

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

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Abstract

In Idrija and its close surroundings the influence of natural dispersion of mercury and of half-a-millennium mining on the environment have been studied. By sampling (69 soil and 65 attic dust samples) of a 51 km² area it was established that on 17.4 km² Hg concentrations in soil exceed the critical values for soil (10 mg/kg). The estimated mercury mean for the studied area is 8.6 mg/kg (0.42 - 973 mg/kg) for soil and 43.5 mg/kg (1.8 - 1055 mg/kg) for attic dust. The Hg concentrations in attic dust are on an average 3.6 times higher than in soil. The highest ratios between Hg abundances in dust versus soil were found in the most distant localities and on higher altitudes above the sea level. Hg in soil exceeds Hg in attic dust only in localities in which the source of the metal is rock next to atmospheric emission.

The spatial Hg distribution in soil and attic dust correlate well ($r=0.87$) and depends very much upon morphology of terrain. High values occur in the Idrijca river valley and at base of slopes, while lower values prevail at higher elevations and at margins of the investigated area.

Kratka vsebina

Na območju Idrije in bližnje okolice smo raziskovali vpliv 500 letnega rudarjenja in naravnih danosti na stanje obremenjenosti okolja z živim srebrom. Z vzorčevanjem smo zajeli 51 km² (69 vzorcev tal in 65 vzorcev podstrešnega prahu) in ugotovili, da na ozemlju velikem 17 km² vsebnosti Hg v tleh presegajo kritično dovoljeno vrednost za tla (10 mg/kg). Vsebnost živega srebra na raziskanem območju znaša v tleh v povprečju 8.6 mg/kg (0.42 - 973 mg/kg) in v podstrešnem prahu 43.5 mg/kg (1.8 - 1055 mg/kg). Vsebnosti Hg v podstrešnem prahu so povprečno 3.6-krat višje kot v tleh. Najvišja razmerja med Hg v prahu in Hg v tleh smo določili na lokacijah najbolj oddaljenih od Idrije. V tleh je več Hg kot v prahu le na območjih, kjer je talna podlaga poleg atmosferskih emisij prevladujoči vir živega srebra.

Prostorski porazdelitvi Hg v tleh in podstrešnem prahu se dobro ujemata ($r = 0.87$) in sta zelo odvisni od morfologije ozemlja. Visoke vrednosti so v dolini reke Idrijce in ob vznožju vzpetin, nižje vrednosti pa so v višjih delih in na obrobju obravnavanega ozemlja.

Introduction

The Idrija mercury mine is situated 50 km west of Ljubljana, Slovenia, in the narrow valley of the Idrijca river and its confluent Nikova (Figure 1). The Idrija mine has been the second largest mercury mine in the world surpassed only by the Almaden mine (Ferrara, 1999). During the operating period of the mine, 107,000 tones of mercury were produced. By taking into account losses during mining and inefficient smelting, the total volume of mined mercury is estimated to be at least 147.000 tons (Mlakar, 1974; Miklavčič, 1999). The Idrija mine is, after more than five hundred years of mining, in the final stage of its gradual shut down because of lack of reserves, low ore grade, low mercury prices and environmental reasons.

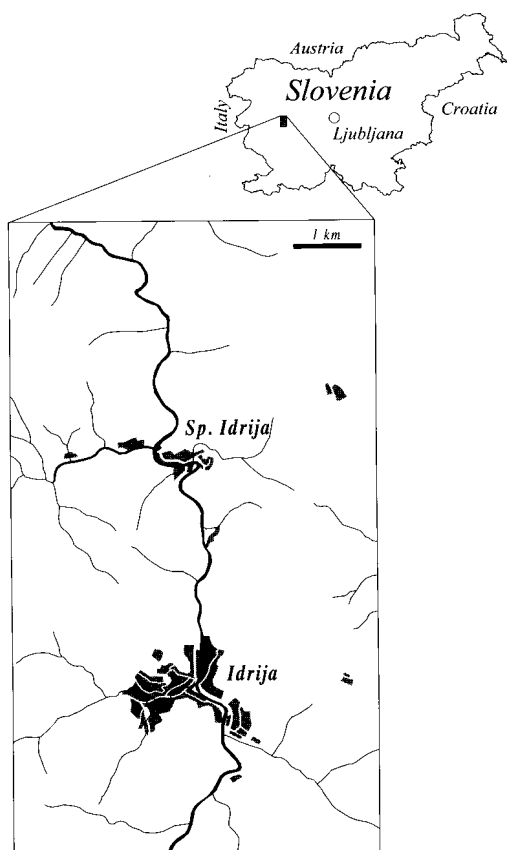


Figure 1. Researched area

Slika 1. Lega raziskanega območja

Owing to naturally increased abundances of mercury in certain rocks, mining and ore processing operations, Idrija and its surroundings have been polluted with Hg. At the time of full mine and smelter production, about 20 kg of Hg were emitted daily from the smelter chimney alone according to the estimate of Kosta et al. (1974), or 30 kg according to an estimate made by Kavčič (1974).

The first known extensive mass intoxications with mercury occurred in Japan between 1953 and 1956, and in 1965 when in Minamata and Niigata more than 100 persons suffered heavy nervous system damages. It was established that the catastrophes were caused by Hg compounds that came into the marine environment with waste waters from the chemical factories (Takeuchi et al., 1963, in: Förstner & Müller, 1974).

Outbreak of mass poisoning took place in Iraq in 1971/72. Seed grain treated with methylmercury fungicide was used to prepare homemade bread. More than 400 persons died, and several thousands of them were critically damaged (WHO, 1990).

These tragic ecological catastrophes warned the world about the heavy danger of intoxication with mercury and other toxic heavy metals. Most western European countries accepted very severe legislation on allowed levels of mercury and other metals in sediments, soils and food. Mercury came into focus of environmental investigations all around the world. Interest also arose in the geochemical mercury halo at Idrija, and detailed investigations on influence of mercury production on the environment were conducted (Byrne & Kosta, 1970; Kosta et al., 1974; Dermelj, 1974; Kavčič, 1974).

History of investigations of mercury environmental impact in Idrija

Mercury pollution in the surroundings of the Idrija mine was studied by Byrne and Kosta (1970). Mercury was determined in water, soil and plant samples taken at two localities in Idrija. In the area around the roasting plant, the established amounts of mercury in investigated plants were about 5

times higher than in the Pront area (ore deposit outcrop), although soils at both localities contained about the same amounts of mercury (200 - 600 mg/kg). They concluded that the finely dispersed mercury is easier assimilated than mercury from the ore particles in the soil of the Pront area. It is interesting, however, that the experimental determination of mercury available to plants did not show significant differences between the two localities. The river that flows through the town was also examined. The samples taken about 1 km above the plant contained between 0.1 and 1 ng Hg/ml. Those taken at two sites near and below the plant showed in case of still water little Hg (0.5 ng/ml) but turbulent water containing a suspension of fine ash particles gave values of 4 to 74 ng Hg/ml (Byrne & Kosta, 1970).

Studies of the distribution, uptake and transformation of mercury in the environment, plant life, animals and man in the area of Idrija and the site of an abandoned mine at Podljubelj are described by Kosta et al. (1974). Important results on distribution of mercury in plants were obtained, especially on its accumulation and methylation. Studies of fish and aquatic life contributed new information on behavior of mercury and some other elements in animals. It was established that contamination of water in the Idrija river is transferred to a large degree to water animals, whereas the degree of methylation increases with distance from the source (Kosta et al., 1974; Dermelj, 1974). To obtain data on the degree of methylation in waters that carry away the roasted ore tailings, Hg in muscle and liver of trouts caught at Marof, Stopnik and at confluence of Bača into Idrija were measured. It was interesting to note that total mercury determined in muscles of fishes fell off sharply downstream, while methylmercury in both organs remained roughly constant. Thus in muscle, the average methylmercury fraction rose from 15.5% at Marof over 83% at Stopnik to 98% at Most na Soči, while for liver methylmercury fraction was much lower (Kosta et al., 1974). This increasing relative methylation is result of the rapid elimination of inorganic mercury and the long biological half life of the methyl form, and also of the increasing degree of meth-

ylation in the aquatic system downstream (Kosta et al., 1974).

Mercury uptake, distribution and elimination were determined also in other animals (rabbits, hens) at the most exposed localities around the main stack (Stegnar, 1973).

Measurements of mercury in the air during the 1970's, at the time of full production of the mine and roasting plant, showed very high values. By collecting 24-h samples during 1971-1972 at six localities in Idrija, Kavčič (1974) found values of 100-4,000 ng Hg/m³ with mean of 2,000 ng Hg/m³. In the smelter courtyard the contents were 10,000 to 30,000 ng Hg/m³. A year later with a different analytical method at the roasting plant 8,500 ng Hg/m³ was determined, and in the town center 570 Hg/m³ (Grašič, 1973; Kosta et al., 1974). There were great differences between the contents owing to weather changes. In the years 1986 (Kobal et al., 1991), 1991 (Pirc, 1991; Lupšina et al., 1992) and in 1992/93 (Lupšina-Miklavčič, 1994) drastic drops of Hg in the air were found (all measurements below 500 ng Hg/m³, and mostly below 300 ng Hg/m³) after the production of the mine and smelter had almost halted. Measurements in September 1994 with portable Zeeman atomic absorption spectrometer PA-915 (Gosar, 1997; Gosar et al., 1997a) showed rather high mercury concentrations in the air in spite of the fact that the smelter was stopped ten months before measurements and the only activity in the mine was ventilation. Concentrations above 300 ng Hg/m³ (in places even up to 2,000 ng Hg/m³) were observed in the surroundings of the two main sources of mercury vapors in Idrija. Three traverses of the same itinerary at various times were measured. The results show rapid variation of mercury in air, probably depending mostly upon rapidly changing weather conditions.

Lupšina et al. (1992) investigated mercury in lichens that are considered a confirmed reliable bioindicator of air pollution. Samples were collected in six localities at Idrija, two in its surroundings, at the abandoned mine at Podljubelj and in the reference point in the Julian Alps. At Idrija very high concentrations in lichens were determined (25 - 188 ng Hg/m³), with only 0.4

ng Hg/m³ at the reference locality. In continuation of these studies (Miklavčič, 1999) next to lichens also garden vegetables were investigated (carrots and beans) in several localities in Idrija. In carrots 60-760 ng Hg/g dry sample was determined and in beans 2 - 23 ng Hg/g d.s. The author considers that Hg in carrots reflects air pollution with Hg, and the bean soil pollution. The study confirmed heavy mercury impact on the environment in Idrija in the 1990's after the closing down of mercury production.

Gnamuš (1992) presented in his work the use of biologic indicators for monitoring and assessing the mercury impact on terrestrial ecosystems. Total mercury concentrations in higher plants from the Idrija area were found above 1 mg/kg dry weight as an average of two samplings. At a somewhat more distant locality at Srednja Kanomlja they were about 100 times lower. In continuation of the study (Gnamuš & Horvat, 1999; Gnamuš et al., 2000) also abundance of mercury in soil close to smelter were determined (mean 1256 mg/kg, n=14) and in plants growing on them (mean 41.8 mg/kg). In the wider surroundings of Idrija, the averages in soil amount to 288 mg/kg (n=96) and in plants to 14.4 mg/kg (n=48).

