were 100 soil samples collected (0–15 cm) in an area of 160 km^2 (GOSAR & ŠAJN, 2001, 2003; GOSAR et al., 2006). The results revealed the highest median (47 mg/kg) in Area 1, which includes the towns of Idrija and Spodnja Idrija, and the Idrijca River valley between them. Median in the intermediate Area 2 was 3.2 mg/kg and in the most distant Area 3 1 mg/kg (GOSAR et al., 2006). It was established that on 19 km^2 Hg contents in soil exceed the The New Dutchlist action value for Hg (10 mg/kg; MHSPE, 1994) which is also the critical values according to Slovenian legislation (Uradni list RS – Official Gazette RS, 1996). Spatial distributions of mercury contents in soil depended very much upon the morphology of terrain (GOSAR & ŠAJN, 2001, 2003; GOSAR et al., 2006). We can come to the conclusion that the pollution is primarily related to the River Idrijca Valley, while the effect on the farther surroundings is less significant, but still important. It is of most interest to compare the Hg contents in samples taken higher or lower than the main exhaust stack of the roasting factory. The average of Hg in soil, which lies in lower altitudes than the main exhaust stack is 42 mg/kg. In higher altitudes the average is 2.8 mg/kg. High values occur in the Idrijca River valley and at the base of slopes, while lower values prevail at higher elevations and at margins of the investigated area (GOSAR et al., 2006). Strong relationship between the Hg contents in soil and between height above sea level and the distance from the smokestack of the roasting plant, which was the main anthropogenic source of mercury, was determined. Also Hg contents in soils along the Idrijca River depend mostly on the distance from the source of pollution, shape of the valley and local winds blowing along the valley. The highest concentrations were found near the source of pollution, i.e. the smokestack of the roasting plant and they decrease exponentially down the valley. Exceptions are alluvial soils which will be presented in paragraph "Contaminated floodplain soil". With geochemical mapping results we proved that the influence of atmospheric emissions caused by the Idrija roasting plant resulted in impacts on the environment on a regional scale (Gosar et al., 2006).

The results of Hg thermo-desorption measurements showed the presence of the cinnabar- and non-cinnabar-bound Hg. Metallic mercury was not detected (Gosar et al., 2002; Gosar et al., 2006). In the total researched area the weighted average of total cinnabar-bound Hg in soils was 18 %. The highest median (49 %) was identified in Area 1. The portions of non-cinnabar compounds increased with the distance from the mercury source. It has been assumed that there were two different transport mechanisms of dust particles and gaseous Hg^0 during the mercury production period. Coarse-grained particles with mostly cinnabar-bound Hg settled in the immediate vicinity of the smokestack of the roasting plant, whereas the fine grained fraction could be dispersed further ahead. As a consequence, fine grained material with Hg^{2+} and Hg^0 prevails in remote localities and is bound to soils with matrix and organic matter (Gosar et al., 2006).

Contaminated floodplain soil

Besides soil pollution by atmospherically derived mercury, considerable areas with polluted floodplain soils were identified in the areas of the Idrijca and Soča River Valleys. During mining history of the area, considerable amounts of mercury-bearing ore residues and roasting residues were spilled into the River Idrijca. This mercury-rich material was washed away because of the torrential nature of the Idrijca River and some of this material was deposited on the floodplains in the lower part of the Idrijca and Soča River valleys, thus building a large accumulation of mercury-enriched floodplain soils (Gosar et al., 1997b; Gosar, 2008; Žibret & Gosar, 2006: Gosar & Žibret, 2011).

Studies of mercury speciation in sediments and soils from floodplains (Biester et al., 2000) indicated the occurrence of cinnabar and matrix-bound Hg compounds. Accumulation of cinnabar predominately occurred in coarse grained river sediments. In contrast, non-cinnabar Hg was found enriched in areas where fine grained material was deposited reaching up to 40 % of Hg $_{tot}$ (1–60 mg/kg) in floodplain soils (BIESTER et al., 2000).

