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Preliminary results of detailed geochemical study of mercury at the ancient ore roasting site Pšenk (Idrija area, Slovenia)

Preliminarni rezultati geokemične raziskave živega srebra na območju nekdanje žgalnice rude Pšenk (Idrijsko, Slovenija)

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Abstract

Pšenk is one out of 21 localities of ancient roasting sites in the woods surrounding Idrija and one of the largest localities of roasting vessels fragments. The most abundant pottery remains are found in the central western part of the area, which is about 60 m long and up to 50 m wide and is supposed to be the location of the roasting process itself. Detailed soil sampling was performed on 210 x 180 m big area. 156 soil (0–15 cm and 15–30 cm) and humus samples were collected from 73 sampling points. 3 soil profiles were sampled to determine vertical distribution of Hg in soil. The prevailing soil types are Cambisols with the typical A-B-C layers sequence. In general soils are rich in organic matter to the depth of 30–40 cm; deeper the clayey loam prevails. The determined Hg contents in soil and humus samples of the investigated area are in the range 1.6–8,600 mg/kg with the median of 62.5 mg/kg. At the area of supposed roasting site the Hg contents range between 20 and 8,600 mg/kg with the median of 580 mg/kg. Spatial distribution of mercury in humus and soils of the investigated area show the highest Hg concentrations at the supposed roasting site area where the largest quantity of pottery fragments were found and to the east of this area, at the narrow tract between the footpath on the north and the bed of Lačna voda brook on the south. Extremely high Hg contents were found in profile P4 where it riches 37,020 mg/kg at the depth of 20–30 cm; in general Hg concentrations in all three studied profiles show a gradual decrease with depth. The soils of the investigated area are enriched with mercury to a high degree. Further investigations on Hg speciation are needed to determine the mobility and bioavailability of Hg in soil.

Izvleček

Pšenk je ena izmed 21 lokacij nekdanjih žgalniških mest v gozdovih okrog Idrije in eno večjih nahajališč drobirja žgalniških posod. Največje količine lončenine najdemo na približno 60 m dolgem in do 50 m širokem predelu v centralnem zahodnem delu obravnavanega območja, ki domnevno predstavlja ožje območje žgalnice. Na raziskovanem ozemlju v velikosti 210 x 180 m je bilo na 73 vzorčnih lokacijah odvzetih 156 vzorcev tal (0–15 cm and 15–30 cm) in humusa. Za določitev vertikalne razporeditve Hg v tleh so bili vzorčeni 3 talni profili. Prevladujoči talni tip so kambična tla s tipičnim profilom A–B–C. Tla so v splošnem bogata z organsko snovjo do globine 30–40 cm, globlje pa prevladuje glinasta ilovica. Vsebnost živega srebra v obravnavanih vzorčnih medijih znaša v povprečju 62,5 mg/kg in niha v razponu od 1,6 do 8.600 mg/kg. Na ožjem območju žgalnice se vrednosti gibljejo med 20 in 8.600 mg/kg, mediana znaša 580 mg/kg. Prostorska razporeditev živega srebra v humusu in tleh kaže najvišje vrednosti na domnevnem ožjem območju žgalnice in vzhodno od tega območja, na predelu med gozdno potjo na severu in strugo potoka Lačna voda na vzhodu. Ekstremno visoke vsebnosti Hg so bile določene v profilu P4, kjer dosežejo na globini 20–30 cm vrednost 37.020 mg/kg; v splošnem vsebnosti Hg v vseh treh obravnavanih profilih postopoma upadajo z globino. Tla na obravnavanem območju so močno obogatena z živim srebrom, zato so potrebne nadaljnje raziskave zvrsti živega srebra, ki bodo omogočile določitev mobilnosti in bio-dostopnosti živega srebra v tleh.

