GEOLOGIJA *56/2*, 229-241, Ljubljana 2013

doi:10.5474/geologija.2013.015

Heavy metal concentrations in soil in the vicinity of former ironworks in Spodnja Radovna, Slovenia

Vsebnosti težkih kovin v tleh na območju nekdanjih fužin v Spodnji Radovni, Slovenija

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Prejeto / Received 26. 11. 2013; Sprejeto / Accepted 3. 12. 2013

Key words: ironworks, heavy metals, soil, Spodnja Radovna, Slovenia
Ključne besede: fužine, težke kovine, tla, Spodnja Radovna, Slovenija

Abstract

Mining and ore processing represent one of the main anthropogenic sources of heavy metals in Slovenia. To determine the environmental impact of iron ore processing activity in Spodnja Radovna, which finished at the end of the19th century, a sampling campaign was carried out in the area of ironworks and along the river Radovna next to the ironworks. 45 soil samples were collected in three grids at various distances (10, 60 and 110 m) from the former blast furnace location and in two cross-valley profiles stretching from Pokljuka to Mežakla plateau. Along the river Radovna samples were collected 200 m upstream and downstream from the location of blast furnace. The analysis of heavy metal distribution in soil in the area of former ironworks and its vicinity confirmed the influence of former activities on the environment, since elevated concentrations of heavy metals, a distinctive feature of iron industry and tailings, were detected in a quite narrow area around iron foundry. While Cd and Pb indicate areal load of heavy metals in soil, concentrations of As, Cu, Hg and Zn are typical of point pollution sources, where the officially allowed limit and warning values are exceeded. The most significant threat to the environment as a consequence of iron ore processing activities are therefore sources of point pollution (tailings locations) in the ironworks area.

Izvleček

Rudarstvo in predelava rude predstavljata na področju Slovenije enega izmed glavnih vnosov težkih kovin v okolje. Z namenom določanja stopnje vpliva fužinarstva na območju Spodnje Radovne na okolje, je bilo izvedeno vzorčenje tal na območju nekdanjih fužin ter vzdolž reke Radovne. Vzorčeno je bilo na 45 lokacijah, določenih v treh vzorčnih mrežah od mesta nekdanjega plavža oddaljenih 10, 60 in 110 m, v dveh prečnih profilih od pobočja planote Pokljuke do pobočja planote Mežakle ter gorvodno in dolvodno od fužin ob strugi reke do oddaljenosti 200 m od plavža. Analiza prostorske razporeditve težkih kovin v tleh je potrdila vpliv dejavnosti na območju nekdanjih fužin na okolje. Povišane vsebnosti težkih kovin, značilnih za predelovalno industrijo železa in jalovino, se namreč pojavljajo v neposrednem območju plavža. Medtem ko vsebnosti Cd in Pb v tleh kažejo na razpršeno onesnaženje pa vsebnosti As, Cu, Hg in Zn kažejo na prisotnost točkovnega onesnaženja, kjer so prekoračene zakonsko določene mejne in opozorilne vrednosti vnosa težkih kovin v tleh. Največjo grožnjo za okolje kot posledico fužinarstva tako predstavljajo odlagališča jalovine v okolici fužin.

Introduction

In Slovenia there are 46 known mines and ore extraction locations with the largest ones located in Idrija (Hg ore), Mežica (Zn, Pb, Mo ore), Litija (Pb, Ag, Hg ore), Žirovski vrh (uranium ore) and Savske jame (Fe ore). Apart from mines and extraction locations there were also 25 processing plants and smelters present in the Slovenian area (Budkovič et al., 2003). Of all ores and minerals exploited in Slovenia, iron ore represents the most frequently used one, with around 18 different types identified. Small quantities of iron ore are present almost over

Fig. 1. Location of the investigated area

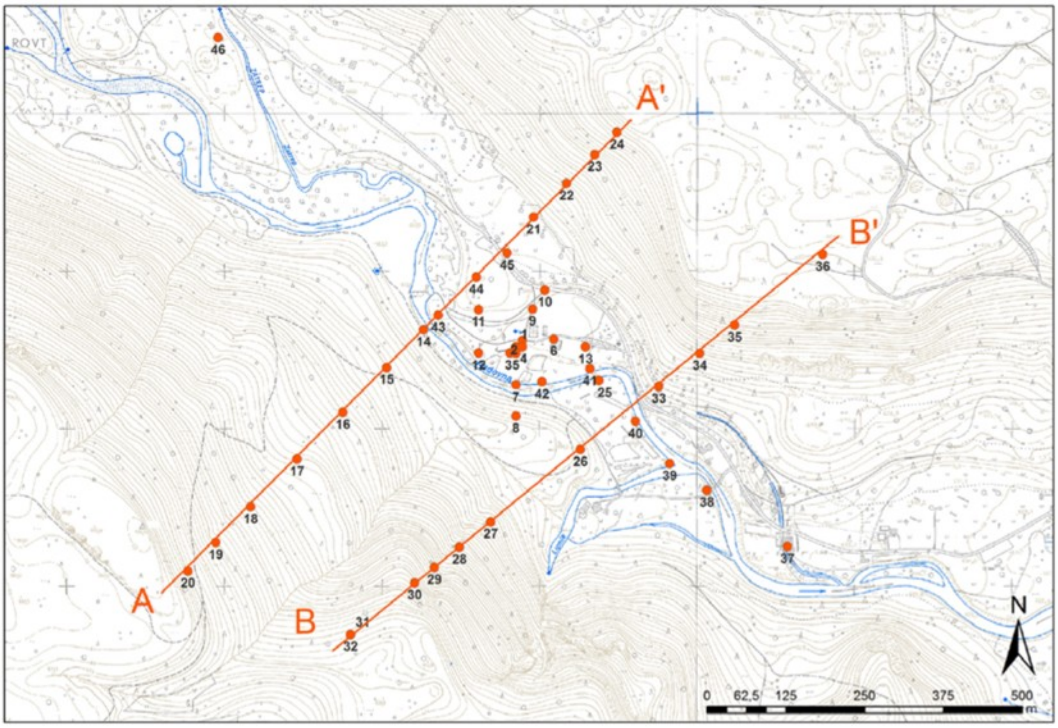

Fig. 2. The area of former ironworks in Spodnja Radovna with indicated sampling locations

the entire Slovenian area, while the largest localities are present in the foothills of the Triglav mountain, in Jelovica plateau and in Karavanke range (Mohorič, 1978). Limonite, also called »bobovec« due to its nugget shape, was the most frequently exploited iron ore in the Gorenjska region, which represented the center of iron ore extraction and processing, dating back to prehistoric times. At first iron was produced in low melting fireplaces with low furnaces. The quality of such iron was poor and needed extra handling to improve its usability and quality. Smelters realized that the height of the furnace was the controlling factor in ensuring an appropriate melting process and consequently good iron quality. With increasing progress in water power use, ironworks with large blast furnaces, sledgehammers and bellows were relocated to locations of higher discharge creeks and rivers. For this reason the ironworks in Spodnja Radovna next to the river Radovna was established in the 16^{th} century. Due to industrial progress in iron industry, ironworks facilities in Spodnja Radovna were shut down in 1901 (Kokošin, 1995).