In continuation the influence of geomorphological factors on the Hg contamination of the Idrijca River alluvial sediments was studied (ŽIBRET & GOSAR, 2006; GOSAR & ŽIBRET, 2011). According to our expectations, floodplains were found to be the most contaminated unit (mean Hg content 335 mg/kg). On the first terrace the identified mean Hg concentration was 155 mg/kg. The least contaminated material was found in the higher terraces (3.8 mg/kg), which most probably reflect only atmospheric influences of the Idrija mercury mine area. Mapping of the Idrijca River terraces was performed in order to estimate the volume of the identified geomorphological units. For the determination of mercury concentrations, the alluvial sediments on different levels were sampled and the analysis of variance was performed. The results showed that the concentration of Hg varies the most between the floodplain and terraces inside the same alluvial plain, but does not change significantly in relation to the distance from the source of pollution, neither in relation to the position inside one terrace or floodplain nor the depth. It was estimated that about 2000 tons of mercury have been stored in the Idrijca River alluvial sediments (ŽIBRET & GOSAR, 2006).

Historical mercury-ore roasting sites

In last couple of years interesting historical small-scale mercury-processing sites, which are non-uniformly distributed in the surroundings of Idrija, have become the subject of our investigations. In 2005 ČAR and TERPIN published interesting paper about different ways of ore roasting techniques in the first 150 years (16th and first half of 17th century) of mercury production in Idrija. They found numerous localities of historical ore roasting sites in the woods around Idrija, where large quantities of broken pottery in which Hg ore was roasted, can be found. Up to now, 21 localities of ancient roasting sites were established on the neighbouring hills and in more distant localities. They also found very interesting and old literature (GRUND, 1911) reporting mercury contamination at the Pšenk ancient ore roasting area that was discovered during cutting down old spruce-trees in the beginning of the 20th century. GRUND (1911) reported that 0.6 m thick layer of roasting vessels fragments was found, which was investigated in detail. In three of the reduced grouped samples, 0.7 %, 0.45 % and 2.09 % of mercury was found. A fragment of a certain earthen vessel contained 0.06 % of Hg, a small piece of recipient 4.92 % of Hg, and soil from one of the earthen vessels 0.52 % of Hg. It was calculated that more than 1850 kg was present at the Pšenk locality (GRUND, 1911).

At the beginning of mercury production in Idrija the technology of excavation and ore processing were very simple. The excavated ore was roasted similar as charcoal in piles and later in earthen vessels at various sites in the woods around Idrija (Valentinitsch, 1981; Čar & Terpin, 2005; Kavčič, 1993, 2008). The ore roasting in earthen vessels lasted without any fundamental changes from 1510 to 1652. The major modification was done merely in 1580, when distilled lime began to be added to the ore in order to prevent the exhaled mercury to re-bind to HgS. At this method a suit of two earthen roasting vessels was used – the bigger upper, in the shape of longish gourd (*earthen vessel*), and smaller lower vessel (*receptacle*). The ore was transported to roasting sites which, due to felling large quantities of trees, were being set up at increasingly greater distances from mine pits. In this procedure, 1.5 kg of rich ore mixed with quicklime was placed in small clay vessels; the vessels were stopped with moss, placed neck downwards onto a receptacle, and their contacts smudged with clay. About 1000 vessels prepared in this way were placed on a piece of treaden ground encircled with stones, covered with sand or ash up to a height of 10 cm above the contact of lower and upper vessels, stacked with wood and ignited. As it grew hotter, the mercury evaporated from the upper vessel and accumulated in the lower, cooler vessel. After one day of burning and several days of cooling, the vessels were separated and the mercury was collected from the bottom vessel. As well as roasting in piles also roasting in earthen vessels gave a very poor yield and resulted in considerable losses. Because of the high temperatures usually a third of earthen vessels cracked during burning and mercury escaped from the vessels (Kavčič, 2008).