Introduction

Numerous extensive and detailed investigations on mercury pollution were performed in Idrija region in the last decades (Gnamuš, 1992, 2002; Hess, 1993; Palinkaš et al., 1995; Gosar, 1997, 2008; Gosar et al., 1997, 2006; Biester et al., 1999, 2000; Horvat et al., 2003; Gnamuš et al., 2000; Gosar & Šajn, 2001, 2003; Kocman et al., 2004; Gosar & Čar, 2006; Hines et al., 2006; Žibret & Gosar, 2006). Owing to naturally increased mercury contents in certain rocks, mining and ore processing,

Idrija and its surroundings are heavily polluted with Hg. Most studies on the environmental legacy of the Hg mining activity in Idrija has focused on soils in the vicinity of the smelter in Idrija or on the draining systems of the Idrijca river, including the Gulf of Trieste, which is seen as the major sink of Hg derived from the mining activity in Idrija. Systematic investigations of mercury contents and its spatial distribution in soil (Hess, 1993; Gosar & Šajn, 2001, 2003; Gosar et al., 2006) demonstrate very high mercury contents in the Idrijca River valley near the pollution source, i.e. smokestack, while lower values prevail at higher elevations and tend to decrease with the distance from Idrija. Until recently, most interpretations of the investigations resulted from the belief that the town of Idrija with the mine, the smelter and waste material dumps, is the only source of pollution. The detailed study on different ways of ore roasting techniques in the first 150 years of mercury production (Čar & Terpin, 2005; Kavčič, 2008), revealed numerous localities of historical ore roasting sites in the woods around Idrija; large quantities of broken pottery can be found at these sites. Up to now 21 localities of ancient roasting sites were established on the neighbouring hills and in more distant localities; taking into account their extent and numerousness they represent a constant source of mercury emissions (Čar & Terpin, 2005; Gosar & Čar, 2006). In certain studies several anomalies were discovered in soils (Hess, 1993; Gosar & Šajn, 2001) and sediments (Gosar, 2008) where increased mercury contents cannot be the consequence of main Hg sources such as atmospheric emissions, mineralized rock dumps and smelting residues or their use in construction. These unexplained mercury anomalies could most likely be the consequence of ancient ore roasting in the woods around Idrija.

Despite the fact that they are known, small roasting sites from the early times (16th and first half of 17th century) of mining activity have been neglected as an important source of Hg pollution of soils and groundwater in the Idrija area. In general, the long term fate of Hg in the soils polluted by the Hg mining activity in Idrija is not sufficiently understood. Among the studies that have focused on soil contamination, none has yet dealt with the former old ore-roasting sites located mainly in the forests, more or less distant from the ore deposit. Studies of these interesting locations have been so far restricted above all to the collection and interpretation of historical data, the assessment of roasting site locations and the reconstruction of ore roasting in earthen vessels. The preliminary investigation of mercury contents in soils at old roasting site locations revealed that mercury contents in soils at these sites are very high, surpassing all hitherto described localities at Idrija and surroundings. It is estimated that there are about 40 tons of mercury still present at all roasting sites in the woods described up to now (Gosar & Čar, 2006). Moreover, it is not known to what extent and how distant Hg from these comparatively primitive ore processing sites had been dispersed by emissions of Hg(0) to the soils in vicinity of those sites.

This study is the continuation of the before mentioned preliminary geochemical investigation in the areas of ancient small scale mercury ore roasting sites in Idrija environments (Gosar & Čar, 2006). The research aims result from the unique situation of the historical contaminated sites, which allows new insight into the long term fate of mercury and its species in the waste dumps and soil environment. The objectives of this work are to define 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. In this paper some preliminary results from old roasting site Pšenk are presented.

Procedure of ore roasting in earthen vessels

In the first decade of mercury mining in Idrija the ore was roasted in piles. This was the most primitive method of extracting mercury and was employed for only a short period of time, from 1490 until 1510. The recovery rate of this method was very low and about half of the mercury was lost. For this reason, a new procedure, roasting of ore in earthen (clay) vessels was introduced in 1494; the ore roasting in this manner was performed at various sites in the woods around Idrija and it lasted for approximately 150 years, until 1656. The reason why this procedure was used for such a long time period lies in very rich mercury ore, which was discovered in 1508 and probably contained on average about 50 % of Hg. The richest excavated ore could contain up to a few percent of elemental Hg. 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 (Kavčič, 2008). 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 (Verbič, 1965). Large quantities of broken pottery can be found at an-

cient roasting sites, especially at localities Pšenk and Frbejžene trate.