Palinkaš et al. (1995) report the results of the investigation of environmental pollution around the Idrija mercury mine on the basis of a two days field work (24 and 25 May 1990). Soils were sampled at 52 points arranged in an irregular grid. The maximum value (87.6 mg/kg) was determined in the mining area and in the vicinity of the smelter. The mean mercury concentration in the soil of the studied area was 15 mg/kg. The distribution of mercury along four vertical profiles suggests a predominant influence of the fallout on the accumulation of the pollutant. An extremely low content of mercury in the stream waters and springs in the Idrija surrounding (3 - 31 ng Hg/l) approximates to the waters in the unpolluted areas and differs greatly from other mining areas. Palinkaš et al. (1995) believe that these low values are due to high pH (7.5-8.3) of well-buffered waters, a characteristic of karst hydrology.

Results of study of Hg phases in tailings (Biester & Gosar, 1999; Biester et

al., 1999) indicate that the binding type of mercury is primarily dependent upon the efficiency of roasting technique and prevailing mercury species in roasted ore. In older tailings the predominant Hg species is cinnabar (HgS) due to incomplete roasting, whereas in tailings of the 20th century the amount of cinnabar in the material decreased because of higher efficiency of the roasting process and the increasing use of ores bearing native Hg. In younger tailings metallic Hg sorbed to mineral matrix components became the predominant Hg binding form in addition to unbound Hg⁰ and traces of HgO. Despite the lower total Hg concentrations found in the younger tailings, the long-term risk potential of its mobile matrix-bound Hg⁰ is higher than in that of older tailings bearing mostly immobile cinnabar (Biester et al., 1999).

Because most roasted ore tailings were dumped into the Idrija riverbed, the contents of mercury in the sediments of Idrija and Soča rivers (Gosar, 1992; Gosar, 1997; Gosar et al., 1997b; Biester et al., 2000; Horvat et al., 2000) and also in marine sediments at the mouth of the Soča river (Kosta et al., 1978; Covelli et al., 1999; Horvat et al., 1999; Širca et al., 1999a; Širca et al., 1999b; Biester et al., 2000; Covelli et al., 2001) are increased. Studies of mercury speciation in sediments (Biester et al., 2000) indicate the occurrence of two major Hg forms; cinnabar the primary ore, and an unspecified group of matrix-bound Hg compounds which were assumed to be potentially bioavailable. The results show that Hg concentrations and dispersion of the two Hg forms in sediments strongly depend on grain size. Accumulation of cinnabar predominately occurs in coarse grained river sediments, where it constitutes on average more than 80% of total Hg (up to 1,000 mg/kg) in present- and past day sediments. In contrast noncinnabar Hg was found to be enriched in areas where fine grained material was deposited reaching up to 40% in flooded soils, and up to 55% in sediments of the Gulf of Trieste.

Hess (1991) investigated in the frame of a short study only a limited number of samples of soil, river sediments and water. In soil he found from 1.8 to 885 mg Hg/kg. Analyzed were also 4 river sediment sam-

ples that contained comparable mercury as in soils, whereas the water samples contained 0.35 and 3.1 mg Hg/l.

Spatial distribution of mercury in soil on an 8 x 14 km area with Idrija in the center was studied by Hess (1993). Owing to topographic and meteorologic reasons the area was elongated in the north-south direction. He sampled in a regular 1 km grid (127 sample sites). On grassland he collected the upper 15 cm of soil, in the forest the upper 20 cm, and on arable soil the upper 30 cm of the soil profile. In forest sample sites in which also the humus horizons were developed next to the mineral soil also the sample of the humus horizon was collected.

Contents above 10 mg Hg/kg were detected in soils in valleys and at foot of slopes, and lower values in higher parts and at margins of the sampled area. In 10 selected samples also the contents of the most dangerous form of mercury, the methylated mercury was determined. Selected samples contained <0.003 to 0.2 mg of methyl Hg/kg which corresponds to a few thousandths to 0.66% of total mercury in samples.

Methods and Materials

The research by Hess (1993) established the dimensions of the Idrija geochemical mercury halo, which is the result of outcropping of mineralized rocks and of half a millenium of mining and processing mercury ore. The impact of the mercury production even exceeds the naturally higher Hg geochemical background. In an area measuring approximately 3 x 6 km with the town of Idrija in the heart of it, very high mercury concentrations in soil were determined. The sampling net used by Hess was not dense enough to separate the most polluted locations. In the year 2000, we carried out a new geochemical research with a better coverage of the area. In the most affected areas, such as Idrija and Spodnja Idrija, we took an average of four samples in a km². At a chosen location, we took a sample of the attic dust from a nearest suitable house as well as a sample of the soil in its immediate vicinity. We considered this sufficient for disclosing the most affected areas in Idrija and estimating the mercury contents in them.

In localities sampled by Hess, this study should document the possible changes that might have happened in the past ten years since Hess's investigation.

Soil was sampled from the surface to a depth of 15 cm; the possible organic horizons were excluded. In the town itself, we sampled urban soil such as soil in the gardens and on the grass verges. In the surroundings of Idrija, we took samples from grasslands, only exceptionally, if there was no other possibility, we sampled forest soil. One soil sample represents the composite material sampled in the sampling point and four points 10 m towards N, E, S and W. The mass of such a composite was about 1 kg. There were 69 soil samples collected.

Of the three materials soil, sediment and dust, which derive primarily from the Earth's crust, and with which human beings come into contact, dust is the most pervasive. It is also the material that has, until last 20-30 years, largely been ignored as a significant source of trace metals in the urban environment. The term dust usually comprises street dust and house dust. However other types, such as playground dust, have also been studied (Ferguson & Kim, 1991). The work of Šajn (1999) represents an introduction of studies of urban sediments (street sediment, house and attic dust) into the geochemical studies in Slovenia. He also sampled a special type of house dust; attic dust. It represents dust that is deposited in the attics, which are abandoned by inhabitants, so that there should be minimal tenant influence on the dust deposited there. It is derived prevalingly from external sources as deposition of aerosols and dusting of soil, and less from household activities. Particles of house dust accumulate in the human organism through inhalation and consummation. In this manner, the intake of heavy metals into the organism also takes place (Schlipkoeter & Brockhaus, 1988).

The attic dust as sampling material has the advantage that its composition remains constant, chemically unchanged with time. Investigations of attic dust chemistry reveal the average historical state of the atmosphere (Šajn, 1999).

The attic dust was collected from wooden construction of attic that was not in imme-

diate contact with roof tiles and floor. This permitted to avoid collecting particles of tiles, wood and other construction materials. For sampling buildings as old as possible were selected. We gathered 65 attic dust samples.

The samples were air-dried. A fraction of attic dust smaller than 0.125 mm was prepared for the chemical analyses by sieving. Soil samples were gently crushed in a ceramic mortar and passed through a sieve with 2 mm openings. Fraction smaller than 2 mm was pulverised before chemical analyses.

Samples were analyzed in the ACME laboratories in Vancouver, Canada. After aqua-regia digestion (1 hour, 95°C) mercury was determined using Cold Vapor Atomic Absorption Spectrometry (CVAA). Quality assurance was carried out by shipment of samples to the laboratory in a random succession to distribute any errors due to laboratory performance. Objectivity was assured through the use of neutral laboratory numbers. Accuracy was estimated by blind determinations of geological standards SJS-1, GXR-6 and SO-1. Reliability of determinations was assessed as very satisfactory.

Results and Discussion

On the basis of the investigated samples, the estimated mercury mean in the soil in Idrija and its surroundings amounts to 8.6 mg/kg with the range from 0.42 to 973 mg/kg and for attic dust 43.5 mg/kg with the range from 1.8 to 1055 mg/kg. The Slovene average for soil is 0.15 mg/kg (Pirc, 1993) and for attic dust 1.1 mg/kg (Šajn, 1999). On 17.4 km² of the studied area, the contents of mercury exceed the critical allowed value for mercury in soil (10 mg/kg, Official Gazette - Ur. list, 1996).

For comparison, we prepared geochemical maps of mercury distribution in same distribution classes for soil based on sampling in year 1990 by Hess (1993) (Figure 2) and for soil and attic dust based on our sampling in year 2000 (Figures 3 and 4). As expected, the state of mercury impact on soils did not change much. The mercury levels of the year 1990 are comparable to those of 2000. However, by means of denser sampling, we could better locate spots of especially high

mercury impact (contents higher than 140 mg/kg). Spatial distribution of mercury in soil depends a lot upon morphology of the area (Figures 3 and 5). The highest mercury content in soil (973 mg/kg, site 507) occurs in the garden soil on Kosovelova Street 21. According to Čar (1998), rocks mineralized with elementary Hg and cinnabar are exposed at this location. Besides, the ancient dumps of unroasted ore also occur here (Čar, 1998). Close to this locality Hess (1991) found a similar concentration (885 mg/kg) in soil. The second highest concentration (924 mg/kg, site 518) was determined on Prejnuta where old ore roasting tailings are situated; the ore was roasted there from mid 17th to mid 19th century (Čar, 1998). Here, the influence of exhaust from chimney stacks of roasting plant was also high. Detailed sampling revealed increased mercury content in the area around the last 500 m of the Ljubevšca brook. (between 40 and 67 mg/kg), which can be probably attributed to the nearby ventilation shaft of the mine. On the Pšenk hill, SW from Idrija, one sample uncovered high mercury content (57 mg/kg) that can be the consequence of ore roasting in the woods in the past, as described by Čar (1998). Hess also sampled close-by, but he did not detect any higher contents.

Mercury contents in the attic dust are on average 3.6 times higher than in the soils. It is only in the locations where soil is, next to the atmospheric emissions, the main source of mercury, that the situation is reversed. That is on the locations of unsmelted ore wastes, primary ore smelting residues, ore residues dumps, outcropping of mineralised rocks and in locations of old ignition facilities or in places where the smelting residues were used for road construction or otherwise. These locations are described by Čar (1998).