Our preliminary investigation of mercury contents in soils at old roasting site locations (Gosar & Čar, 2006) revealed that mercury contents in soils at these sites are very high, surpassing all up to that time described localities at Idrija and surroundings. It was estimated that there are about 40 t of mercury still present at ancient roasting sites (Gosar & Čar, 2006). We started detailed investigations on mercury contents in soils at 2 historical roasting site locations (Gosar & Čar, 2006; Teršič & Gosar, 2009; Teršič et al., 2008; Teršič, 2010, 2011; Teršič et al. 2011a; Teršič et al. 2011b). The main aims were to find out the extension of mercury pollution at old roasting sites and their significance for mercury dispersion locally and also in the wider Idrija area, to determine the contents and vertical distribution of mercury in soils and sediments and to establish the changes in mercury speciation with depth in the soil profile. As several anomalies were discovered during geochemical soil survey (GOSAR et al., 2006) where increased mercury contents could not be the consequence of main Hg sources such as atmospheric emissions, mineralized rock dumps and roasting residues or their use in construction, we wanted to find out if old roasting sites could be the reason for these anomalies.

At Frbejžene trate roasting site the organic matter-rich surface soil layer (SOM) and underlying mineral soil were sampled at 63 sampling locations on an approximately 300 m × 250 m area. The results indicate extremely high Hg concentrations with a maximum of 37 000 mg/kg in SOM and 19 900 mg/kg in mineral soil. The established Hg median in soil was 370 mg/kg and in SOM 96.3 mg/kg. Spatial distributions of Hg in SOM and soil showed very high Hg contents in the central investigated area which decrease rapidly with the distance from this area. The New Dutchlist action value for Hg in soil (10 mg/kg; MHSPE, 1994) was exceeded in soil (5–20 cm) on approximately 95 % of the investigated area. The highest Hg contents were determined at a depth of 5–20 cm, and they decreased with depth in the soil profile. Mercury speciation was performed using Hg thermo-desorption-AAS to distinguish cinnabar from potentially bioavailable forms. The results of Hg thermo-desorption measurements indicated the presence of cinnabar (HgS) and Hg bound to organic or mineral soil matter. A significant portion (35–40 %) of Hg in the investigated soil and SOM samples was comprised of non-cinnabar compounds, which are potentially bioavailable. It has been shown that soils contain high amounts of potentially transformable non-cinnabar Hg, which is available for surface leaching and runoff into the surrounding environment. Therefore, contaminated soils and roasted residues at the studied area are important for the wider spatial contamination of soils and other environmental compartments (TERŠIČ et al., 2011a).

The other investigated ancient roasting site was the Pšenk site, where similar results were obtained. Detailed soil sampling was performed on 210 m × 180 m area to establish the extension of Hg pollution and to investigate Hg transformations and transport characteristics through the 400 year-long period. A total of 156 soil (0–15 cm and 15–30 cm) and SOM (soil organic matter) samples were collected from 73 sampling points. Three soil profiles were sampled to determine vertical distribution of Hg. The main Hg phases were determined by the Hg-thermo-desorption technique. The measured Hg contents in soil samples in the study area vary from 5.5 mg/kg to almost 9 000 mg/kg with a median of 200 mg/kg. In SOM, Hg contents are ranging from 1.4 mg/kg to 4 200 mg/kg with a median of 20 mg/kg. The New Dutchlist action value for Hg (10 mg/kg; MHSPE, 1994) is exceeded on approximately 82 % of the investigated area. Extremely high Hg contents were found in soil profiles where the metal reaches 37 020 mg/kg. In general, Hg concentrations in all three profiles show a gradual decrease with depth with the minimum values between 140 mg/kg and 1 080 mg/kg. The Hg-thermo-desorption curves indicate the presence of Hg in the form of cinnabar and that of Hg bound to organic or mineral soil matter. The distribution of Hg species in soil and SOM samples shows almost equal distribution of cinnabar and non-cinnabar Hg compounds. The non-cinnabar fraction shows a little increase with depth, however, cinnabar represents a high portion of total Hg (about 40 %). Large amounts of potentially mobile and transformable non-cinnabar Hg compounds exist at the roasting site, which are potentially bioavailable (Teršič et al., 2011b).

At roasting site Pšenk we also studied the applicability of earthworm casts as a sampling media for determining soil contamination (Teršič & Gosar, 2012). Earthworm casts were sampled at the same locations as soil and SOM samples. In general the Hg values determined in casts are slightly higher compared to the values in SOM and somewhat lower compared to the Hg contents in soil. Strong correlation between Hg contents in casts and soil was found. Spatial distribution of Hg in earthworm casts is similar to the Hg distribution in soil with somewhat smaller anomaly. For most of the analyzed elements, the determined contents were in the order of soil > cast > SOM, indicating that the material from casts is a mixture of material from soil and SOM. Only Ca, Mg, P, Sr, Cu and Zn contents were higher in earthworm casts compared to soil. Beside Hg, strong correlations between concentrations in casts and soil were found also for U, Cr, Ni and Mo. Earthworm casts proved to be an appropriate sampling media for determining soil contamination at this particular area (Teršič & Gosar, 2012).