Materials and methods

Site description

Pšenk is one of the larger localities of roasting vessels fragments. Its position is represented on Figure 1. Roasting site Pšenk was discovered already in the beginning of 20th century during cutting down old spruce-trees (Grund, 1911). It is located on flattened surface at Lačna voda brook below Hleviše, above its confluence with the Padar ravine. The flattened surface is the result of the thrust along which the Triassic dolomite is thrusted over the Cretaceous limestone. The dolomite is covered with stained quartz conglomerate and sandstone of the Carnian age (Čar & Terpin, 2005). The most abundant pottery remains are found in the central western part of the area, just below the way to Hleviše. This area is about 60 m long and up to 50 m wide and is supposed to be the location of the roasting process itself. The pottery fragments lay just below the surface humus layer and in some parts they stretch more than 1 meter deep. Single parts of pottery fragments can be found along the whole gravelly bed of Lačna voda brook.

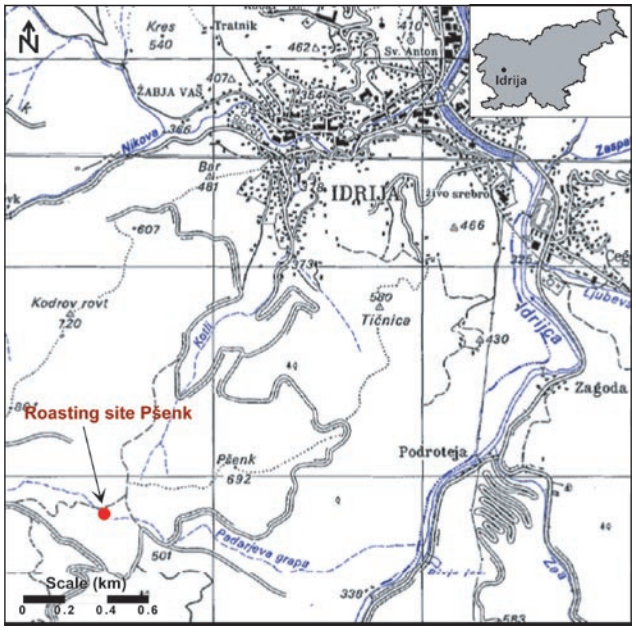

Fig. 1. Locality of ancient roasting site Pšenk

Sampling

Detailed soil sampling was performed on the area of former roasting site and its surroundings, on approximately 210 x 180 m big area (Fig. 2). Soil (0–15 cm) and humus samples were collected from 73 sampling points in the research grid 30 x 30 m. At the area of supposed past roasting processes (approximately 40 x 50 m big area) the sampling was performed in the research grid 10 x 10 m (22 sampling locations) and beside humus and topsoil (0–15 cm) also bottom soil (15–30 cm) samples were collected here. Approximately 1 kg

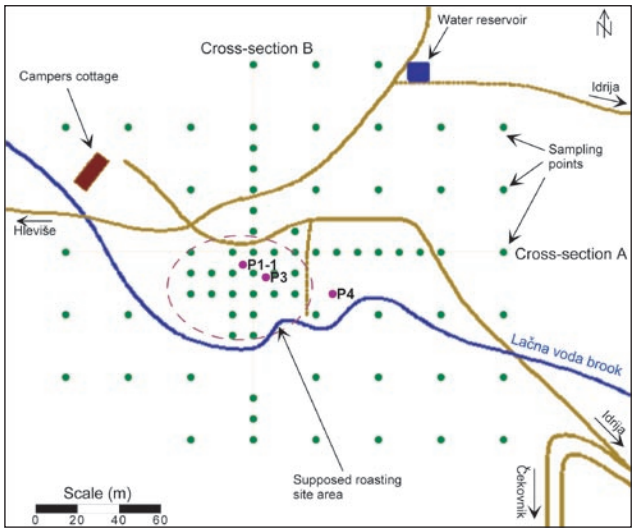

Fig.2. Pšenk roasting site area with sampling locations

of soil and 0.5 kg of humus was collected at each sampling site. To determine vertical distribution of Hg in soil also 3 soil profiles were sampled. The P1-1 profile was taken by digging a ditch of about 35 cm in depth; afterwards it was taken by a hand-drilling tool to a depth of 95 cm. The P1-1 profile was sampled next to the locality of geochemical profile P1, described in the study of Gosar & Čar (2006). Profile P3 was sampled by a hand-drilling tool to 50 cm. Profile P4 was taken by digging a ditch of approximately 50 cm in depth. Samples were then cut from the soil column using a plastic spatula with regard to visible differences of soil characteristics (colour, consistency). Samples were taken on each 20 cm with a hand-drilling tool. The prevailing soil types are Cambisols with the typical A-B-C layers sequence. In general soils are rich in organic matter to the depth of 30–40 cm; deeper the clayey loam prevails. Soil characteristics are shown in Table 2. All soil and humus samples were stored in polyethylene bags at ambient temperature (15–25 °C) before further treatment in the laboratory.