In the last decades exploitation in almost all mines in Slovenia has been stopped and closing activities are still in progress. Environmental effects of ore processing were the subject of many studies (Šajn et al., 1998, Šajn, 2001, 2002, 2003; Gosar & Šajn, 2001, 2003; Šajn & Gosar, 2007; Teršič & Gosar, 2009) and big loads of heavy metals are evident locally (Šajn & Gosar, 2004), proving that mining and ore processing were one of the main anthropogenic sources of heavy metals in the environment in Slovenia (Budkovič et al., 2003). *The decree on limit values, alert thresholds and critical levels of dangerous substances into the soil* (Official Gazette of the RS no. 68/1996, 41/2004) defines the limit, warning and critical values of heavy metal concentration in soil. The limit value is the concentration of a certain harmful substance, which still ensures acceptable living conditions for plants and animals, where groundwater quality or soil fertility does not deteriorate, and effects on humans and the environment are still acceptable. The warning value represents the concentration of a harmful substance where in some cases of ground use damaging effects on human health or the environment might occur. The concentration of a harmful substance that reaches critical value can have damaging effects on human population or the environment and polluted grounds are no longer appropriate for crop production and water retention and filtration (Official Gazette of the RS no. 68/1996, 41/2004).

Previous investigations of soil heavy metal pollution in areas of the largest centers for mining and ore processing (Celje, Idrija, Jesenice, Mežica) showed that heavy metal concentrations did not exceed the officially allowed concentrations only in 7 % of the 466 km^2 of the investigated area. Official limit concentrations were exceeded in 18 %, warning concentrations in 59 % and critical concentrations in 16 % (Šajn & Gosar, 2004).

From the geochemical point of view the former ironworks in Spodnja Radovna is situated in a poorly studied area, where the true environmental impact and consequences of past activities are not clearly specified. Additionally, the ironworks is located in the area of the Triglav national park with strict nature conservation and protection regimes. Therefore the presented detailed geochemical analysis and spatial distributions of heavy metals in upper ground soil horizons in the ironworks area, subjected to possible impact of the past activities, would disclose the actual degree of pollution from former activities as well as reveal the presence of potential problematic areas, representing tailings locations subjected to leaching of harmful substances.

Description of the investigated area

The area of former ironworks in Spodnja Radovna is located in SW Slovenia, 7 km NW of Bled at an altitude of 645 m.a.s.l. in the valley of the Radovna river (Fig. 1). Towards the north and the south the Radovna valley is bounded by two plateaus, Pokljuka and Mežakla, with steep slopes reaching up to around 1400 m. The valley was formed during glacial erosion and is now filled with alluvial and fluvioglacial deposits. The width of the river Radovna alluvial bed varies between 50 and 600 meters, with the thickness of the Radovna alluvial deposits not exceeding 5 m. The area of Pokljuka and Mežakla plateaus consists of Triassic, mostly carbonate rocks, which represent the primary rocks of the area, while Quaternary deposits are present in the valley bottom and as diluvium on the slopes of the plateaus (Drobne, 1975).

According to the soil classification (Ćirić, 1986) the prevailing soil types in the entire study area are rendzina (A – C profile) and brown soil on limestone and dolomite (A – $B_{(RZ)}$ – C profile) with developed grass and mixed beech and spruce forest vegetation. While rendzina with poorly developed horizons is present on the slopes of the Pokljuka and Mežakla plateaus, quite thick brown soil on carbonates, rich in iron and aluminum oxides and clay, is present at the bottom of the valley. In the lower parts poorly sorted medium- to thick-grained pebbles are present. Due to variable morphology of the terrain, the depth of both soil types varies in short distances (Drobne, 1975). Anthropogenic grounds (local gravel roads, forest roads, tailing spots, former residential buildings in the ironworks facilities) are also present in the area.

Materials and methods

Sampling and analytics

The sampling campaign was carried out in September 2006. Soil samples from 45 locations were collected in the area of ironworks, along the Radovna river and in two cross-valley profiles in the proximity. Sampling in the ironworks area was performed in three grids, with the location of ex-blast furnace being the center point. Soil samples were collected at distances of 10, 60 and 110 m from the blast furnace, and 200 m upstream and downstream from the blast furnace along the Radovna river (Fig. 2).

At each sampling location the upper organic horizon was removed and the soil sample collected to the depth of 30 cm regardless of the soil horizons. In cases of poorly developed soils (slopes of Mežakla and Pokljuka plateaus) samples were collected to the available depth, but the quantity of the sample remained the same. Sample preparation was conducted in accordance with generally accepted procedures recommended in the UNESCO project IGCP 259 (Darnley et al., 1994). The collected soil samples weighed around 1 kg, except at locations with well-developed soils, where 2-kg samples were taken. Soil samples were air dried, halved and sieved (2 mm mesh) to remove possible remains of vegetation and rocks. Samples were then crushed and sieved to analytical granulation (<0.063 mm). Soil samples (n=45), repeated samples (n=6) and standard materials (BCR No109, CRM No141R, CRM No143R) (n=6) (IRMM, 2013) were coded prior to shipping to the laboratory to ensure an unbiased treatment of samples.

The chemical analysis of samples was conducted in the analytical laboratory ACMELabs Analytical Laboratories Ltd., Vancouver, Canada. Samples were analyzed for SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, MnO, Cr_2O_3, Ba, Ni, Sc, trace elements (As, Bi, Cd, Co, Cs, Cu, Ga, Hf, Mo, Nb, Ni, Pb, Rb, Sb, Sn, Sr, Ta, Th, Tl, U, V, W, Zn, Zr, Y), rare earth elements - REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and loss on ignition (LOI). Multielemental analysis and trace element analysis (As, Bi, Cd, Cu, Mo, Ni, Pb, Sb, Zn) were conducted with inductively coupled plasma emission spectrometry (ICP-ES), while determinations of remaining trace elements and rare earth elements was conducted with inductively coupled plasma mass spectrometry (ICP-MS). The loss on ignition was determined on the basis of sample loss after 1 hour of heating at 100 °C.