Regarding the investigation of Hg distribution in soils of the wider Idrija area (Gosar et al., 2006), the determined Hg values of the studied roasting site areas are much higher. Compared to the established Hg median (3.2 mg/kg) and maximum (75 mg/kg) values for soils in the surroundings of Idrija town (Gosar et al., 2006), the Hg median in soils of the studied areas are about 100-fold higher and the maximum value was almost 300-fold higher (Teršič, 2010). However, it should be taken into account that the roasting sites are of a small size and that Hg contents in soils and SOM decrease rapidly with the distance from the source of pollution.

Microanalysis of contaminated soils and roasting vessels fragments using scanning electron microscope coupled with energy dispersive spectrometer (SEM/EDS) has been applied to better characterize the Hg-bearing species in investigated materials (Teršič, 2011). Mercuric sulphide (HgS) was found to be the main mercury compound present in the samples. Analysis of earthen vessels fragments showed abundant HgS coatings on the surface of ceramics, forming either crust-like aggregates on matrix or isolated grains. Some well-shaped grains with indicated structure and the size of up to 200 μm could also be observed. In soil HgS was present as powder-like concentrations scattered in soil samples, frequently coating silicate and quartz crystals and clay-minerals. Polycristalline, mercury- and sulphur- rich particles comprising silica, clay minerals and Al-, Fe- and Mg-oxides that were also observed in the samples were interpreted as soil aggregates infiltrated by mercuric and sulphur vapours and by liquid mercury spilled during roasting. These particles suggest a possible presence of mercury-sulphur associations other than HgS (Teršič, 2011).

Detailed geochemical surveys carried out at these two ancient roasting sites proved that the unique way of historical ore processing in the surroundings of Idrija resulted in extremely polluted sites which influence today's extension and spatial distribution of mercury in the Idrija area. Several Hg anomalies in sediments which were discovered in upper Idrijca River Valley (Gosar, 2008; Gosar & Žibret, 2011) and in the soils on the hills around Idrija (Hess, 1993; Gosar & Šajn, 2001; Gosar et al., 2006), where increased mercury contents could not be the consequence of main anthropogenic Hg sources, are now interpreted as a consequence of ancient ore roasting sites impacts.

Comparison of mercury contents in soils of the Idrija area to other mercury mining sites

The Idrija mine was the second largest mercury mine in the world being surpassed only by the Almadén mine in central Spain that has produced one-third of the total world production of mercury. As it was presented in this paper, five hundred years of intensive mercury mining activities in Idrija left a legacy of highly polluted environment. Idrija area can be compared to the Almadén area which is regarded as the largest geochemical anomaly of mercury on Earth. The district includes a series of mercury mineral deposits, having in common a simple mineralogy (dominant cinnabar, minor pyrite). The ore deposits have been mined for more than 2000 years, and the main mine of the district (Almadén), has been active from Roman times to pre-

Table 1. Hg concentrations in soils from mining contaminated areas worldwide

Location	Hg (mg/kg)	Reference
Idrija: historical mercury-ore roasting sites	3.4–19 900	Teršič, 2010, Teršič et al., 2011a; 2011b
Idrija: soil survey 160 km^2	0.3–973	Gosar et al., 2006
Idrija: alluvial soils in the Idrijca Valley	0.595– 1 970	Gosar & Žibret, 2011
Almadén district	6–8 889	Higueras et al., 2006
Mieres mining sites (N Spain)	1.7–2 224	Loredo et al., 1999
Mieres mining sites (N Spain)	54–29 304	Fernandéz-Martinez et al., 2006
Azogue Valley mining sites (SE Spain)	6–1 400	Viladevall et al., 1999
Andacollo Cu-Au-Hg mining district (Chile)	2.5–47	Higueras et al., 2004
Punitaqui Cu-Au-Hg mining district (Chile)	3.2–16	Higueras et al., 2004
Tongren district, Guizhou Province (China)	0.18–47	Li et al., 2008

sent day with almost no interruptions. The mercury distribution in soils of the Almadén district revealed the existence of high, and extremely high mercury values (6–8 889 mg/kg) (Higueras et al., 2003, 2006; Table 1). The soil contents in both districts are in the same range, but the contaminated area in the case of Idrija is much smaller. In both areas extremely contaminated areas of historical ore roasting are due to low recovery rate.