Sampling preparation and analytical methods

The soil samples were air-dried and gently crushed in a ceramic mortar and passed through a sieve with 2 mm openings. Fraction smaller than 2 mm was pulverized prior to chemical analysis. Hg was determined by cold vapour atomic absorption spectrometry (CV-AAS) after digestion of the sample material in aqua regia for 3 h at 160 °C. Samples with very high Hg concentrations (>100 mg/kg) were analyzed at the Institute for Environmental Geochemistry at Technical University Braunschweig. To determine total mercury, 0.10 g of soil samples was digested with a mixture of HNO_3 and HCl at a ratio 1:3, left to react for 24 hours at room temperature and after that for 1 hour at 160 °C. The mixture was then filtered through folded filter (∅ 185 mm) and diluted with ionized water to 100 ml. Then the sample was reduced with stannous chloride ($SnCl_2$) to convert Hg^{2+} to gaseous mercury (Hg^0) and then detected using mercury analyzer.

Quality assurance was carried out by shipment of samples, duplicates and geological standards to the laboratory in a random succession to distribute evenly any errors due to laboratory performance. Objectivity was assured through the use of neutral laboratory numbers. The reliability of analytical procedures was considered adequate for using the determined Hg contents in further statistical analyses.

Data analysis and production of maps were performed on a PC using the Statistica (ver. 6.1), Autocad (ver. 2000) and Surfer (ver. 8.0) software. The universal kriging with linear variogram interpolation method (Davis, 1986) was applied to construct the maps of areal distribution of Hg in humus and soil (0–15 cm). For class limits the percentile values of the Hg distribution in investigated samples were chosen. Five classes of the following percentile values were selected: 0–10, 10–25, 25–75, 75–90 and 90–100.

Results and discussion

The Hg contents in soil and humus samples of the investigated area are in the range 1.6–8,600 mg/kg (*N=156*) with the median of 62.5 mg/kg. The Hg median in humus samples (*N=67*) amounts to 20.0 mg/kg with individual contents ranging between 1.4 and 4,200 mg/kg. Hg concentrations in soil (*N=73*) vary from minimum 5.5 to maximum 8,600 mg/kg with the median of 70.0 mg/kg. At the area of roasting site itself the Hg contents range between 20 and 8,600 mg/kg with the median of 580 mg/kg (*N=58*). The median in humus samples is 435 mg/kg (20–2,100 mg/kg; *N=20*), in topsoil 695 mg/kg (60–8,600 mg/kg; *N=22*) and in subsoil 535 mg/kg (50–7,900 mg/kg; *N=16*). Table 1 summarizes the determined Hg values in humus and soil samples of the investigated area.

The determined Hg values in the investigated area are extremely high, surpassing all hitherto described localities at Idrija and surroundings. Compared to Hg average for Slovenian soils (0.065 mg/kg; Šajn, 2003), the studied soils from the investigated area are enriched in mercury by a factor of 10^2–10^6. The Slovenian critical value for Hg in soil (10 mg/kg; Ur. list RS 68/96 – Off. Gaz. RS 68/96) is exceeded on approximately 82 % of the investigated area. The highest Hg contents were determined in upper soil horizon (0–15 cm) and the lowest in humus samples. Compared to Hg contents in soils of Idrija area in the size of about 160 km^2 (Gosar et al., 2006; Table 1), the determined Hg values of the investigated area are much higher. According to Gosar et al. (2006) the studied area belongs to Area 2, which includes the area in the vicinity of the towns of Idrija and Spodnja Idrija and on the whole comprises 51 km^2. Compared to the established Hg median (3.2 mg/kg) and maximum (75 mg/kg) for this area, the Hg median in soils of the investigated area is 20-times higher and the maximum value is more than 100-times higher.