The detection limit for As and Zn was 1 mg/kg, for determinations of Cd, Mo, Ni, Pb and Co 0.1 mg/kg, and for Hg 0.01 mg/kg. Accuracy of the analytical method for the determination of heavy metals, studied in the presented paper, was estimated according to the calculation of relative error between the analyzed and recommended values of geological standards. The comparison of heavy metal concentrations in the analyzed standards and the recommended values generally show differences lower than 15 %. For precision control, relative differences in element determinations between duplicates of the same sample were studied. Precision was considered good, since relative differences for determinations of heavy metals were generally lower than 30 %. According to the satisfactory reliability of analytical procedures, determinations of soil heavy metal concentrations can be used in further data analyses.

Data treatment

Statistical package Statistica (StatSoft, Inc., 2013) was used for statistical analyses of the available dataset. Maps of spatial distribution of analyzed variables in soil were produced using the interpolation method of universal kriging with linear variogram (Davis, 2002) and created with software packages Surfer (Golden Software, Inc., 2013) and AutoCAD (AutoDesk, Inc., 2013).

Results

In the presented paper the focus is only on the concentrations and spatial distribution of heavy metals governed by the *Decree on limit values,*

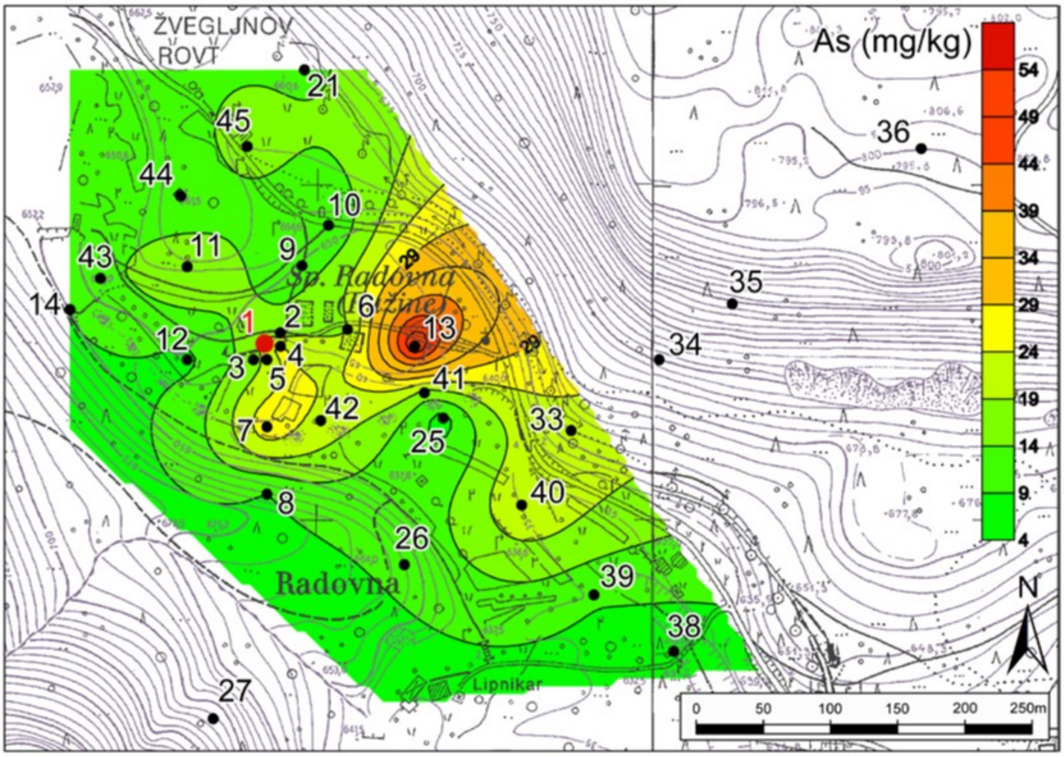

Fig. 3. Spatial distribution of As in soil samples in the area of former ironworks in Spodnja Radovna

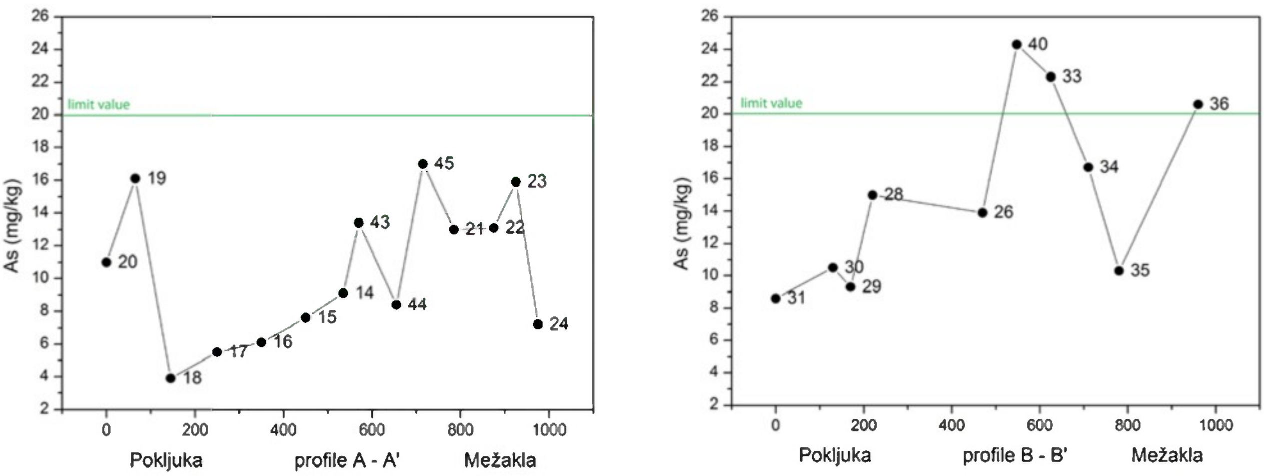

Fig. 4. As concentrations in cross-valley profiles A-A' (valley bottom points: 14, 43, 44, 45, 21) and B-B' (valley bottom point: 40)

alert thresholds and critical levels of dangerous substances into the soil (Official Gazette of the RS no. 68/1996, 41/2004) (Table 1), while a detailed investigation of remaining elements included in the soil analysis is given elsewhere (Ferjan, 2007). Detailed spatial distributions of heavy metals are shown only for the area of the ironworks and its proximity, since elevated concentrations of heavy metals are expected to occur within this area, where the largest impact of former activities is expected.