Highly elevated mercury contents were reported also from Mieres (northern Spain) by Loredo et al. (1999), who determined in soil samples near spoil heaps Hg values of up to 2 224 mg/kg. In continuation, extremely high Hg content (29 304 mg/kg) was reported from La Peña-El Terronal site (Mieres, N Spain) (Fernandéz-Martinez et al., 2006). Viladeval et al. (1999) report the contents of 6–1 400 mg/kg Hg in soils and overburden from a mineralized area in Azogue Valley (SE Spain) (Table 2).

Conclusions

Idrija certainly represents one of the areas where natural elevated mercury concentrations are technologically enhanced due to the 500 years long Hg mining, and therefore requires special attention. Presented studies have shown that Hg mining in Idrija caused intense pollution of local and regional soils. Although numerous studies have already been performed at Idrija mercury mining area, which have shown on complexity of mercury contamination problem, they also open new scientific questions and challenges for future work.

Acknowledgments

The presented research and preparation of paper are funded by Slovenian Research Agency (ARRS) in the frame of the research programme Groundwater and Geochemistry (P1-0020) and the research project Environmental geochemistry of metal contaminated sites (J1-2065) which are performed on the Geological Survey of Slovenia.

REFERENCES

ADRIANO, D. C. (1986): Trace elements in the terrestrial environment, *Springer-Verlag, New York, Berlin, Heidelberg, Tokyo*, 533 p.

BIESTER, H., GOSAR, M. & COVELLI, S. (2000): Mercury speciation in sediments affected by dumped mining residues in the drainage area of the Idrija mercury mine, Slovenia. *Environmental Science and Technology*. Vol. 34/16, 3330–3336.

BIESTER, H., GOSAR, M. & MÜLLER, G. (1999): Mercury Speciation in Tailings of the Idrija Mercury Mine. *Journal of Geochemical Exploration.* Vol. 65/3, 195–204.

BIESTER, H., GOSAR, M., COVELLI, S. (2000): Mercury speciation in Sediments affected by Dumped Mining Residues in the Drainage Area of the Idrija Mercury Mine, Slovenia. Environment Science Technology, Vol. 34/16, 3330–3336.

BYRNE, A. R. & KOSTA, L. (1970):Studies on the distribution and uptake of mercury in the area of mercury mine at Idrija, Slovenia. *Vestnik SK 17*. 5–11.

ČAR, J. & TERPIN, R. (2005): Stare žgalnice živosrebrove rude v okolici Idrije. *Idrijski razgledi, Idrija.* Vol. 50/1, 80–105.

CIGALE, M. (2006): Rudnik živega srebra Idrija od 1490 do 2006. In: B. Režun, U. Eržen, M. Petrič, I. Gantar (Eds.), 2. Slovenski Geološki Kongres, Zbornik povzetkov, *Rudnik živega srebra v zapiranju d.o.o., Idrija,* 13–16.

DERMELJ, M. (1974): Idrija spet v središču mednarodne pozornosti. *Idrijski razgledi, Idrija.* Vol. 19/3–4, 126–132.

DIZDAREVIČ, T. (2001): The influence of mercury production in Idrija mine on the environment in the Idrija region and over a broad area. *RMZ - Materials and Geoenvironment.* Vol. 48/1, 56–64.

DUDKA, S. & ADRIANO, D. C. (1997): Environmental impacts of Metal Ore Mining and processing: A Review. *Journal of Environmental Quality*. Vol. 2, 590–602.