The geographical distributions of mercury contents in the soil and attic dust are in good agreement (Figures 3 and 4). The correlation coefficient (*r*) between contents in the two sampling media is 0.87 (Figure 6). There is also a strong correlation between Hg in soil and attic dust and the altitude (*r* = 0.84 respectively *r* = 0.80; Figures 7 and 8). This suggests the conclusion that the pollution is spread mainly along the Idrija val-

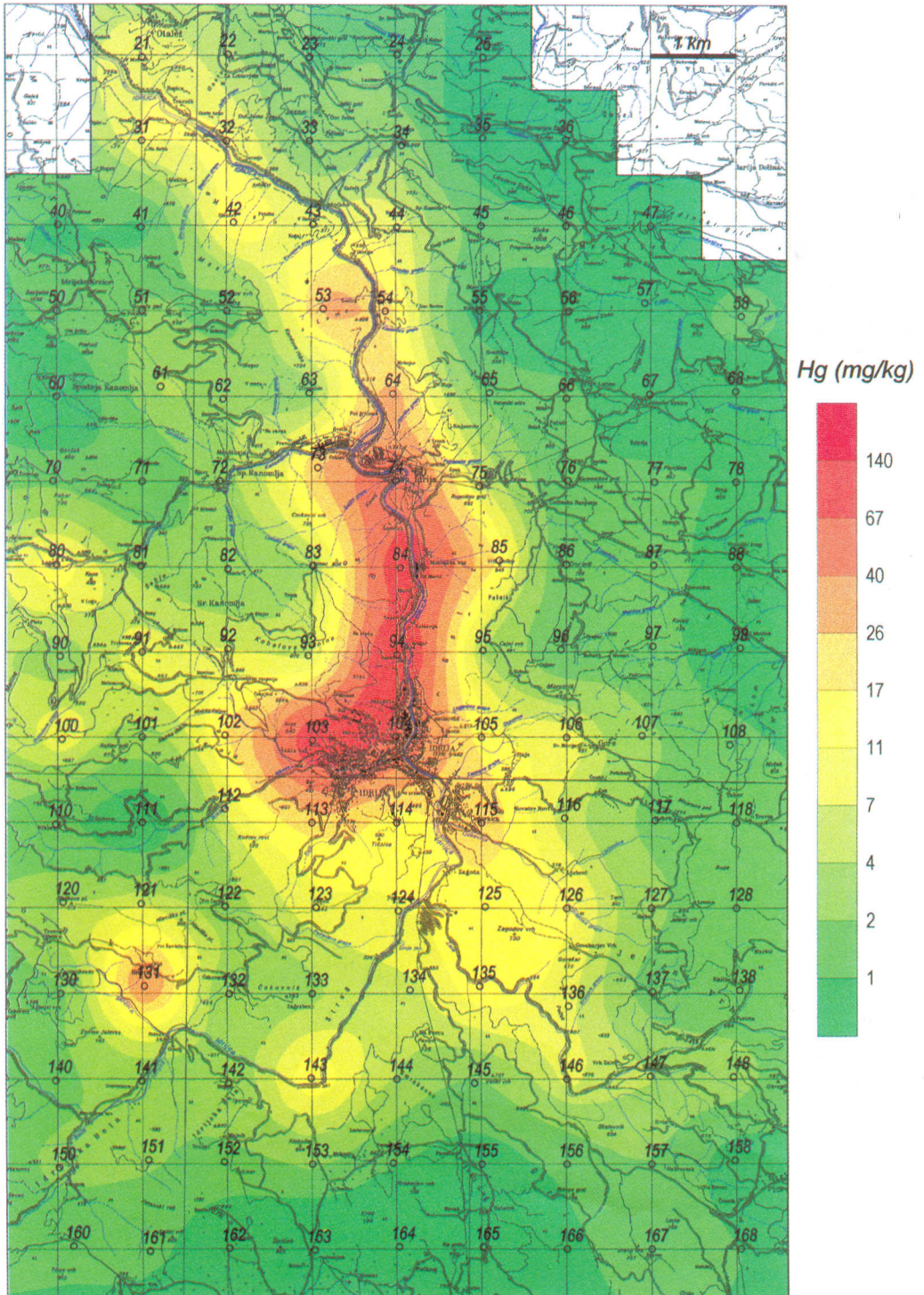


Figure 2. Mercury distribution in soil in year 1990 (data after Hess, 1993)

Slika 2. Porazdelitev Hg v tleh v letu 1990 (podatki po Hessu, 1993)