Table 1. Limit, warning and critical values for heavy metals in soil governed by the *Decree on limit values, alert thresholds and critical levels of dangerous substances into the soil* (Official Gazette of the RS no. 68/1996, 41/2004)

Element	Limit value (mg/kg)	Warning value (mg/kg)	Critical value (mg/kg)
As	20	30	55
Cd	1	2	12
Co	20	50	240
Cr	100	150	380
Cu	60	100	300
Hg	0,8	2	10
Mo	10	40	200
Ni	50	70	210
Pb	85	100	530
Zn	200	300	720

Arsenic - As

The highest As concentration which is almost at the critical value (Table 1) was determined at sampling point 13 (54.6 mg/kg), located 110 m from the former blast furnace – point 1 (Fig. 3). Elevated values of more than 20 mg/kg which exceed the officially allowed limit value for As are present in the area east of the blast furnace. The median value of As concentration in the area of former ironworks is 13.1 mg/kg. A comparison of the median As value in Radovna with the Slovenian median and the median for the Jesenice area (Table 2), which once represented the center of iron industry, shows comparable values with Slovenian average, while a comparison with the Jesenice median shows by almost 10 mg/kg lower value for the former ironworks area.

As concentrations in cross-valley profiles A-A' and B-B' (Fig. 4) compared to valley bottom show lower values. Somewhat higher concentrations of As in profile A-A' are present at sampling points 19 and 20 on the slope of the Pokljuka plateau. The comparison between profiles shows higher As concentrations on the slopes of the Mežakla plateau. It can also be noted that in profile B-B', which lies southeast from the ironworks location, concentrations of As in the valley bottom are higher than in profile A-A'.

Cadmium – Cd

Concentrations of Cd with a median of 1.6 mg/kg are elevated in the entire area and exceed or are close to the warning value of 2 mg/kg (Table 1). The median value for the research area is higher than the Slovenian median (0.52 mg/kg), but with comparable ranges, and below the median value for the Jesenice area (3.7 mg/kg) (Table 2).

Cd concentrations in cross-valley profiles are generally lower compared to valley bottom (Fig. 5). Extremes are present at sampling points 19 and 22 in profile A-A'. A comparison of Cd concentrations in valley bottom shows higher values in profile B-B'.

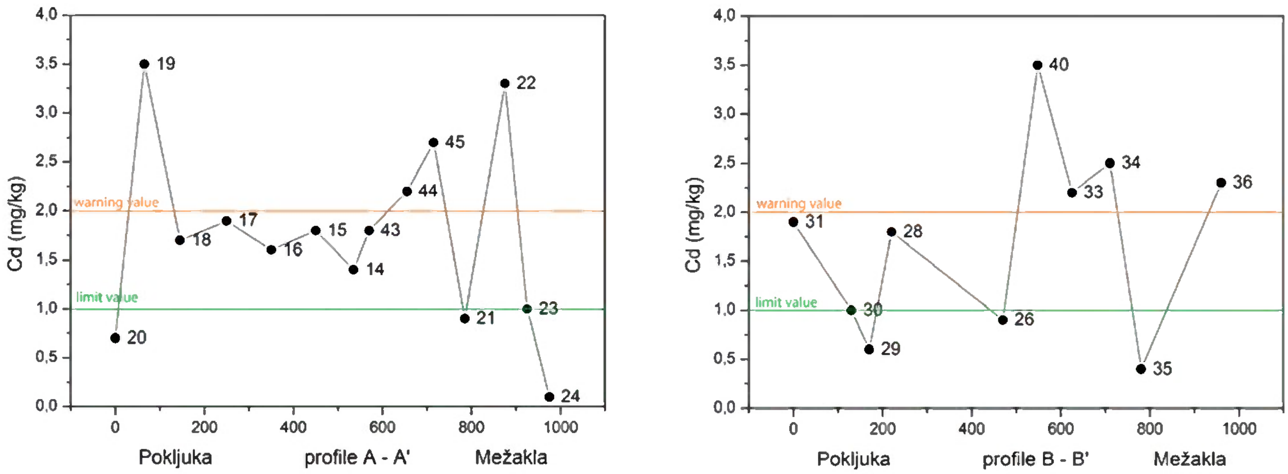

Fig. 5. Cd concentrations in cross-valley profiles A-A' (valley bottom points: 14, 43, 44, 45, 21) and B-B' (valley bottom point: 40)

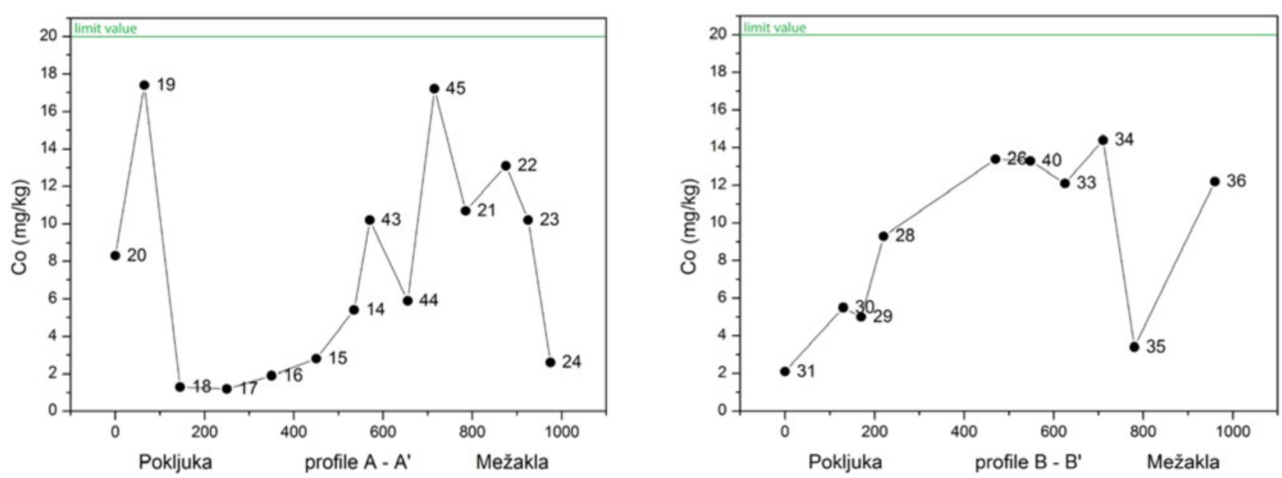

Fig. 6. Co concentrations in cross-valley profiles A-A' (valley bottom points: 14, 43, 44, 45, 21) and B-B' (valley bottom point: 40)