FERNANDÉZ-MARTINEZ, R., LOREDO, L., ORDÓÑEZ, A., RUCANDIO, M. I. (2006): Physiochemical characterization and mercury speciation of particle-size soil fractions from an abandoned mining area in Mieres, Asturias (Spain). *Environmental Pollution.* Vol. 142/2, 217–226.

GNAMUŠ, A. (1992): Uporaba bioloških indikatorjev za spremljanje in ovrednotenje obremenjenosti kopenskih ekosistemov z živim srebrom, *B. Sc. thesis, University of Ljubljana, Biotechnical Faculty, Department of Biology, Ljubljana,* 160 p.

GNAMUŠ, A. (2002): Živo srebro v kopenski prehranski verigi – Indikatorski organizmi, privzem in kopičenje, *Institut »Jožef Stefan«, Ljubljana*.

Gnamuš, A., Byrne, A. R. & Horvat, M. (2000): Mercury in the soil-plant-deer-predator food chain on a temperate forest in Slovenia. *Environ. Sci. Technol*. Vol. 34/16, 3337–3345.

Gosar, M. & Šajn, R. (2001): Mercury in soil and attic dust as a reflection of Idrija mining and mineralization (Slovenia) = Živo srebro v tleh in podstrešnem prahu v Idriji in okolici kot posledica orudenja in rudarjenja. *Geologija.* Vol. 44/1, 137–159.

Gosar, M. & Šajn, R. (2003):Geochemical soil and attic dust survey in Idrija, Slovenia. *Journal de Physique.* Vol. 107, 561–564.

Gosar, M. (1997): Živo srebro v sedimentih in zraku na ozemlju Idrije kot posledica orudenja in rudarjenja = Mercury in sediments and air as a reflection of Idrija mineralization and minin, *Ph. D. Thesis, University of Ljubljana, Ljubljana*.

Gosar, M. (2008): Mercury in River Sediments, Floodplains and Plants Growing thereon in Drainage area of Idrija Mine, Slovenia. *Polish Journal of Environmental Studies.* Vol. 17/2, 227–236.

Gosar, M., Čar, J. (2006): Vpliv žgalnic živosrebrove rude iz 16. in 17. stoletja na razširjenost živega srebra v okolici Idrije = Influence of mercury ore roasting sites from 16th and 17th century on the mercury dispersion in surroundings of Idrija. *Geologija.* Vol. 49/1, 91–101.

Gosar, M., Teršič, T. (2012): Environmental geochemistry studies in the area of Idrija mercury mine, Slovenia. *Environ. geochem. health*, Vol. 34, suppl. 1, 27–41.

Gosar, M., Pirc, S. & Bidovec, M. (1997b): Mercury in the Idrijca river sediments as a reflection of mining and smelting activities of the mercury mine Idrija. *Journal of Geochemical Exploration.* Vol. 58, 125–131.

Gosar, M., Pirc, S., Šajn, R., Bidovec, M., Mashayanov, N. R., Sholupov, S. E. (1997a): Distribution of mercury in the atmosphere over Idrija. *Environment Geochemistry Health.* Vol. 19, 101–110.

Gosar, M., Šajn, R. & Biester, H. (2006): Binding of mercury in soils and attic dust in the Idrija mercury mine area (Slovenia). *Sci. total environ.* Vol. 369/1–3, 150–162.

Gosar, M., Šajn, R. & Biester, H. (2002): Zvrsti živega srebra v tleh in podstrešnem prahu na Idrijskem = Mercury speciation in soils and attic dust in the Idrija area. *Geologija.* Vol. 45/2, 373–378.

Gosar, M., Žibret, G. (2011): Mercury contents in the vertical profiles through alluvial sediments as a reflection of mining in Idrija (Slovenia). *Journal of Geochemical Exploration.,* Vol. 110/2, 81–91.

Grund, R. (1911): Geschichtliches aus Idria, *Berg und Hüttenwessen, Wien,* Vol. 59/34, 457–461.

Greičiūtė, K., Juozulynas, A., Šurkienė, G., & Valeikienė, V. (2007): Research on soil disturbance and pollution with heavy metals in military grounds. *Geologija.* Vol. 57, 14–20.

Hess, A. (1993): Verteilung, Mobilität

und Verfügbarkeit von Hg in Böden und Sedimenten am Beispiel zweier hochbelasteter Industriestandorte, *Heidelberger Geowissenschaftliche Abhandlungen, Heidelberg*.