In profiles P1-1, P3 and P4 the determined Hg contents are very high, ranging from 140 to 37,020 mg/kg (Table 2, figs. 3 and 4). In profile P3 the contents decrease proportionally with depth, from 960 mg/kg in the top, with organic matter rich soil layer (0–20 cm) cm to 190 mg/kg in the bottom soil layer (40–50 cm). In profile P1-1 the Hg content increase from 1,880 mg/kg in the top soil horizon (0–15 cm) to 3,330 mg/kg at the depth of 15–35 cm; then the contents decrease with depth and reach 140 mg/kg at 75–95 cm. Compared to geochemical profile P1, described in the preliminary investigation in the areas of historical ore roasting sites (Gosar & Čar, 2006), the determined Hg contents in profile P1-1 have similar values and distribution. In P1 the established Hg contents were very high in the top 45 cm thick layer (4,000 to 5,000 mg/kg) and fall quite rapidly with depth to around 100 mg/kg at 60 cm. Extremely high Hg contents were found in profile P4 where it riches 37,020 mg/kg at the depth of 20–30 cm. The value declines quite rapidly with depth and in depth range 30–50 cm only 1,080 mg/kg of mercury was found. In general Hg concentrations in all three studied profiles show a gradual decrease with depth which is in accordance with the decrease in organic matter content. This behaviour,

Area		*Depth (cm)*		*Hg content (mg/kg)*			
				N	Median	Min	Max
total investigated area		all samples		156	62.5	1.4	8,600
		humus		67	20	1.4	4,200
		soil	0–15 cm	73	70	5.5	8,600
roasting site area		all samples		58	580	20	8,600
		humus		20	435	20	2,100
		soil	0–15 cm	22	695	60	8,600
			15–30 cm	16	535	50	7,900
Idrija*	**Area 1**	soil	0–15 cm	32	47	3.3	973
	Area 2			31	3.2	0.4	75
	Area 3			37	1.0	0.3	13
Europe**		subsoil	>25 cm		0.022		
		topsoil	0–25 cm		0.037		
		humus			0.202		
Slovenia***		soil	0–5 cm		0.065		

*after Gosar et al., 2006
**after Salminen et al., 2005
***after Šajn, 2003

Table 1.
Mercury contents in humus and soils of the investigated area and comparison to mercury contents in soils of Idrija area, and to Slovenian and European averages of mercury in soil