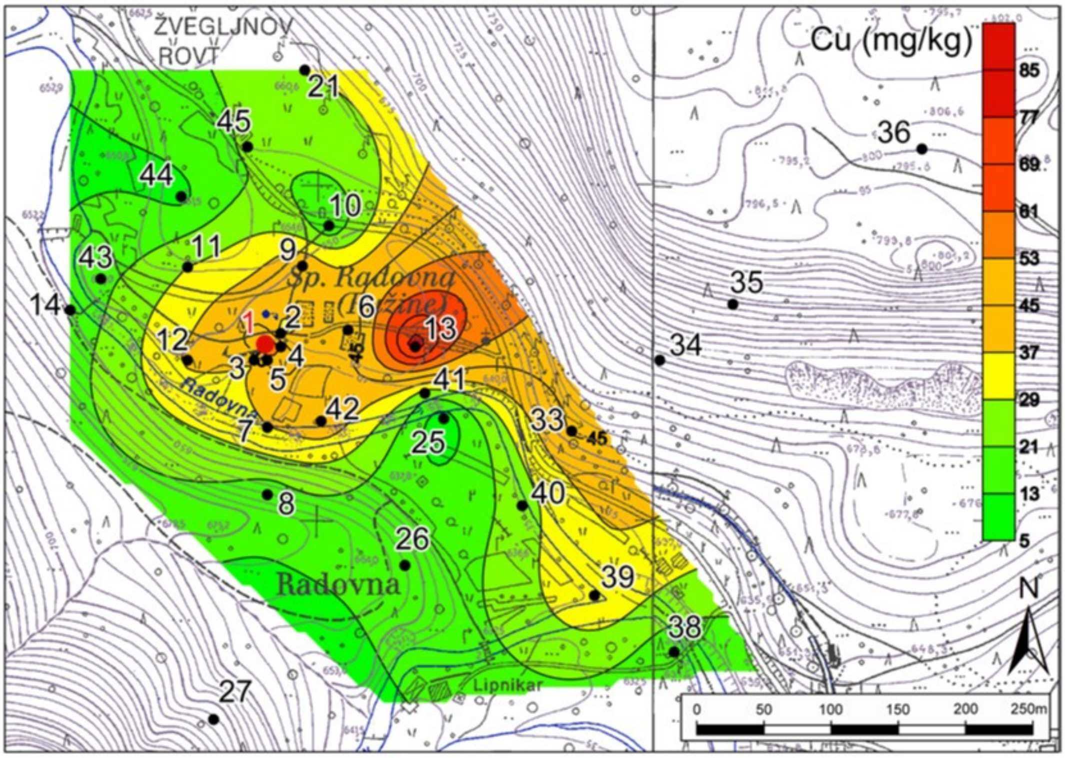

Fig. 7. Spatial distribution of Cu in soil samples in the area of former ironworks in Spodnja Radovna

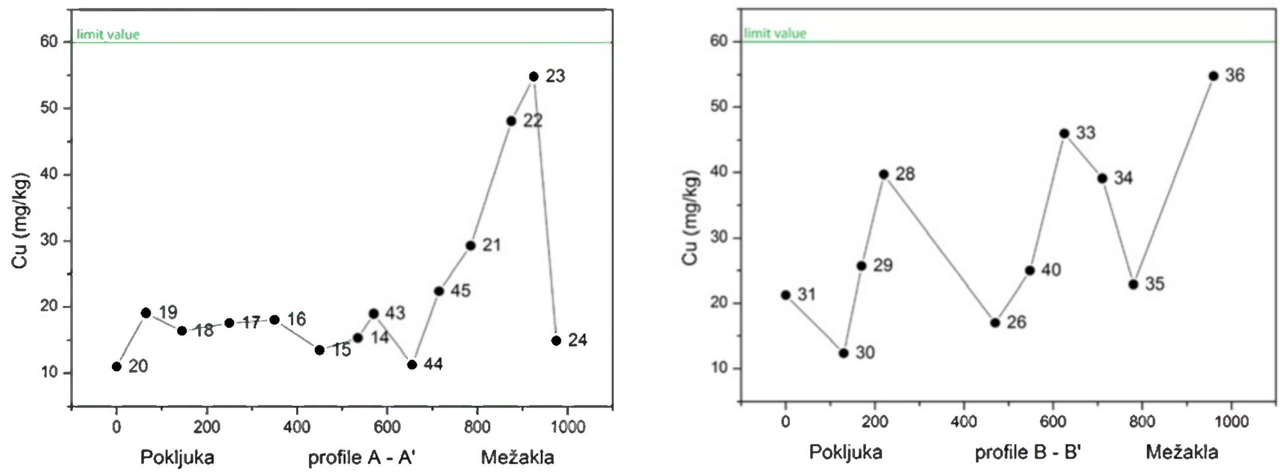

Fig. 8. Cu concentrations in cross-valley profiles A-A' (valley bottom points: 14, 43, 44, 45, 21) and B-B' (valley bottom point: 40)

Cobalt – Co

Co concentrations at all sampling points are below the limit value (20 mg/kg) (Table 1), with a median value of 6.3 mg/kg. The median value is also below the Slovenian median and the median value determined for the Jesenice area (Table 2). The distribution of Co in both cross-valley profiles (Fig. 6) shows elevated values on the slopes of the Mežakla plateau, while in the Pokljuka area concentrations in both profiles are lower, with the exception of locations 19 and 20. Valley bottom parts of the profiles show similar concentrations of Co.

Copper – Cu

Cu concentrations in the area are elevated at the location of former blast furnace (65.3 mg/kg) and at sampling point 13 (83.1 mg/kg), located 110 m away (Fig. 7). In both cases concentrations exceed the officially allowed limit values for Cu (60 mg/kg) (Table 1). Values around 30 mg/kg are present in the entire ironworks area and show similar distribution as As, with elevated values in the eastern direction from the blast furnace. The median value of 24.4 mg/kg is below both compared areas (Slovenia, Jesenice) (Table 2).