HIGUERAS, P., OYARZUN, R., BIESTER, H., LILLO, J. & LORENZO, S. (2003): A first insight into mercury distribution and speciation in soils from the Almaden mining district, Spain. *Journal of geochemical exploration.* Vol. 80/1, 95–104.

HIGUERAS, P., OYARZUN, R., LILLO, J., SÁNCHEZ-HERNÁNDEZ, J. C., MOLINA, J. A., ESBRI, J. M., LORENZO, S. (2006): The Almadén district (Spain): Anatomy of one of the world's largest Hg-contaminated sites. *Science of the total environment.* Vol. 356/1–3, 112–114.

HINES, M. E., FAGANELI, J., ADATTO, I. & HORVAT, M. (2006): Microbial mercury transformations in marine, estuarine and freshwater sediment downstream of the Idrija Mercury Mine, Slovenia. *Applied Geochemistry.* Vol. 21/11, 1924–1939.

HORVAT, M., COVELLI, S., FAGANELI, J., LOGAR, M., FAJON, V., RAJAR, R., ŠIRCA, A., ŢAGAR, D. (1999): Mercury in contaminated coastal environments; a case study: the Gulf of Trieste. *Science total environment.* Vol. 237/238, 43–56.

HORVAT, M., KONTIĆ, B., KOTNIK, J., OGRINC, N., JEREB, V., LOGAR, M., FAGANELI, J., RAJAR, R., ŠIRCA, A., PETKOVŠEK, G., ŽAGAR, D. & DIZDAREVIČ, T. (2003): Remediation of mercury polluted sites due to mining activities. *Crit. rev. anal. chem*. Vol. 33, 291–296.

HOSKIN, W., BIRD, G. & STANLEY, T. (2000): Mining - facts, figures and environment. *Industry and environment.* Vol. 23, 4–8.

IDZELIS, R., GREIČIŪTĖ, K. & DAINIUS, L. P. (2006): Investigation and evaluation of surface water pollution with heavy metals and oil products in kairiai military ground territory. *Journal of Environmental Engineering & Landscape Management.* Vol. 14/4, 183–190.

JORDAN, G. (2009): Sustainable mineral resources management: from regional mineral resources exploration to spatial contamination risk assessment of mining. *Environ. Geol.* on line first, 17 p.

KAVČIČ, I. (1974): Kakšna je stopnja onečiščenosti zraka v Idriji. *Idrijski razgledi.* Vol. 19/1–2, 25–29.

KAVČIČ, I. (1993): Pridobivanje in uporaba živega srebra, In S. Bevk, J. Kavčič, I. Leskovec (Eds.) Idrijska obzorja, Pet stoletij rudnika in mesta, *Mestni muzej Idrija, Idrija,* 83–93.

KAVČIČ, I. (2008): Živo srebro: zgodovina idrijskega žgalništva = History of smelting in Idrija, *Založba Bogataj, Idrija*.

KESLER, S. E. (1994): Mineral resources, economics, and the environment, *Maxwell Macmillan International, New York,* 391 p.

KOCMAN, D., HORVAT, M. & KOTNIK, J. (2004): Mercury fractionation in contaminated soils from the Idrija mercury mine region. *Journal of Environmental Monitoring.* Vol. 6, 696–703.

KOCMAN, D., HORVAT, M. (2010): A laboratory based experimental study of mercury emission from contaminated soils in the River Idrijca catchment.

Atmospheric Chemistry Physics. Vol. 10, 1417–1426.

Kocman, D., Kanduč, T., Ogrinc, N., Horvat, M. (2011a): Distribution and partitioning of mercury in a river catchment impacted by former mercury mining activity. *Biogeochemistry*. Vol. 104/1–3, 183–201.

Kocman, D., Vreča, P., Fajon, V., Horvat, M. (2011b): Atmospheric distribution and deposition of mercury in the Idrija Hg mine region, Slovenia. *Environmental research*. Vol. 11, 1–9.