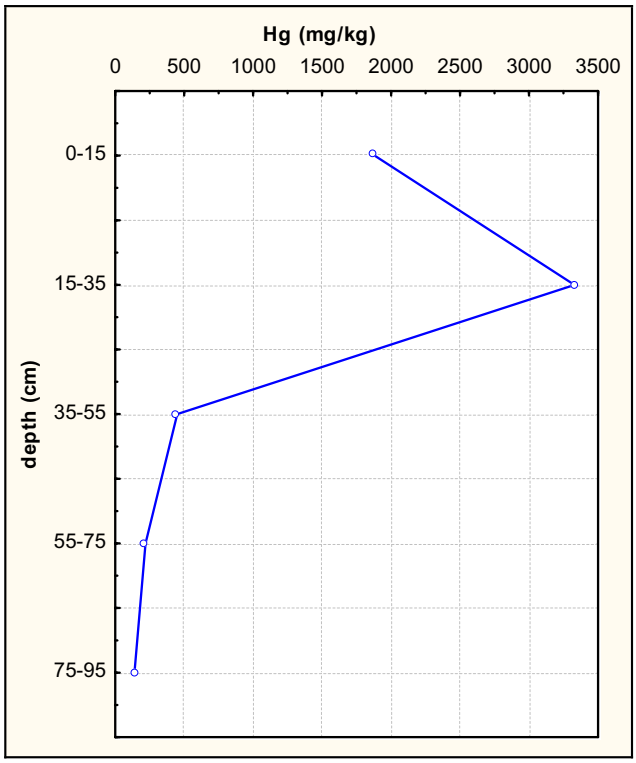

Fig. 3. Mercury contents in P1-1 profile

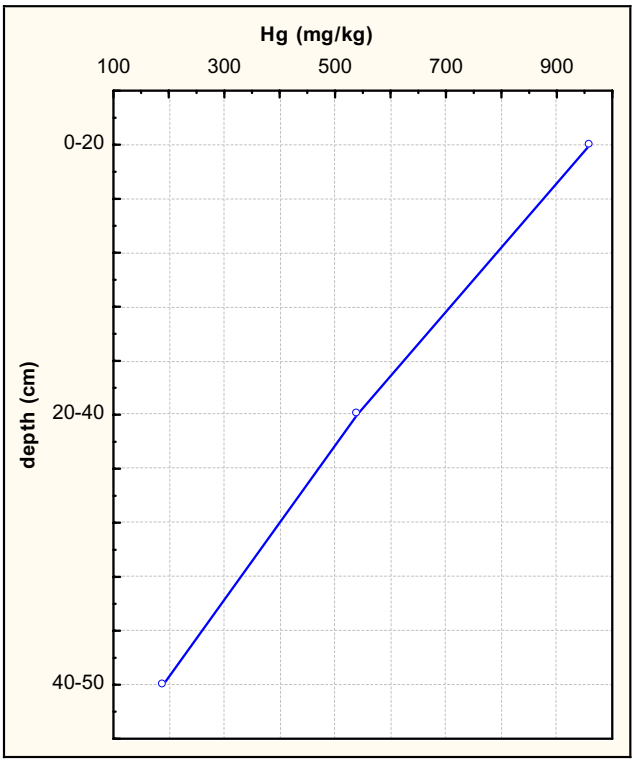

Fig. 4. Mercury contents in P3 profile

which was observed in several studies (Biester et al., 2002, Palmieri et al., 2005) indicates that retention of Hg is strongly related to organic matter content, which is the highest in uppermost soil layer. However, the increase of Hg content from the topsoil layer to the highest value in the depth range from 15–35 cm in profile P1-1 and 20–30 cm in profile P3 could imply that adsorption of Hg to mineral soil components is as much or even more important than binding of Hg to organic matter content. The situation could also be the result of Hg transportation to deeper soil layers as soluble organic complexes. Nevertheless, to ascertain any of these assumptions, further analyses on mercury speciation and organic carbon content are in progress.

Spatial distribution of mercury in humus and soil of the investigated area (Figs. 5 and 6) show the highest Hg concentrations at the supposed roasting site area where the largest quantity of pottery fragments were found and to the east of this area, at the narrow tract between the footpath on the north and the bed of Lačna voda brook on the south. In humus the Hg contents decrease quite rapidly with the distance from this area and they reach the values of less than 10 mg/kg at the margins of the studied area. Hg distribution in soil shows a little larger region of highly contaminated area with slower decreasing of Hg concentrations to the margins of the studied area. High Hg contents (> 200 mg/kg) are continuing to the central western part and also to the north-eastern and

Profile	*Depth (cm)*	*Soil characteristics*	*Hg (mg/kg)*
P1-1	0–15	A horizon with pottery fragments	1,880
	15–35	organic matter rich soil; a lot of pottery fragments	3,330
	35–55	clayey loam	450
	55–75	loam with dolomitic fragments	220
	75–95	loam with a lot of dolomitic fragments from rock substrate	140
P3	0–20	A horizon	960
	20–40	organic matter rich soil mixed with clayey loam	540
	40–50	clay loam with sandstone fragments from rock substrate	190
P4	0–20	humic A horizon	13,845
	20–30	mixed layer (bituminous soil and clayey loam)	37,020
	30–50	clayey loam	1,080

Table 2. Mercury contents in profiles P1-1, P3 and P4

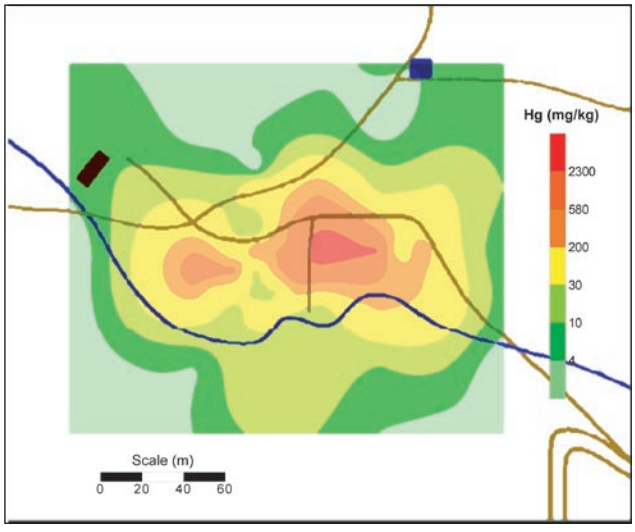

Fig. 5. Spatial distribution of mercury in humus (see Fig. 2 for orientation)