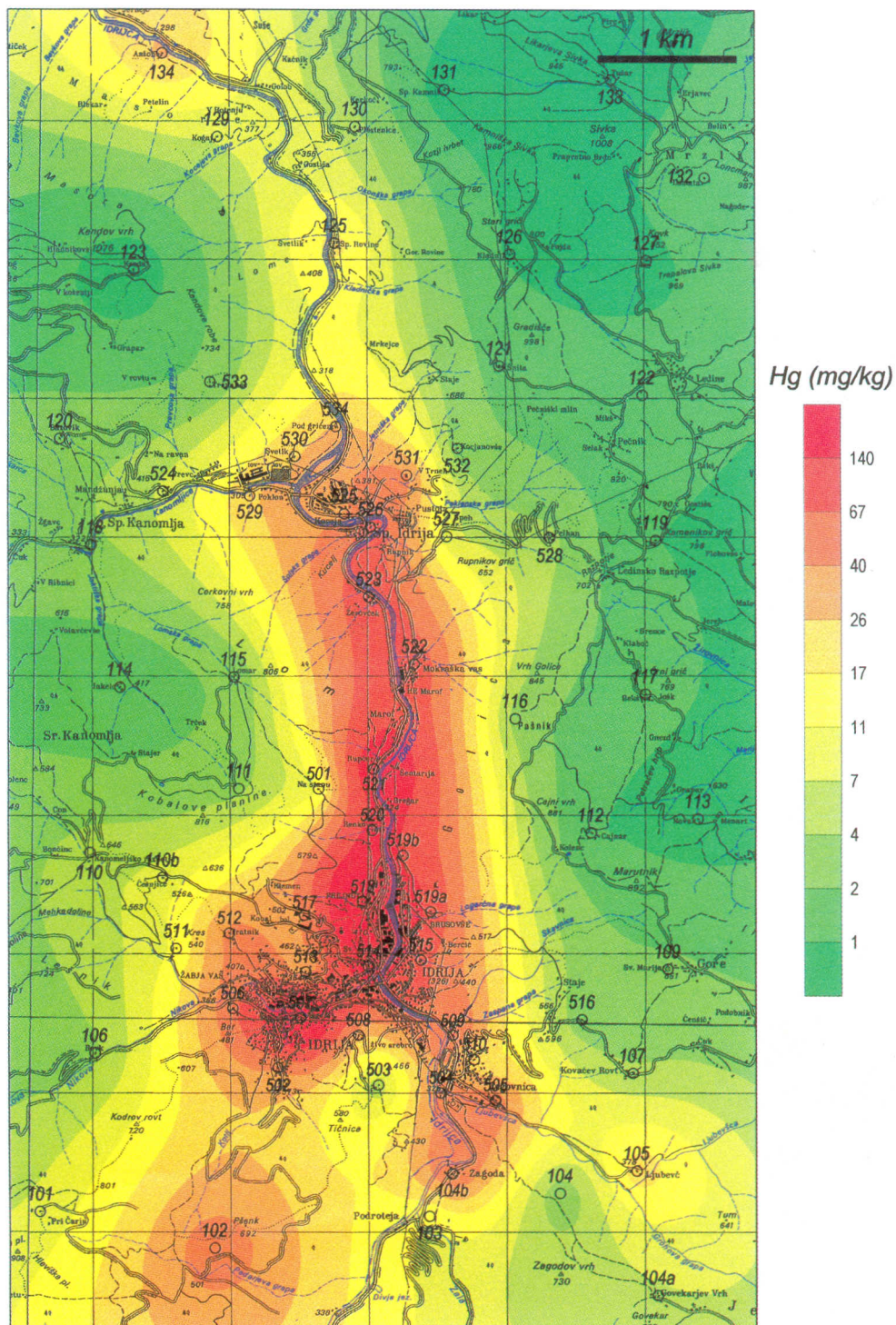


Figure 3. Mercury distribution in soil in year 2000

Slika 3. Porazdelitev Hg v tleh v letu 2000

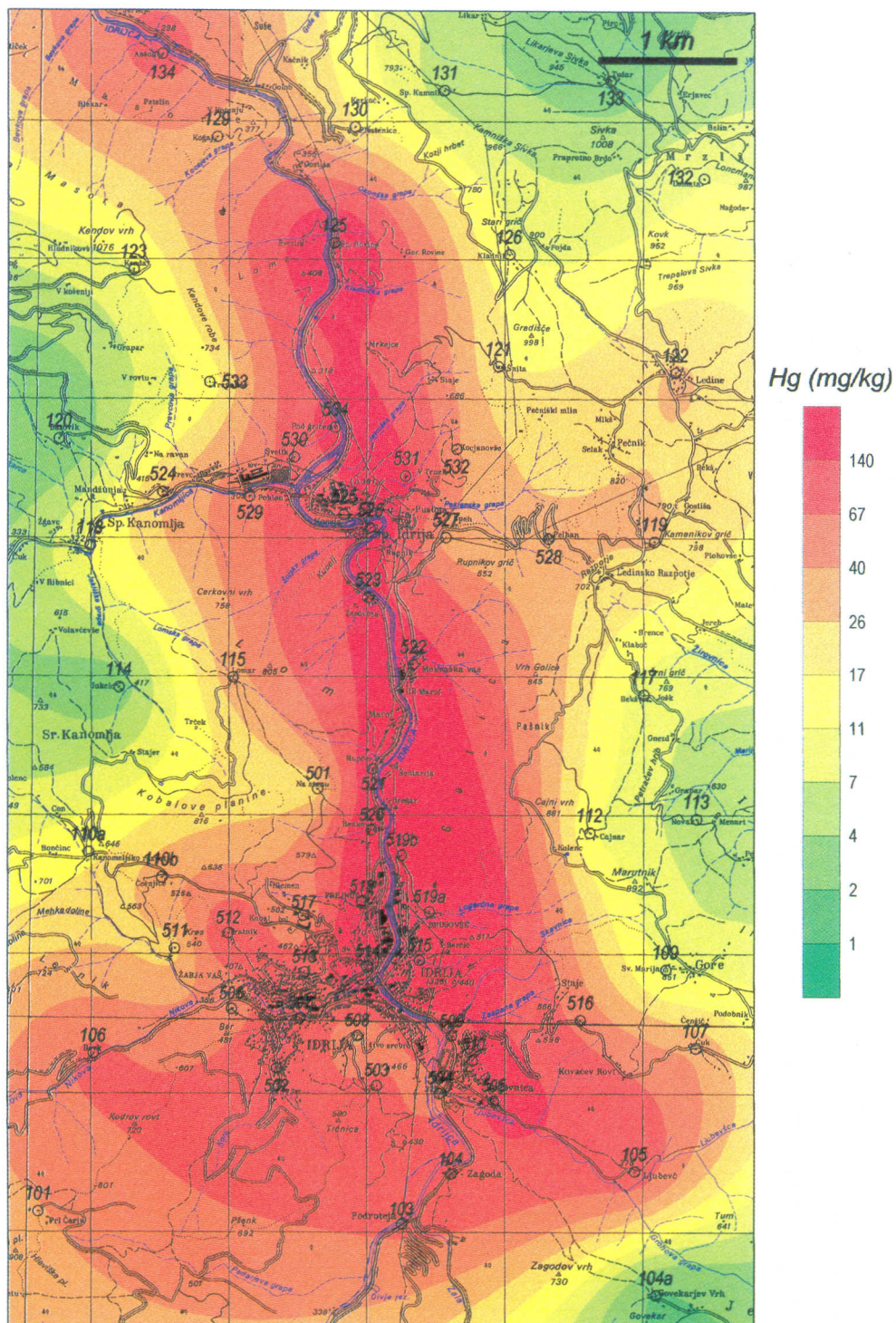


Figure 4. Mercury distribution in attic dust in year 2000

Slika 4. Porazdelitev Hg v podstrešnem prahu v letu 2000

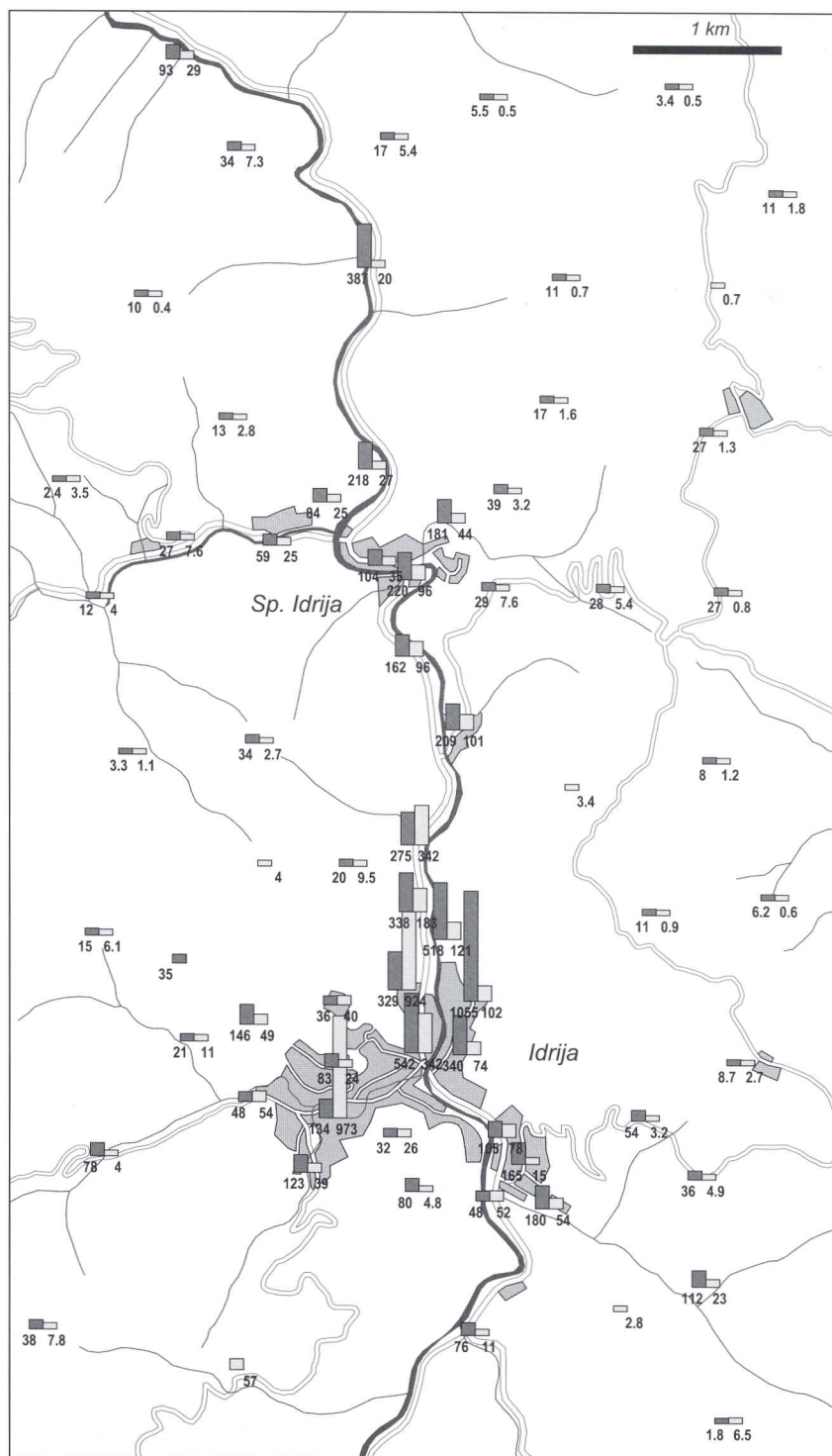


Figure 5. Mercury contents (mg/kg) in attic dust (dark grey columns) and in soil (light grey columns)
 Slika 5. Porazdelitev Hg (mg/kg) v podstrešnem prahu (temno sivi stolpci) in tleh (svetlo sivi stolpci)

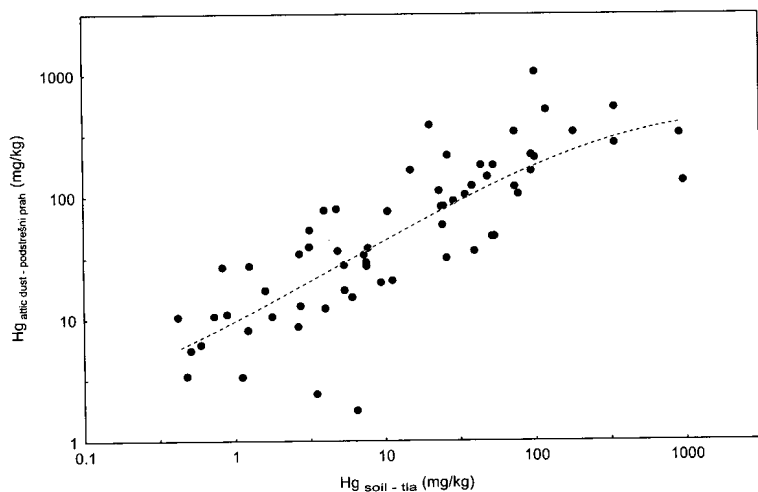


Figure 6. Relationship between Hg in attic dust and in soil

Slika 6. Soodvisnost Hg v podstrešnem prahu in v tleh

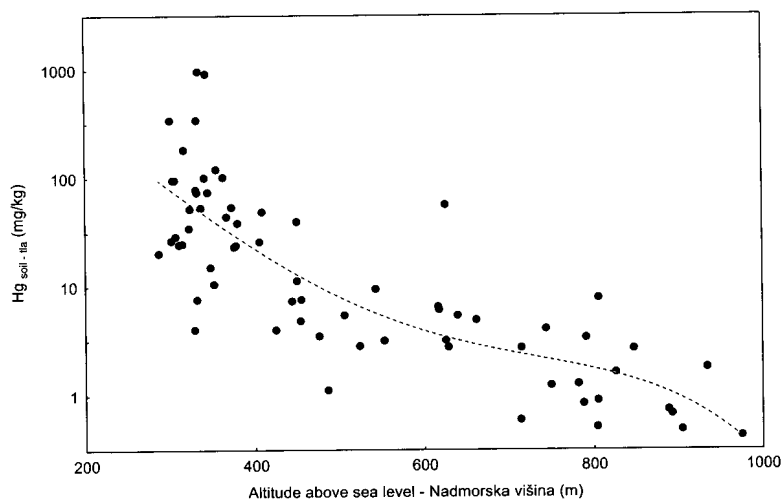


Figure 7. Distribution of Hg content in soil depended on altitude above sea level

Slika 7. Porazdelitev vsebnosti Hg v tleh v odvisnosti od nadmorske višine

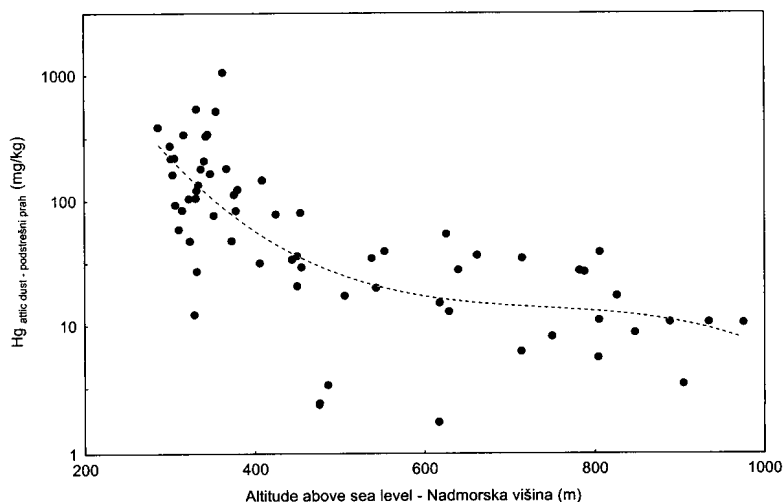


Figure 8. Distribution of Hg content in attic dust depended on altitude above sea level

Slika 8. Porazdelitev vsebnosti Hg v podstrešnem prahu v odvisnosti od nadmorske višine

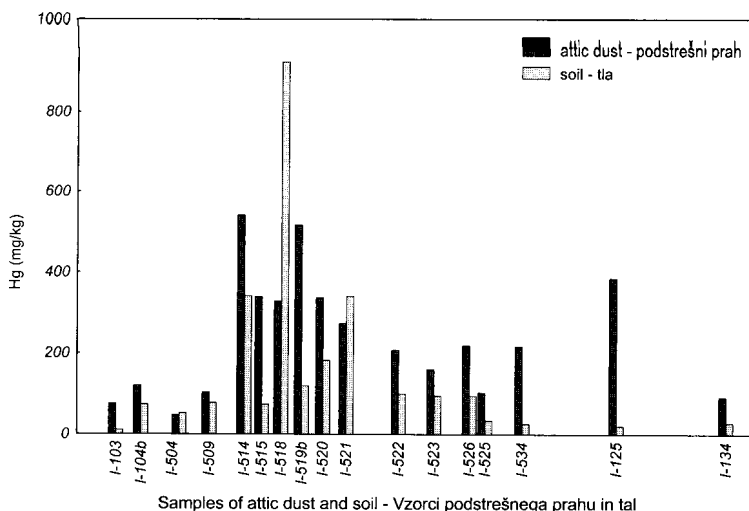


Figure 9. Hg in soil and attic dust in the Idrija river valley from the confluence with Zala northwards

Slika 9. Vsebnosti Hg v tleh in podstrešnem prahu v dolini reke Idrijce od so-točja z Zalo proti severu

ley, while the distant influence seems to be of secondary importance only.

Of particular interest are the data of mercury contents in the attic dust. The map of mercury distribution in the attic dust (Figure 4) shows that the influence of atmospheric emissions caused by the Idrija smelter extended outside the researched area. Obviously, the impact on environment was also considered on the regional scale.

Extremely high contents in the attic dust were determined in the vicinity of the smoke stack (1055 mg/kg) and in the valley of Idrija between the Idrija bridge in Idrija and the hydroelectric power plant Marof (from 275 to 542 mg/kg) (Figures 5 and 9). Prevailing southern winds spread the pollution from the smelter far northwards along the Idrija valley (Figure 9). High mercury contents occur also in the Ljubevšca valley, probably owing to the ventilation shaft situated there.

It is of special interest to compare the Hg samples taken higher or lower than the main exhaust stack of the smelter. The average of Hg in soil, which lies in lower altitudes than the main exhaust stack, is 42 mg/kg and in the attic dust samples is 122 mg/kg. In higher altitudes the average is 2.8 for soil and 16 mg/kg for attic dust.