Kosta, L., Byrne, A. R., Zelenko, V., Stegnar, P., Dermelj, V. Ravnik, V. (1974): Studies on the uptake, distribution and transformations of mercury in living organisms in the Idrija region and comparative areas. *Vestnik SKD*. Vol. 21, 49–76.

Loredo, J., Ordóñez, A., Gallego, J. R., Baldo, C., Garcia-Iglesias, J. (1999): Geochemical characterization of mercury mining spoil heaps in the area of Mieres (Asturias, northern Spain). *Journal of Geochemical Exploration*. Vol. 67(1–3), 377–390.

Miklavčič, V. (1999): Mercury in the town of Idrija (Slovenia) after 500 years of mining and smelting, In: R. Ebinghaus, R.R. Turner, L.D. de Lacedra, O. Vasiljev, W. Salomons (Eds.), Mercury contaminated sites, *Springer-Verlag, Berlin,* 259–270.

Mlakar, I. (1974): Osnovni parametri proizvodnje rudnika Idrija skozi stoletja do danes. *Idrijski razgledi.* Vol. 19(3–4), 1–40.

Official Gazette – Uradni list RS, Uredba o mejnih, opozorilnih in kritičnih imisijskih vrednostih nevarnih snovi v tleh. *Uradni list*. 1996: 68, 5773–5774.

Palinkaš, L. A., Pirc, S., Miko, S. F., Durn, G., Namjesnik, K., Kapelj, S. (1995): The Idrija mercury mine, Slovenia, a semi-millennium of continuous operation: an ecological impact, In: Richardson, M. (ed.), Environmental toxicology assessment, *Taylor & Francis, London,* 317–341.

Pirc, S., Budkovič, T. (1996): Remains of World War 1 geochemical pollution in the landscape, In: Richardson, M. (ed.), Environmental xenobiotics, *Taylor & Francis, London,* 375–418.

Siegel, F. R. (2002): Environmental Geochemistry of Potentialy Toxic Metals, *Springer, Verlag Berlin, Heidelberg,* 218 p.

Teršič, T. (2010): Environmental influences of historical small scale ore processing at Idrija area, Ph.D. thesis, *University of Ljubljana, Ljubljana*.

Teršič, T. (2011): SEM/EDS analysis of soil and roasting vessels fragments from ancient mercury ore roasting sites at Idrija area. *Geologija.* Vol. 54/1, 31–40.

Teršič, T., Gosar, M. (2009): Preliminary results of detailed geochemical study of mercury at the ancient roasting site Pšenk (Idrija area, Slovenia). *Geologija.* Vol. 52/1, 79–86.

Teršič, T., Gosar, M. (2012): Comparison of elemental contents in earthworm cast and soil from a mercury-contaminated site (Idrija area, Slovenia). *Science of the Total Environment*, 430, 28–33.

Teršič, T., Gosar, M., Biester, H. (2008): Historical ore processing in Idrija: case study of a unique mercury waste disposal site. In: 18th Annual V.M. Goldschmidt Conference, Vancouver, 13–18 July 2008. Awards ceremony speeches and abstracts. *Geochimica et cosmochimica acta, 72, Amsterdam.* Vol. 12/1, A942p.

TERŠIČ, T., GOSAR, M., BIESTER, H. (2011a): Distribution and speciation of mercury in soil in the area of an ancient mercury ore roasting site, Frbejžene trate (Idrija area, Slovenia). *Journal of Geochemical Exploration.* Vol. 110, 136–145.

TERŠIČ, T., GOSAR, M., BIESTER, H. (2011b): Environmental impact of ancient small-scale mercury ore processing at Pšenk on soil (Idrija area, Slovenia). *Applied Geochemistry.* Vol. 26, 1867–1876.

VALENTINITSCH, H. (1981): Das landesfürstliche Quecksilberbergwerk Idria 1575–1659, *Historische Landeskommission für Steiermark, Graz*.

VILADEVALL, M., FONT, X., NAVARRO, A. (1999): Geochemical mercury survey in the Azogue Valley (Betic Area, SE Spain). *Journal of Geochemical Exploration.* Vol. 66/1–2, 27–35.

ŽIBRET, G. & GOSAR, M. (2006): Calculation of the mercury accumulation in the Idrijca river alluvial plain sediments. *The Science of the Total Environment.* 368, 291–297.