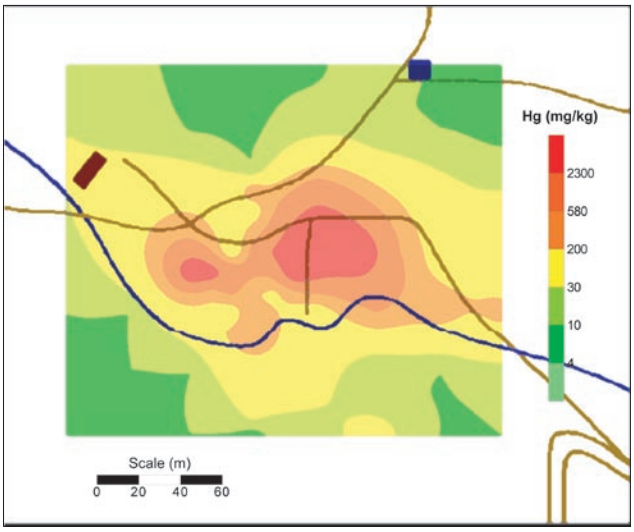

Fig. 6. Spatial distribution of mercury in soil (0–15 cm) (see Fig. 2 for orientation)

southern part of the investigated area where they are remaining in the range above 30 mg/kg. Hg distributions in cross-sections A and B show similar pattern (Figs. 7 and 8). The Hg contents in soil of cross-section A are very high, reaching up to 8,000 mg/kg Hg. The contents gradually increase from the west towards the central part of the investigated profile with the maximum in the distance 130 m from the western point of sampling and then the contents gradually decrease to the east. Similar can be observed in cross-section B from the north to the east, though the pattern is not so regular and the Hg contents are much lower, with the maximum of about 900 mg/kg Hg. Very low Hg values in the northern part of cross-section B are the result of the elevated area in this region which means that the increased Hg concentrations here are probably only the consequence of smoke emissions during ore roasting and not of the roasting process itself. The main effects of the past roasting processes can be seen in increased Hg values in soils and humus in the narrow region between the footpath on the north and the Lačna voda brook on the south in the length of approximately 120 m and width about 50 m. Very high Hg concentrations in this area are presumably the consequence of considerable losses of Hg during the roasting process and many years of ore roasting at this site.

A major point regarding mercury in soils relates the chemical and/or mineralogical species present in them. Mercury deposited to soil is known to be subject to a wide array of chemical and biological transformation processes such as Hg(0) oxidation,

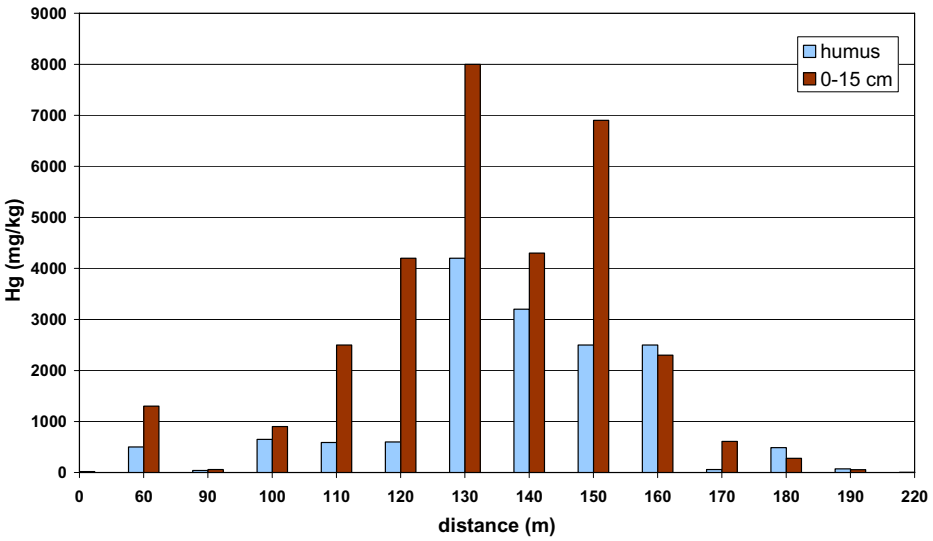

Fig. 7. Mercury contents in cross-section A (from the west on the left to the east on the right) *the position of the cross-section is shown on Fig. 2