Concentration ratios (Fergusson & Kim, 1991) of mercury in the attic dust and soil, respectively, are significantly dependant on the altitude. Lower from the altitude of the main exhaust stack the concentration

ratio average is about 3, and in higher elevations it is about 7, which is similar to the Slovene concentration ratio (7.3) (Figure 10). In localities of pronounced atmospheric emissions, the Hg contents in the attic dust are much higher than in the corresponding soils. The highest ratios were determined at the most distant localities that lie most frequently also at highest altitudes (sampling points 119, 123, 122, 106)

In the case of Idrija, the attic dust was first used for geochemical mapping of a small area at a dense spacing. It proved itself a very applicable and stable sampling medium showing small variability at short distances.

Mechanisms of mercury dispersion in Idrija

Mechanisms of mercury dispersion in Idrija and its surroundings are of various nature. The most important mercury sources are atmospheric emissions, ore and smelting residue dumps, and outcrops of mineralized rocks.

The main cause of Hg pollution in Idrija and its surroundings were the *atmospheric emissions*. The strongest sources - smelter and roasting tailings dumps - are on the north edge of the town of Idrija where by the winds prevailing in the north-south direction, with a emphasized southern component (Petkovšek & Rakovec, 1980), the polluted gases and dust particles are spread mainly along the Idrija valley north

of Idrija, and much less southwards. This is evident also from Figure 9 showing the concentrations of mercury in soil and attic dust along the Idrijca valley. Since that valley is bordered by steep slopes of relative elevation reaching even above 700 m, the polluted air is directed mostly northwards along the valley, and not eastwards or westwards. The second important source of atmospheric emissions are the two ventilation shafts of the mine. At the Inzaghi shaft in the center of Idrija also after abandoning of production high mercury concentrations in the air were measured (Gosar et al., 1997a; Miklavčič, 1999). The second shaft in the Ljubevšca valley should not have much influence, as indicated by established mercury in carrots (Miklavčič, 1999). On the displayed mercury distributions in attic dust and soil (Figures 3 and 4), however, increase of mercury in the Ljubevšca valley is evident.

The other causes of mercury pollution are *mineralized rock dumps* and especially *smelting residues* that still contain rather high amounts of mercury. The main reason for complex spatial distribution of roasting tailings in Idrija and surroundings are changes in combustion technology over centuries, continuous growth of quantities of processed ore accompanied by decreasing Hg content and various method of further treatment of ore residues (Čar, 1998). Up to the middle of 17th century, the ore was roasted on the neighboring hills (Pront, Pringl), and in more distant localities (Čekovnik, Kanomlja). Several localities of old ignition facilities were found by Mlakar during geological mapping, others were located later (Čar, 1998). The first established permanent roasting plant was at Lenštat. In 1652, the roasting plant at Prejnuta was built. It was in operation till the 19th century. After 1868, the new roasting plant at Brusovš was gradually installed. Until 1977, most roasting remains were dumped directly into the river Idrijca that carried the material to the Soča river and Adriatic Sea. In this way, extensive river deposits with high mercury contents that are and will continue to be a source of mercury impacted sediments also in the future were formed in the lower Idrijca valley (Gosar, 1997; Gosar et al., 1997b; Biester et al., 2000). New dumps of roasted ore occur also

on the right banks of Idrijca. After the renewal of production in 1983 dumping of tailings into the river was not allowed (Čar, 1998). At rainshowers nevertheless polluted material was washed into the drainage. Spatial distribution of roasting remains was described by Čar (1998). The highest mercury contents in soil (sites 518 and in part 507) we attribute to roasted material.

Mercury levels in the environment at Idrija are increased also owing to natural, geogene reasons. Syngenetically mineralized and lithologically very diverse Ladinian beds were deposited in sedimentation conditions of the tectonic graben of the Idrija structure. They were deposited on partly eroded older Anisian, Scythian, Permian and Carboniferous rocks that were epigenetically mineralized (Mlakar, 1967; Placer & Čar, 1977; Čar 1985; Čar, 1998). During later tectonic events the present very complex structure of the deposit formed. However, a more extensive natural migration of mercury into the wider surroundings of the deposit was limited owing to impermeable Carboniferous clastites and to tectonic zones filled with clay (Čar, 1998). The western part of the deposit was uplifted along a fault and by erosion a part of mineralized rocks, especially of the Carboniferous clastites with native mercury, and at western edge the tectonized Skonca beds and tuffites were exposed (Čar, 1998). On an average the mineralized clastites contain 0.38% Hg, about half in the form of cinnabar, and the rest as native metal (Čar, 1998).

Carboniferous beds, enriched with cinnabar and native Hg, lie below the center of Idrija, and they outcrop in slopes of Kurji vrh and lower part of Pront (Čar, 1998). The Skonca beds and tuffites are exposed on Pront between Karnik and Albreht (Čar, 1998).

The results of our investigations lead to the conclusion that Idrija with its surroundings represents an environment that is highly polluted with mercury. It is an example of a case study in the frame of which the impacts of natural (geogene) sources of mercury, as well as those caused by human activity during the five hundred years long exploitation, can be studied in a relatively small area.

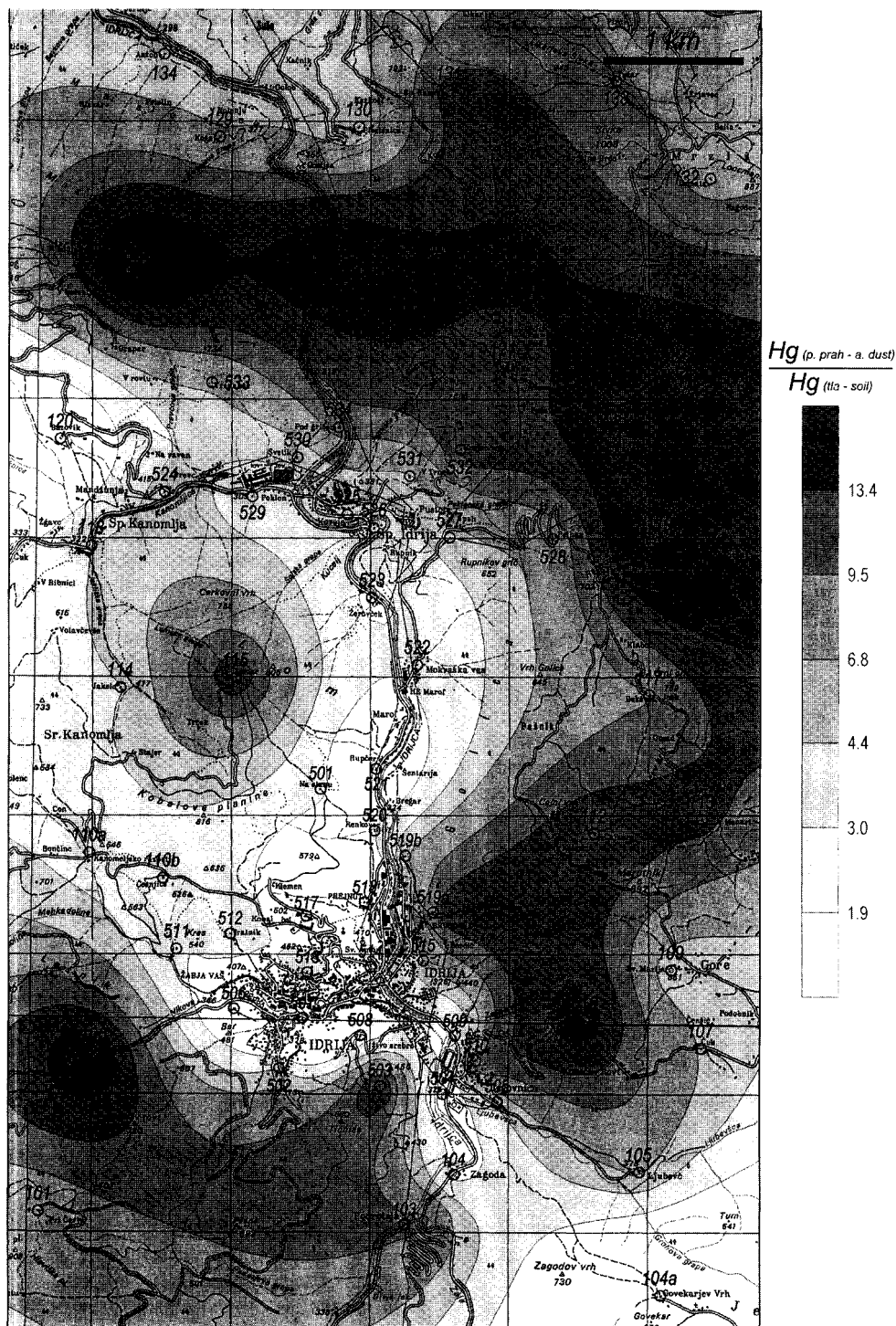


Figure 10. Spatial presentation of ratio of Hg in attic dust to Hg in soil.

Slika 10. Prostorski prikaz razmerja Hg v podstrešnem prahu proti Hg v tleh

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Živo srebro v tleh in podstrešnem prahu v Idriji in okolici kot posledica orudenja in rudarjenja

Uvod

Rudnik živega srebra v Idriji leži v ozki dolini med idrijskim hribovjem in se razprostira med reko Idrijco in njenim pritokom Nikovo (slika 1). Glede na celotno proizvodnjo živega srebra prekaša Idrijo samo rudnik v španskem Almadenu (Ferrara, 1999). V celotni zgodovini rudnika so idrijski rudarji pridobili 107.000 ton živega srebra. Upoštevajoč vse ocenjene izgube, do katerih je prihajalo zlasti v starejših obdobjih, pa bi lahko znašala celotna proizvodnja živega srebra kar 147.000 ton (Mlakar, 1974; Miklavčič, 1999). Po več kot petsto letih delovanja je danes idrijski rudnik zaradi izčrpanosti, nizke cene živega srebra na svetovnem tržišču ter okoljevarstvenih razlogov v zadnji fazi postopnega zapiranja.

Zaradi naravno povečane vsebnosti živega srebra v nekaterih kamninah ter zaradi rudniške in predelovalne dejavnosti je širša okolica Idrije onesnažena s to kovino. Samo iz dimnika topilnice je pred letom 1977, ko sta rudnik in topilnica delovala še v polni meri, po oceni Koste in sodelavcev (1974) uhajalo v atmosfero okrog 20 kg živega srebra na dan, ali po oceni Kavčičeve (1974) 30 kg živega srebra na dan.

Do prvih znanih velikih množičnih zastrupitev z živim srebrom je prišlo na Japonskem v letih 1953 do 1956 in 1965, ko je v Minamati in Niigati zbolelo več kot 100 ljudi za težkimi poškodbami živčnega sistema. Ugotovili so, da so katastrofe povzročile različne Hg spojine, ki so z odpadnimi vodami kemičnih tovarn prihajale v morsko okolje (Takeuchi et al., 1963 v: Förstner & Müller, 1974).

Pozimi 1971/1972 je prišlo v Iraku do množične zastrupitve s kruhom iz moke zrnja, ki so bila prej obdelana s fungicidom metilnega Hg. Umrlo je več kot 400 ljudi, nekaj tisoč pa jih je bilo resno poškodovanih (WHO, 1990).