Cu concentrations in profile A-A' show elevated values in the Mežakla slopes (location 22, 23), since higher values are present in profile B-B' over the entire profile, with extremes in the slopes of the Mežakla plateau, which are close to the official limit value of 60 mg/kg. The lowest values are present in the valley bottom, where concentrations in both profiles are comparable (Fig. 8).

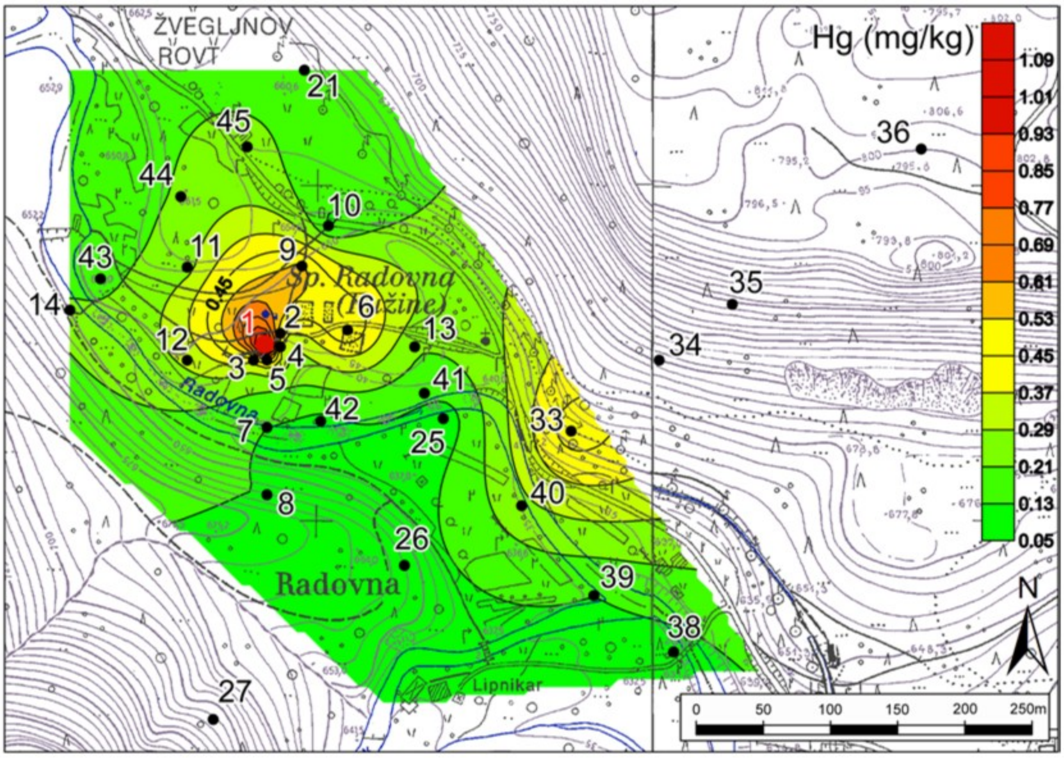

Fig. 9. Spatial distribution of Hg in soil samples in the area of former ironworks in Spodnja Radovna

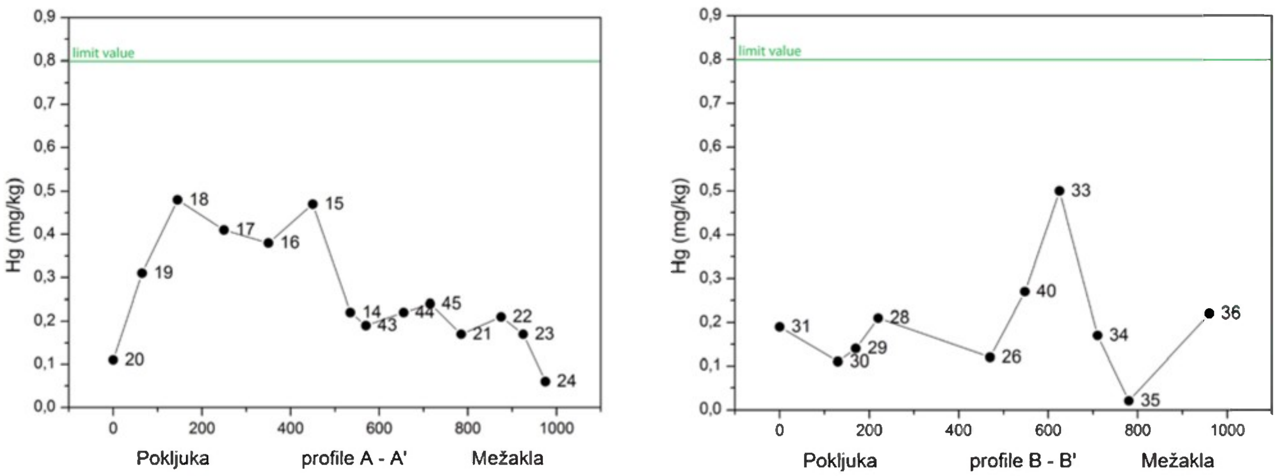

Fig. 10. Hg concentrations in cross-valley profiles A-A' (valley bottom points: 14, 43, 44, 45, 21) and B-B' (valley bottom point: 40)

Mercury – Hg

Hg concentrations with a median value of 0.21 mg/kg are below the median determined for Jesenice, but four times higher than the Slovenian median (0.066 mg/kg) (Table 2). The highest concentration of 1.2 mg/kg, which exceeds the officially determined limit value for Hg, was determined at the blast furnace location, while elevated values are present in the entire area of ironworks and in the southeastern direction from the blast furnace (Fig. 9).

In profile A-A' elevated concentrations of Hg are present in the slopes of the Pokljuka plateau, where values are significantly higher than in the valley bottom (Fig. 10). In profile B-B' Hg concentrations in the Mežakla and Pokljuka area are comparable, with sampling point 33 on Mežakla slope as an extreme.

Molybdenum - Mo

Concentrations of Mo in the entire research area are far below the limit value of 10 mg/kg, having a median value of 0.8 mg/kg, comparable with the Slovenian median. The distribution of Mo over the cross-valley profiles shows no trends in distribution, while somewhat higher values were determined in profile B-B' (Fig. 11).