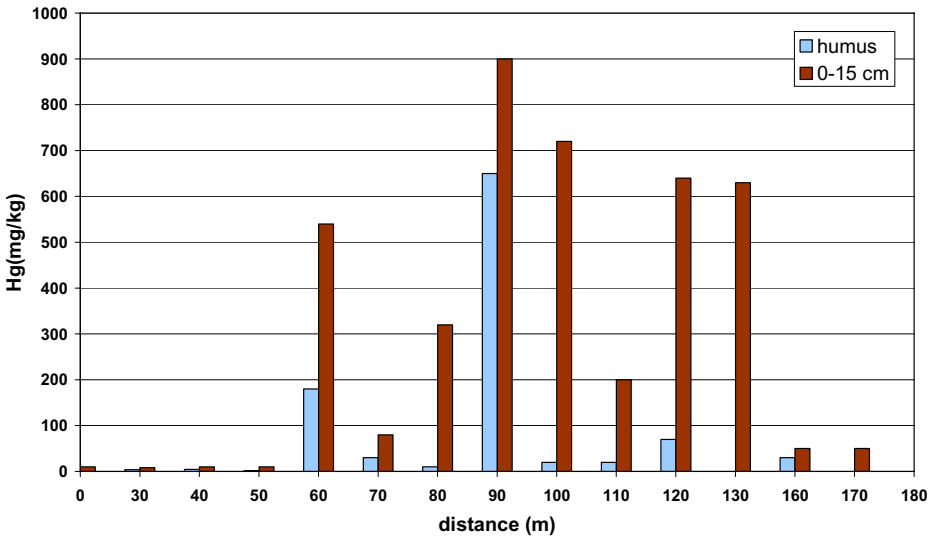

Fig. 8. Mercury contents in cross-section B (from the north on the left to the south on the right) *the position of the cross-section is shown on Fig. 2

and Hg(II) reduction or methylation depending on soil pH, temperature and soil humic substances. Hg mobilization in soils through formation of inorganic soluble Hg compounds such as $HgCl_2$ and $Hg(OH)_2$, are of minor importance in the presence of organic matter as Hg is known to be effectively bound to soil humic substances. The formation of organic Hg(II) complexes is known to be the dominating process, which is due largely to the affinity of Hg(II) and its inorganic compounds to sulphur-containing functional groups (Weber, 1988). Therefore mercury speciation analyses in the solid phase and in soil solution are going to be performed in the continuation of this study to determine Hg leachability, mobility, and bioavailability.

Conclusions

The study has shown that the ancient roasting site Pšenk and its surroundings are highly contaminated with Hg. The established median Hg content in soil and humus samples of the investigated area is 62.5 mg/kg (1.6–8,600 mg/kg). At the area of roasting site itself the median Hg content is 580 mg/kg with the individual contents ranging between 20 and 8600 mg/kg. The highest Hg values were found in topsoil (0–15 cm) of the roasting site alone, where the determined median is 695 mg/kg (60–8,600 mg/kg). Spatial distribution of mercury in humus and soil of the investigated area show the highest Hg concentrations at the supposed roasting site area where the largest quantity of pottery fragments were found and to the east of this area, at the narrow region between the footpath on the north and the bed of Lačna voda brook on the south in the length of approximately 120 m and width about 50 m. In humus the Hg contents decrease quite rapidly with the distance from this area, while Hg distribution in soil shows a little larger region of highly contaminated area with slower decreasing of Hg concentrations to the margins of the studied area. Extremely high Hg concentrations were found in profile P4 (37,020 mg/kg at the depth 20–30 cm). The value declines quite rapidly with depth and in depth range 30–50 cm the soil contains only 1,080 mg/kg of mercury. In general Hg concentrations in all three studied profiles show a gradual decrease with depth. It should be emphasized that despite the fact that more then 400 years has already passed since small-scale ore roasting in the woods surrounding Idrija, these sites are still extremely contaminated with mercury. In fact, no world literature reports such high mercury values in soils of the mining or industry regions.

Acknowledgments

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