Ti tragični primeri so opozorili svet na veliko nevarnost zastrupitev z živim srebrom in drugimi nevarnimi težkimi kovinami. V večini zahodnoevropskih držav so sprejeli zelo stroge predpise o dovoljenih količinah Hg in drugih kovin v sedimentih, tleh in hrani. Živo srebro se je znašlo v središču ekoloških raziskav po celem svetu. Za raziskovalce je postala tako tudi z ekološkega stališča zelo zanimiva idrijska živosrebrova geokemična avreola. Zato so se začele v tistem času poglobljene raziskave o vplivu rudarjenja, ki je bilo takrat še v polnem zamahu, na okolje (Byrne & Kosta, 1970; Kosta et al., 1974; Dermelj, 1974; Kavčič, 1974).

Zgodovina raziskav obremenjenosti okolja z živim srebrom v Idriji

Onesnaženost okolja z živim srebrom v okolici idrijskega rudnika sta raziskovala Byrne in Kosta (1970). Vsebnosti Hg so bile določene v vzorcih voda, tal in rastlin na dveh mestih v Idriji. Prva lokacija v bližini topilnice je bila onesnažena z drobno razpršenim elementarnim živim srebrom v zraku, druga lokacija pa je znana pod lokalnim imenom Pront, kjer izdanjajo karbonski skrila glinavci in meljevci s samorodnim živim srebrom. Ugotovili so, da so na območju topilnice količine živega srebra v preiskovanih rastlinah približno 5-krat večje kot na Prontu, kljub temu, da so tla na obeh območjih vsebovala podobne količine živega srebra (200 - 600 mg/kg). Sklepali so, da se drobno dispergirano živo srebro v okolici topilnice dosti lažje asimilira v rastlinah kot tisto na območju Pronta. Zanimivo je, da poskus določitve rastlinam dostopnega živega srebra ni pokazal značilnih razlik med obema lokacijama. V okviru iste raziskave so določili tudi koncentracije živega srebra v vodi reke Idrijce. Kilometer nad topilnico rude so izmerili od 0,1 do 1 ng Hg/ml, v bližini in tik pod njo so izmerili 0.5 ng/ml v mirni vodi in v primeru turbulentnih tokov

v vodi z drobno suspendiranimi delci od 4 do 74 ng Hg/ml (Byrne & Kosta, 1970).

Raziskave o porazdelitvi, privzemu in presnovah živega srebra v okolju, vegetaciji, živalih in ljudeh na območju Idrije v primerjavi z okolico opuščenega rudnika so opravili Kosta in sodelavci (1974). Pomembni so rezultati o porazdelitvi živega srebra v rastlinah, zlasti o njegovi akumulaciji in metilaciji. Raziskave vodnih živali so pokazale, da se kontaminacija reke Idrije v veliki meri prenaša na njih; stopnja metilacije v ribah narašča z oddaljenostjo od izvora (Kosta et al., 1974; Dermelj, 1974). Da bi dobili podatke o stopnji metilacije v vodah, ki odplavljajo prežgano rudo, so analizirali meso in jetra postrvi, ulovljenih pri Marofu, Stopniku in pred izlivom Bače v Idrijo. Zanimivo je, da vsebnost celotnega živega srebra v mišicah rib s tokom reke pada, medtem ko razmerje med metilnim živim srebrom in celotnim živim srebrom v mesu rib narašča od 15,5% pri Marofu do 83% pri Stopniku in 98% pri Mostu na Soči. To pomeni, da je v mesu rib, ulovljenih pri Mostu na Soči, skoraj vse živo srebro v metilni obliki, medtem ko je to razmerje v jetrih rib znatno nižje (Kosta et al., 1974). Porast razmerja med organsko in anorgansko vezanim živim srebrom pripisuje Dermelj (1974) hitremu izločanju anorgansko vezanega Hg, dolgi biološki razpolovni dobi metilnega živega srebra in tudi povečani stopnji metilacije v vodnem sistemu spodnjega toka Idrije.

Privzemanje, razdelitev in izločanje živega srebra so merili tudi na nekaterih drugih živalih (zajci, kokoši) na najbolj izpostavljenih mestih v bližini glavnega dimnika topilnice (Stegnar, 1973).

Meritve v zraku iz 70-ih let, ko sta rudnik in topilnica še polno obratovala, so pokazale zelo visoke vsebnosti živega srebra. Kavčičeva (1974) je proučevala stopnjo onesnaženosti zraka v letih 1971/72. Jemali so 24-urne vzorce in določili na 6 vzorčnih mestih v Idriji od 100 do 4.000, povprečno 2.000 ng Hg/m³. Na dvorišču topilnice so določili kar od 10.000 do 30.000 ng Hg/m³. Leto kasneje so z drugo metodo pri topilnici izmerili 8.500 ng Hg/m³, v centru mesta pa 570 ng Hg/m³ (Grašič, 1973; Kosta et al., 1974). Ugotovili so tudi, da prihaja zaradi spremenjenih vremenskih pogojev

med posameznimi meritvami do precejšnjih razlik. V letih 1986 (Kobal et al., 1991), 1991 (Pirc, 1991; Lupšina et al., 1992) in 1992/93 (Lupšina-Miklavčič, 1994) so meritve pokazale veliko zmanjšanje količine živega srebra v zraku (vse pod 500 ng/m³, večina celo pod 300 ng/m³). To je razumljivo, saj sta topilnica rude in rudnik v tem času delovala v zelo zmanjšanem obsegu. Meritve septembra 1994 s prenosnim spektrometrom PA-915 (Gosar, 1997; Gosar et al., 1997a) so pokazale, da so bile koncentracije Hg v zraku še vedno precej visoke, kljub temu, da predelovalnica rude že več kot deset mesecev pred meritvami ni delovala in da je bila v času meritev edina dejavnost rudnika prezračevanje. Koncentracije nad 300 ng Hg/m³ zraka (ponekod tudi do 2.000 ng Hg/m³ zraka) so bile izmerjene v okolici obeh glavnih virov Hg hlapov v Idriji. Izmerjeni so bili trije profili na isti poti ob različnih časovnih obdobjih. Prikazujejo hitro spreminjanje koncentracij živega srebra v zraku, verjetno predvsem v odvisnosti od hitro se spreminjajočih vremenskih pogojev.

Vesna Lupšina in sodelavci (1992) so raziskovali vsebnosti živega srebra v lišajih, ki so priznani dober bioindikator onesnaženosti zraka. Lišaje so nabrali na šestih vzorčnih lokacijah v Idriji, dveh v bližnji okolici Idrije, v Podljubelju (opuščeni rudnik živega srebra) in na referenčnem mestu v Julijskih Alpah. V Idriji so izmerili zelo visoke koncentracije živega srebra v lišaju (od 25 do 188 µg/g), medtem ko je bila koncentracija na referenčnem mestu le 0,4 µg/g. V nadaljevanju teh raziskav (Miklavčič, 1999) so bile poleg lišajev obravnavane še nekatere vrtnine (korenje in fižol) na različnih lokacijah v Idriji. V korenju je bilo določeno od 60 do 760 ng Hg/g v suhi snovi, v fižolu pa 2 do 23 ng Hg/g v suhi snovi. Avtorica je mnenja, da odraža vsebnost Hg v korenju nivo živega srebra v zraku, vsebnost Hg v fižolu pa nivo Hg v tleh. Vsekakor je raziskava potrdila veliko obremenjenost okolja v Idriji z živim srebrom tudi v devetdesetih letih 20. stoletja, ko v Idriji ni bilo več proizvodnje Hg.

Gnamuš (1992) je izdelal diplomsko nalogo, v kateri je predstavil uporabo bioloških indikatorjev za spremljanje in vrednotenje obremenjenosti kopenskih ekosiste-

mov z živim srebrom. Celotne koncentracije živega srebra v višjih rastlinah z območja Idrije so bile v povprečju dveh vzorčenj nad 1 mg/kg suhe teže. Na nekoliko oddaljenejši lokaciji v Srednji Kanomlji so bile te približno 100-krat manjše. V nadaljevanju raziskav (Gnamuš & Horvat, 1999; Gnamuš et al., 2000) so bile določene tudi koncentracije živega srebra v tleh v bližini topilnice (povprečno 2456 mg/kg, $n=14$) in v rastlinah v bližini topilnice (povprečno 41,8 mg/kg). Na širšem območju mesta Idrija so izmerili v tleh povprečno 288 mg/kg Hg ($n=96$) in v rastlinah povprečno 14,4 mg/kg ($n=48$).

Palinkaš s sodelavci (1995) poroča o rezultatih raziskave onesnaženosti okolja v bližini rudnika na podlagi dvodnevnega terenskega dela (24. in 25. 5. 1990). Tla so vzorčevali na 52 vzorčnih mestih v nepravilni mreži. Največje izmerjene koncentracije (87,6 mg/kg) so bile določene na antropogenih tleh in regosolih na območju rudnika in v bližini topilnice. Da bi ločili naravno stanje od antropogeno povzročenega, so preiskali 4 talne profile. Porazdelitev živega srebra v profilih nakazuje večinoma antropogeni, z zračnim depozitom pogojeni vnos živega srebra v tla. Povprečje talnih vzorcev je 15 mg/kg, kar priča o veliki obremenitvi območja. V vzorcih vod in vodnih izvirov so določili zelo nizke vsebnosti živega srebra (3–31 ng/l). Avtorji ugotavljajo, da je to zelo nenavadno ter da vode v bližini drugih rudnikov živega srebra vsebujejo bistveno višje koncentracije Hg, zato interpretirajo nizke koncentracije kot posledico nevtralnega do rahlo bazičnega okolja (pH med 7.5 in 8.3), ki ga povzroča karbonatno zaledje.

Rezultati raziskave zvrsti živega srebra v prežgani rudi kažejo (Biester et al., 1999; Gosar, 1999; Biester et al., 1999), da so vrste vezave Hg odvisne predvsem od učinkovitosti žgalne tehnike in prevladujočih zvrsti Hg v žgani rudi. V starih deponijah prevladuje cinabarit, v deponijah iz 20. stoletja pa je vsebnost cinabarita zelo majhna. To je posledica učinkovitejšega žganja in predelave karbonskih skrilavcev, ki vsebujejo samorodno živo srebro. V teh deponijah prevladuje Hg^0 , ki je vezano na mineralne komponente osnove, poleg tega pa nastopata še nevezan Hg^0 in v sledovih HgO . Kljub temu, da vsebujejo mlajše deponije manj celotne-

ga Hg, so dolgoročno lahko bolj nevarne za okolje kot starejše, v katerih je Hg trdno vezan v cinabaritu (Biester et al., 1999).