Nickel – Ni

Ni concentrations with a median value of 12.2 mg/kg are almost four times lower than the Slo-

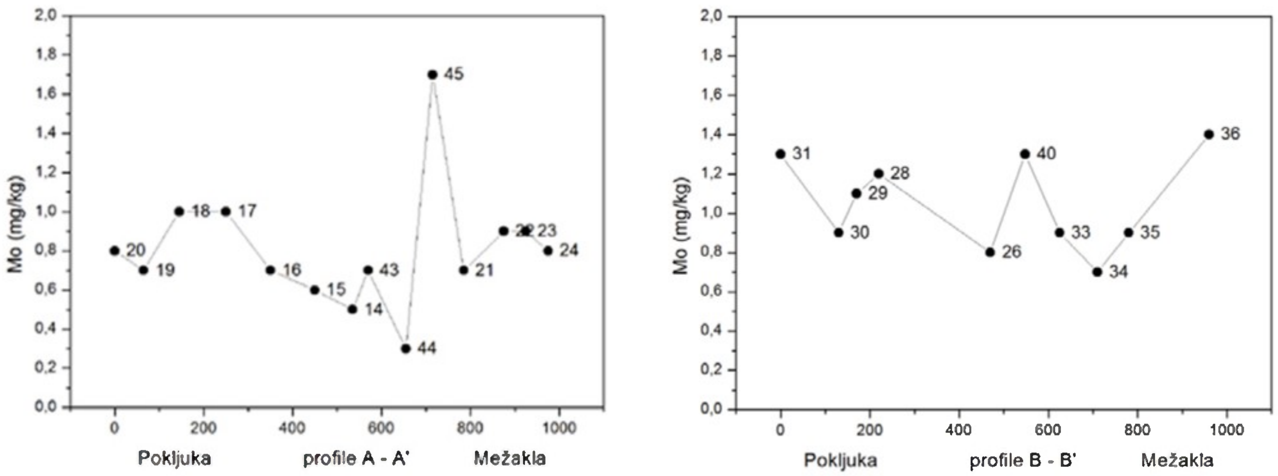

Fig. 11. Mo concentrations in cross-valley profiles A-A' (valley bottom points: 14, 43, 44, 45, 21) and B-B' (valley bottom point: 40)

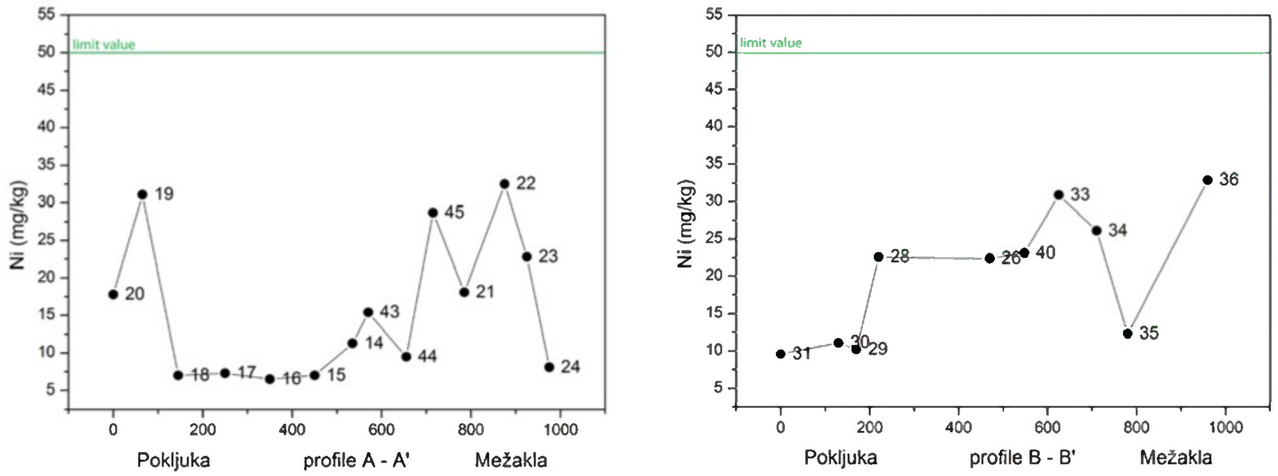

Fig. 12. Ni concentrations in cross-valley profiles A-A' (valley bottom points: 14, 43, 44, 45, 21) and B-B' (valley bottom point: 40)

venian median, and lower than the median for Jesenice (Table 2). In cross-valley profile comparison (Fig. 12) lower values are detected in the Pokljuka area in both profiles, while in the Mežakla area concentrations are higher. Elevated values in the Pokljuka area were identified at sampling points 19 and 20.

Lead - Pb

The median for Pb concentrations in the investigated area with a value of 62.6 mg/kg is above the Slovenian value (42 mg/kg) and almost ten times lower than the median for the Jesenice area (655 mg/kg) (Table 2). However, it does not exceed the official limit value (85 mg/kg). The highest Pb concentration was determined at sampling point 13 (468.1 mg/kg), similar to As and Cu, from where elevated concentrations are followed in the northeast direction (Fig. 13), where at sampling points 40 and 42 Pb concentrations are close to warning values (100 mg/kg).

Elevated concentrations of Pb are present in profile A-A' on the Pokljuka slopes (locations 16, 17, 18) where the warning value of 100 mg/kg is exceeded, while in profile B-B' values in the Pokljuka and Mežakla areas are similar (Fig. 14). Comparison of distributions of Pb in valley bottom shows enrichment in profile B-B'.

Zinc - Zn

The median of 84 mg/kg is lower than the Slovenian median and eight times lower than the Jesenice area median (708 mg/kg) (Table 2). Zn concentrations exceed the officially determined limit value at the location of blast furnace with a concentration of 221 mg/kg. Apart from the ironworks area, elevated values (>100 mg/kg) are also present in profile A-A' on the slopes of Pokljuka and Mežakla and in profile B-B' on the slopes of the Mežakla plateau (Fig. 15). Concentrations on the slopes are even higher than those in the valley bottom. Comparison of Zn concentrations in the valley bottom shows higher values in the bottom area of profile B-B'.