Ker so večino žgalniških ostankov vsipavali v strugo Idrijce, so vsebnosti živega srebra v sedimentih reke Idrijce in Soče (Gosar, 1992; Gosar, 1997; Gosar et al., 1997b; Biester et al., 2000; Horvat et al., 2000) ter tudi v morskih sedimentih ob ustju reke Soče (Kosta et al., 1978; Covelli et al., 1999; Horvat et al., 1999; Širca et al., 1999a; Širca et al., 1999b; Biester et al., 2000; Covelli et al., 2001) povišane. Študija speciacij živega srebra v sedimentih (Biester et al., 2000) je pokazala, da nastopa živo srebro v dveh oblikah: kot cinabarit in kot Hg, vezan na komponente osnove (ne-cinabaritna frakcija). Vsebnost ne-cinabaritne frakcije je močno odvisna od zrnivosti sedimenta. Akumulacija cinabarita nastopa v bolj debelozrnatih rečnih sedimentih, kjer je več kot 80% Hg vezanega v cinabaritu. Ne-cinabaritne komponente pa so vezane na lokacije, kjer se kopiči najdrobnejši sediment: v poplavnih ravninah je ne-cinabaritnega deleža do 40%, v Tržaškem zalivu pa do 55%.

Hess (1991) je v okviru kratke študije preiskal nekaj vzorcev tal, rečnih sedimentov ter vode. V tleh je ugotovil od 1,8 do 885 mg Hg/kg, štirje vzorci rečnih sedimentov kažejo podobno vsebnost kot tla, vzorca vode pa sta vsebovala 0,35 in 3,1 $\mu g Hg/l$.

Prostorsko razporeditev koncentracij Hg v tleh na ozemlju velikem 8 x 14 km z Idrije v sredini je raziskoval Hess (1993). Vzorčeval je v pravilni mreži 1 x 1 km (127 vzorčnih lokacij) in sicer na travnikih prvih 15 cm tal, v gozdu prvih 20 cm in na oranih tleh prvih 30 cm tal. V gozdu, kjer so bili razviti tudi humusni horizonti, je bil na vsaki lokaciji vzet poleg vzorca mineralnega dela tal še vzorec humusnega horizonta.

Vrednosti nad 10 mg Hg/kg tal so v dolinah in ob vznožju vzpetin, nižje vrednosti pa so v višjih delih in na obrobju obravnavanega ozemlja. Najvišja vrednost je bila izmerjena v vzorcu s skrajnega severnega roba Idrije v dolini Idrijce (148,2 mg Hg/kg), najnižje vrednosti (0,2 mg Hg/kg) pa v severovzhodnih in južnih predelih obravnavanega ozemlja (Hess, 1993).

V desetih vzorcih je bila določena tudi količina najbolj nevarne oblike Hg - metil-

no živo srebro (skupno dimetilno - $\text{CH}_3\text{-Hg-}$

CH_3 in monometilno $\text{CH}_3\text{-Hg}^+$). Vsebujejo od manj kot 0,003 pa do 0,2 mg metilnega Hg/kg, kar ustreza od nekaj tisočink pa do 0,66 % celotnega Hg v vzorcih. Aritmetična srednja vrednost v analiziranih vzorcih je 0,065 mg metilnega Hg/kg in jo presegata le dva vzorca: vzorec humusa iz doline reke Idrijce med Idrijo in Spodnjo Idrijo, ki vsebuje kar 0,2 mg metilnega Hg/kg (0,13 % celotnega Hg), in vzorec mineralnega dela tal iz doline zgornjega toka Idrijce (0,12 mg metilnega Hg/kg; 0,66 % celotnega Hg). Statistično značilne korelacije med celotno količino Hg v vzorcih in vsebnostjo metilnega živega srebra v vzorcih niso ugotovili. Delež metilnega Hg je v primerjavi s celotnim živim srebrom v vzorcih razmeroma majhen, v vseh vzorcih pod 0,7% (Hess, 1993).

Metode in materiali

S študijo Hessa (1993) je bila ugotovljena razsežnost idrijske živosrebrove geokemične avreole, ki je nastala zaradi naravnih danosti (izdanjanja rudosnosnih kamnin) in zaradi pol tisočletja trajajočega rudniškega in topilniškega delovanja, katerega vpliv je zasenčil naravno povišano geokemično ozadje za Hg. Na območju velikem približno $3 \times 6 \text{ km}$ z Idrijo v sredini so bile ugotovljene zelo visoke koncentracije Hg v tleh. Ker pa takratna mreža vzorčevanja ni bila dovolj gosta, da bi ločila najbolj obremenjene lokacije, smo v letu 2000 opravili novo geokemično raziskavo z gostejšo mrežo vzorčevanja. Na najbolj obremenjenih območjih v Idriji in Spodnji Idriji smo vzorčevanje pogostili tako, da smo vzeli približno 4 vzorce na km^2 . Na naključno izbranih lokacijah smo vzeli vzorec podstrešnega prahu v najbližji ustrezni hiši ter v neposredni bližini hiše še vzorec tal. Predvidevamo, da je to dovolj, za določitev najbolj obremenjenih površin v Idriji in nivoja Hg v njih. Na lokacijah, kjer je vzorčeval že Hess, pa študija dokumentira tudi morebitne spremembe, ki jih je prineslo zadnje 10 letno obdobje od njegovega vzorčevanja.

Tla so bila vzorčena do globine 15 cm, brez morebitnega organskega horizonta. Izven naselij smo vzorčevali travniška tla (le izjemoma gozdna, če travnika ni bilo v bli-

žini), v naseljih pa urbana tla (vrtna tla in

tla obcestnih zelenic). Posamezen vzorec je predstavljal kompozit vzorca v osrednji točki in štirih 10 m oddaljenih točkah severno, vzhodno, južno in zahodno od osrednje. Celotni tako zbrani vzorec tal je tehtal približno 1 kg. Skupno smo raziskali 69 vzorcev tako odvzetih tal.

Podstrešni prah je v geokemične raziskave v Sloveniji vpeljal Šajn (1999). Predstavlja zvrst bivalnega prahu, ki se kopiči na podstrešjih. To je v prostorih, kjer se prebivalci zelo redko ali sploh ne zadržujejo in na katere vsakdanja dejavnost prebivalcev nima večjega vpliva. Izvira pretežno iz zunanjih virov, kot sta usedanje aerosolov in prašenje tal ter podrejeno iz gospodinskih dejavnosti. Delci bivalnega prahu se z vdihavanjem ali zaužitjem kopičijo v človeškem organizmu. Na ta način s prahom vnašamo v organizem tudi težke kovine (Schlipkoeter & Brockhaus, 1988).

Pomen podstrešnega prahu kot vzorčnega sredstva je v tem, da predstavlja edino snov, ki je ostala ohranjena in kemično nespremenjena skozi daljši čas. Raziskave kemizma podstrešnega prahu odkrivajo povprečno stanje ozračja v preteklosti (Šajn, 1999).

Podstrešni prah smo vzorčevali tako, da smo zbrali prah z lesene konstrukcije podstrešja, ki ni bila v neposrednem stiku s strešniki ali tlemi. Na ta način smo se izognili pobiranju delcev strešnikov, ostankov lesa in gradbenih materialov. Pri vzorčenju podstrešnega prahu smo izbrali čim starejše objekte. Skupno smo odvzeli 65 vzorcev podstrešnega prahu.

Zbrani vzorci so bili posušeni na zraku. Za kemijsko analizo podstrešnega prahu smo s sejanjem pripravili frakcijo manjšo od 0.125 mm. Talni vzorci so bili presejani skozi sito z velikostjo odprtin 2 mm, presevek pa zmlet na analizno zrnastost.

Vzorci so bili analizirani v laboratoriju ACME v Vancouvru v Kanadi. Za določitev vsebnosti Hg je bilo 0.5 g vzorca prelito s 3 ml zlatotopke (mešanica kislin $\text{HCl} : \text{HNO}_3 : \text{H}_2\text{O}$ v razmerju 3:1:2), eno uro segrevano na 95°C in potem razredčeno do 100 ml z destilirano vodo. V raztopini je bila določena vsebnost Hg z neplamensko AAS. Vzorce in naključno izbrane dvojnike ter geološke standardne materiale smo poslali v labora-

torij po naključnem vrstnem zaporedju. S tem smo zagotovili nepristranskost analitike in enakomerno porazdelitev morebitnega spreminjanja analiznih pogojev preko vseh vzorcev. Zanesljivost kemičnih analiz smo ocenili kot zelo zadovoljivo.

Rezultati in razprava

Na podlagi raziskanih vzorcev znaša ocenjeno povprečje živega srebra na območju Idrije v tleh 8.6 mg/kg in niha v razponu od 0.42 do 973 mg/kg in v podstrešnem prahu 43.5 mg/kg od najnižje vrednosti 1.8 do najvišje 1055 mg/kg. Slovensko povprečje za tla znaša 0.15 mg/kg (Pirc, 1993) in za podstrešni prah 1.1 mg/kg (Šajn, 1999). Kar na 17,4 km² obravnavanega ozemlja vsebnosti v tleh presegajo kritično dovoljeno vrednost za Hg v tleh (10 mg/kg - Ur. list RS, 1996).

Za lažjo primerjavo smo v enakih porazdelitvenih razredih pripravili geokemične karte porazdelitve Hg v tleh na podlagi podatkov vzorčevanja leta 1990 (Hess, 1993) (slika 2) in geokemične karte porazdelitve Hg v tleh in podstrešnem prahu na podlagi našega vzorčevanja leta 2000 (sliki 3 in 4). Stanje obremenjenosti tal se v desetih letih, kot smo tudi pričakovali, ni bistveno spremenilo. Nivo Hg je v tleh v letu 1990 zelo primerljiv s stanjem v letu 2000. Smo pa z gostejšim vzorčevanjem v lanskem letu uspeli določiti lokacije, ki so še posebno obremenjene s Hg (koncentracije večje od 140 mg/kg). Prostorska razporeditev živega srebra v tleh je zelo odvisna od morfologije ozemlja (sliki 3 in 5). Najvišja koncentracija živega srebra v tleh (973 mg/kg) je bila določena v vzorcu št. 507. To so vrtna tla na Kosovelovi ulici 21 v Idriji. Po podatkih Čarja (1998) je omenjena lokacija na robu izdanjanja orudenih kamnin, ki vsebujejo tako elementarno živo srebro kot tisto vezano v cinabaritu. Poleg tega segajo na to območje tudi orudeni neprežgani odvali (Čar, 1998). V neposredni bližini omenjene lokacije je podobno koncentracijo v tleh (885 mg/kg) določil tudi Hess (1991). Drugo najvišjo koncentracijo Hg (924 mg/kg) smo določili na Prejnuti (vzorec št. 518). Tu so prisotni primarni žgalniški ostanki, saj so tam rudo žgali od sredine 17. do sredine 19.

stoletja, žgalniški ostanki pa so se kopičili v okolici (Čar, 1998). Na tem območju je bil velik tudi neposreden vpliv dimnih plinov iz topilnice. Nadalje se je pri podrobnejšem vzorčevanju pokazalo povišanje vsebnosti Hg v območju med zadnjimi 500 m Ljubevšce in Idrijo (vrednosti med 40 in 67 mg/kg), kar gre morda pripisati vplivu prezračevalnega jaška, ki je v bližini. Z enim vzorcem smo ugotovili povišane vrednosti Hg tudi na območju hriba Pšenk, JZ od Idrije. Verjetno tako visoka koncentracija živega srebra (57 mg/kg) ni posledica atmosferskih emisij ali naravnih danosti, ker na tem območju ne izdajajo rudonosne kamnine. Lahko pa je posledica žganja rude v preteklosti po gozdovih, kot omenja Čar (1998). V bližini je vzorčeval tudi Hess, a povišanja vrednosti ni zaznal.

Vsebnosti Hg v podstrešnem prahu so v povprečju za 3.6-krat višje kot v tleh. Živega srebra je več v tleh kot v prahu le na lokacijah, kjer je njegov poglavitni vir poleg atmosferskih emisij tudi talna podlaga. To je na prej omenjenih deponijah starih prežganih in neprežganih rudniških odvalov, na območju izdanjanja rudonosnih kamnin ter na lokacijah, kjer so žgali rudo v prejšnjih stoletjih ali uporabljali žgalniške ostanke v cestogradnji in podobno. Lokacije s povečano vsebnostjo živega srebra v talni podlagi je opisal Čar (1998).

Porazdelitvi Hg v podstrešnem prahu in v tleh v Idriji in okolici sta si zelo podobni (sliki 3 in 4). Korelacijski koeficient (r) med vsebnostjo Hg v obeh vzorčnih sredstvih znaša 0.87 (slika 6). Močno povezavo smo odkrili tudi med vsebnostjo Hg v tleh in v podstrešnem prahu ter nadmorsko višino ($r = 0.84$ oz. $r = 0.80$; sliki 7 in 8). Iz tega lahko sklepamo, da je onesnaženje vezano predvsem na dolino reke Idrije, daljinski vpliv pa je podrejenega pomena.

Še posebno so zanimive vsebnosti živega srebra v podstrešnem prahu. Na karti porazdelitve Hg v njem (slika 4) je razvidno, da je vpliv rudniške, predvsem topilniške dejavnosti zaznaven še izven robov raziskane ozemlja in da je bil vpliv rudarjenja v Idriji pomemben tudi v regionalnem merilu.

Najvišje vsebnosti Hg v podstrešnem prahu so bile določene v neposredni bližini topilnice (1055 mg/kg) in v dolini Idrije od sotočja z Nikovo do HE Marof (vsebnosti od

275 do 542 mg/kg) (sliki 5 in 9). Zaradi prevladujočih južnih vetrov se je onesnaženje širilo od glavnega vira onesnaženja, to je od topilnice, po dolini Idrije daleč proti severu. To je lepo razvidno iz porazdelitve vsebnosti živega srebra v vzorcih tal in podstrešnega prahu, ki je prikazana na sliki 9. Visoke so tudi vsebnosti v dolini Ljubevšče, kar je verjetno odraz prezračevalnega jaška v tej dolini.

Zelo zanimiva je tudi primerjava vsebnosti živega srebra v vzorcih, ki leže nižje oz. višje od topilniškega dimnika. Ocenjeno povprečje Hg v vzorcih tal oz. podstrešnega prahu, ki so nižje od dimnika znaša 42 oz. 122 mg/kg, v vzorcih zbranih višje od dimnika pa 2.8 mg/kg v tleh in 16 mg/kg v podstrešnem prahu. Razvidno je, da vsebnosti Hg v tleh rečne doline za 15-krat presegajo vsebnosti v okolici, v podstrešnem prahu pa za skoraj 8-krat.

Ugotovili smo tudi, da je obogatitveni odnos (Fergusson & Kim, 1991) med Hg v podstrešnem prahu in Hg v tleh odvisen od nadmorske višine. Pod dimnikom je vsebnost Hg v podstrešnem prahu za 3-krat večja kot v tleh, nad dimnikom pa več kot 7-krat, kar je podobno razmerju slovenskih povprečij (7.3) (slika 10). Na lokacijah, kjer so bile za obremenitve okolja najpomembnejše atmosferske emisije, so vsebnosti v podstrešnem prahu mnogo višje kot v tleh na isti lokaciji. Najvišja razmerja med Hg v prahu in Hg v tleh smo ugotovili na najbolj oddaljenih lokacijah, ki so navadno tudi na višji nadmorski višini (npr. vzorci št. 119, 123, 122, 106).

Na območju Idrije smo prvič uporabili podstrešni prah za geokemično kartiranje z gosto mrežo vzorčevanja na majhnem območju. Izkazal se je kot izjemno uporabno in za geokemično kartiranje zelo stabilno vzorčno sredstvo z nizkim deležem variance na majhnih razdaljah.

Mehanizmi razširjanja živega srebra v Idriji

Na podlagi raziskav o razširjenosti Hg v okolju v preteklosti in na podlagi naših meritev lahko ugotovimo, da so mehanizmi razširjanja živega srebra in vzroki kontaminacije okolja z njim na Idrijskem mnogov-

stne narave. Najpomembnejši viri živega srebra so: atmosferske emisije, odvali rude in žgalniških ostankov ter izdanki rudonosnih kamnin.

V samem mestu Idrija in bližnji okolici so bile pomembne *atmosferske emisije*. Samo iz dimnika topilnice je pred letom 1977, ko sta rudnik in topilnica delovala še v polni meri uhajalo v atmosfero okrog 20 kg Hg/dan (Kosta et al., 1974; Kavčič, 1974). Zato so bile glavni vzrok obremenjenosti okolja z živim srebrom v Idriji in njeni okolici atmosferske emisije. Ker je bil najpomembnejši vir onesnaženega zraka topilnica z odlagališčem žgalniških ostankov, na severnem robu Idrije, kjer prevladujejo vetrovi v smeri sever-jug s poudarjeno južno komponento (Petkovšek & Rakovec, 1980), so se onesnaženi plini in prašni delci širili v glavnem po dolini Idrije severno od Idrije. To je razvidno tudi s slike 9, kjer so prikazane koncentracije Hg v tleh in podstrešnem prahu vzdolž doline Idrije. Ker dolino Idrije omejujejo strma pobočja z višinsko razliko tudi več kot 700 m, se širi onesnažen zrak predvsem po dolini. Drugi pomemben vir atmosferskih emisij Hg sta prezračevalna jaška. Ob jašku Inzaghi, ki leži v centru mesta Idrija, so bile tudi v času po ukinitvi proizvodnje živega srebra v Idriji izmerjene visoke vsebnosti živega srebra v zraku (Gosar et al., 1997a; Miklavčič, 1999). Prezračevalni jašek v dolini Ljubevšče naj po mnenju Miklavčičeve (1999), glede na vsebnosti Hg v korenju, ne bi imel velikega vpliva. Vsebnosti Hg v podstrešnem prahu in tleh (sliki 3 in 4) pa kažejo povišane koncentracije Hg v dolini Ljubevšče, ki jih verjetno lahko pripišemo vplivu tega zračnika.

Drugi vzrok obremenitve okolja z živim srebrom so odvali rude in predvsem odvali *žgalniških ostankov*, ki vsebujejo še precej Hg. Osnovni vzrok za veliko razširjenost in zapleteno prostorsko razporeditev žgalniških ostankov v Idriji in njeni okolici je v načinu žganja rude v preteklosti in uporabi žgalniških ostankov v gradbene namene v povojnem obdobju (Čar, 1998). Do srede 17. stoletja so žgali rudo na bližnjih gričih Pront, Pringl, pa tudi na bolj oddaljenih krajih v Čekovniku in Kanomlji, o čemer pričajo številni ostanki razbite lončevine. Več lokacij starih žgalnic je našel I. Mlakar

pri geološkem kartiranju idrijske okolice, nekaj pa so jih našli tudi kasneje (Čar, 1998). Prva trajneje locirana žgalnica v mestu je bila na Lenštat. Leta 1652 so začeli graditi žgalnico na Prejnuti, ki je delovala vse do 19. stoletja. Po letu 1868 so postopoma zgradili novo žgalnico na Brusovšu, na Prejnuti pa so žganje opustili. Večino žgalniških ostankov so potem vse do leta 1977 neposredno vsipavali v Idrijo, ki je material ob visokih vodah odnašala po dolini Idrijce in Soče v Jadransko morje. Tako so v spodnjem toku Idrijce nastali obsežni rečni nanosi z visokimi vsebnostmi Hg (Gosar, 1997; Gosar et al., 1997b; Biester et al., 2000), ki so in bodo vir z živim srebrom obremenjenega sedimenta tudi v prihodnosti. Nastale pa so tudi nove deponije prežgane rude vzdolž desnega brega Idrijce. Po obnovitvi proizvodnje po letu 1983 zaradi ekoloških razlogov ni bilo več dovoljeno vsipavati žgalniških ostankov v strugo Idrijce (Čar, 1998). Kljub temu pa se je zaradi slabo utrjenih brežin ob večjih nalivih spiral material v Idrijo še naprej. Prostorsko razporeditev žgalniških ostankov je prikazal Čar (1998). Najvišje koncentracije Hg, ki smo jih določili v obravnavanih talnih vzorcih (lokacija 518 in delno lokacija 507) smo pripisali vplivu žganiških ostankov.

Raven živega srebra je v okolju na Idrijskem povečana tudi zaradi *naravnih - geogenih dejavnikov*. Singenetsko orudene anizijske in litološko pestro razvite ladinijske plasti so nastajale v svojih sedimentacijskih pogojih tektonskega jarka idrijske srednjetasne tektonske zgradbe. Odložene so na erodirane starejše anizijske, skitijske, permske in karbonske kamnine, ki so epigenetsko orudene (Mlakar, 1967; Placer & Čar, 1977; Čar 1985; Čar, 1998). Pri kasnejših tektonskih dogajanjih je nastala današnja izjemno zapletena zgradba rudišča. Za preprečitev obsežnejše naravne migracije živega srebra v širšo okolico je pomembno predvsem to, da je rudišče obdano z neprepustnimi karbonskimi klastičnimi kamninami ali pa omejeno z zaglinjenimi tektonskimi conami (Čar, 1998). Zahodni del rudišča je bil ob prelomu dvignjen, tako da je erozija odkrila del orudenih kamnin, predvsem karbonske klastite s samorodnim živim srebrom ter ob skrajnem zahodnem obrobju rudišča tudi pretrte orudene Skon-

ca plasti in tufite. V povprečju vsebujejo orudeni klastiti 0,38% živega srebra, približno 50% v obliki minerala cinabarita, ostalo kot samorodno živo srebro (Čar, 1998).

S Hg obogatene karbonske plasti gradijo podlago mestnega središča in izdanjajo na pobočju Kurjega vrha in spodnjega dela Pronta, Skonca plasti in tufiti pa izdanjajo na Prontu med Karčnikom in Albrehtom (Čar, 1998).

Na območjih, kjer izdanjajo kamnine orudene s Hg, vsebujejo tudi tla naravno povišane vsebnosti živega srebra. Tako območje je npr. Pront, kjer izdanjajo karbonski klastiti s samorodnim živim srebrom.

Iz rezultatov opravljenih raziskav lahko zaključimo, da je Idrija z njeno okolico specifičen primer okolja, ki je zelo obremenjeno z živim srebrom. Predstavlja hvaležen študijski model, ker je na relativno majhnem območju mogoče raziskovati vpliv naravnih (geogenih) virov živega srebra in tistih, ki jih je zaradi petstoletnega pridobivanja Hg povzročilo človekovo delovanje v okolju.

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