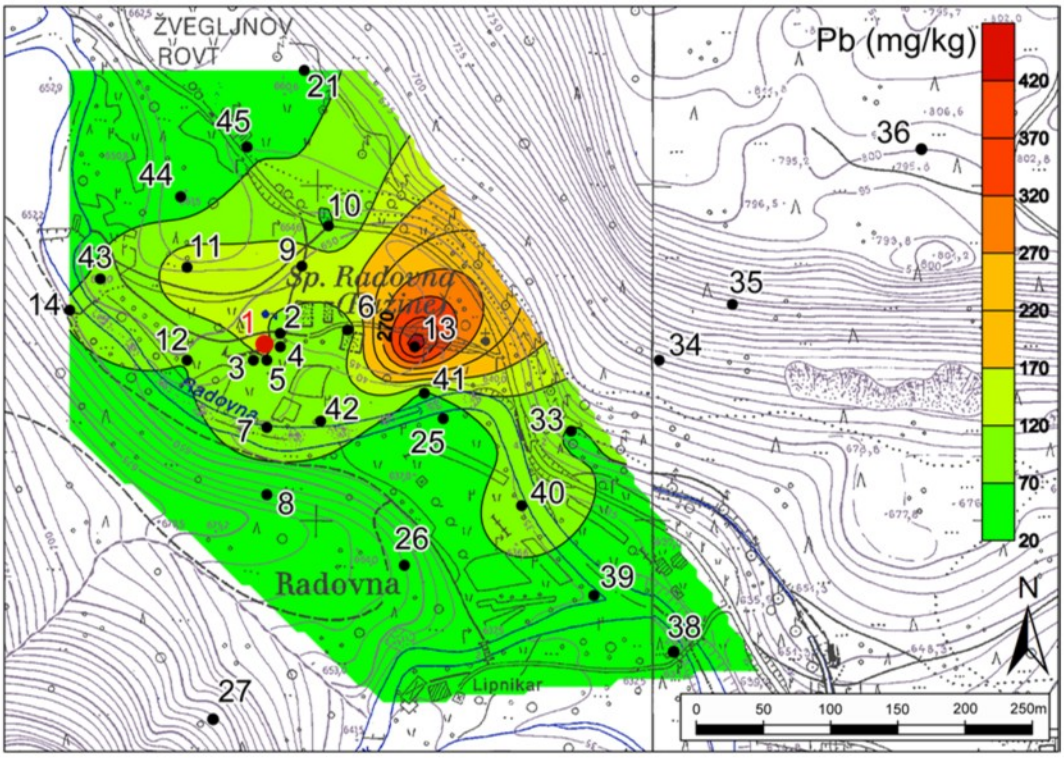

Fig. 13. Spatial distribution of Pb in soil samples in the area of former ironworks in Spodnja Radovna

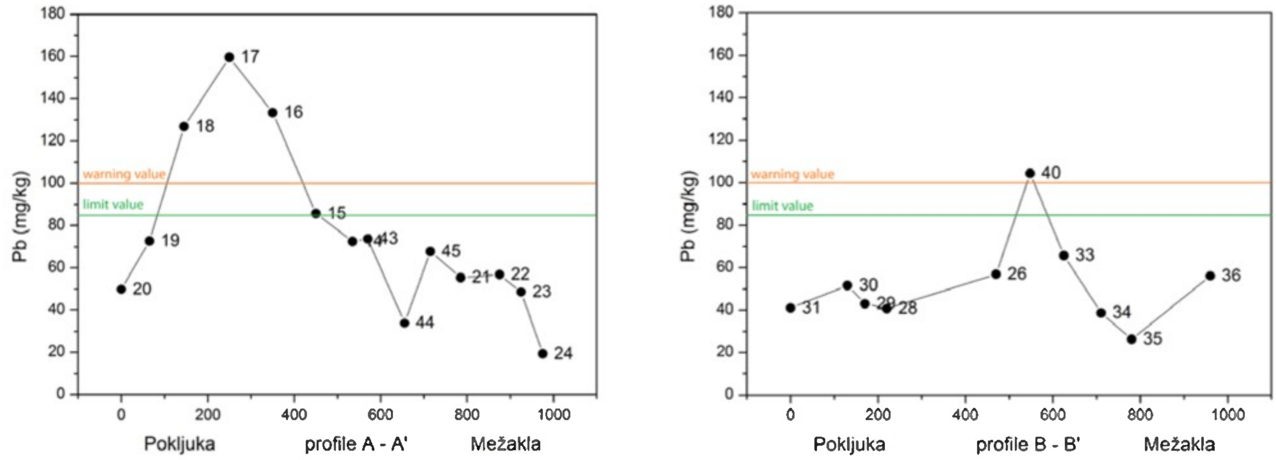

Fig. 14. Pb concentrations in cross-valley profiles A-A' (valley bottom points: 14, 43, 44, 45, 21) and B-B' (valley bottom point: 40)

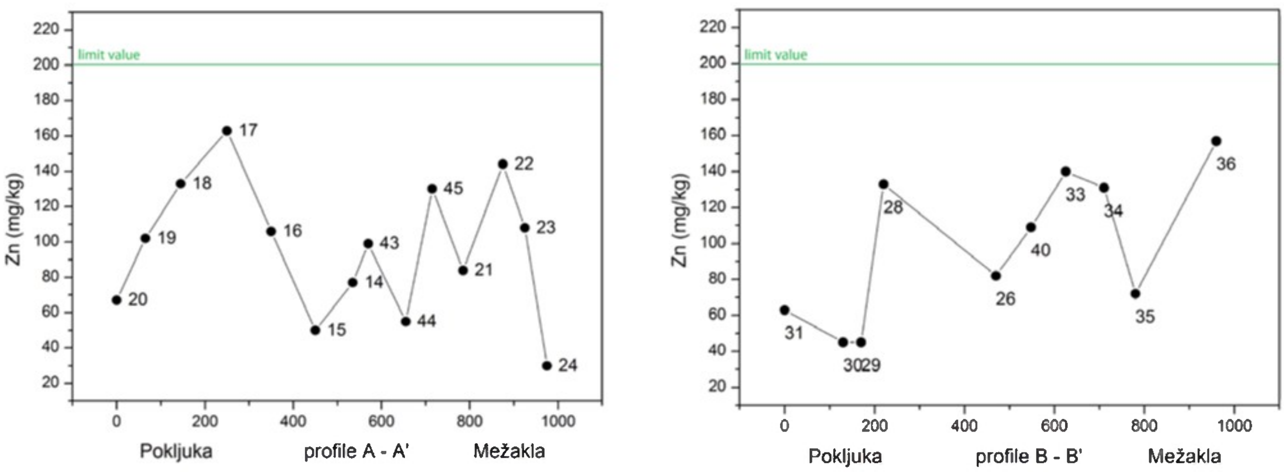

Fig. 15. Zn concentrations in cross-valley profiles A-A' (valley bottom points 14, 43, 44, 45, 21) and B-B' (valley bottom point: 40)

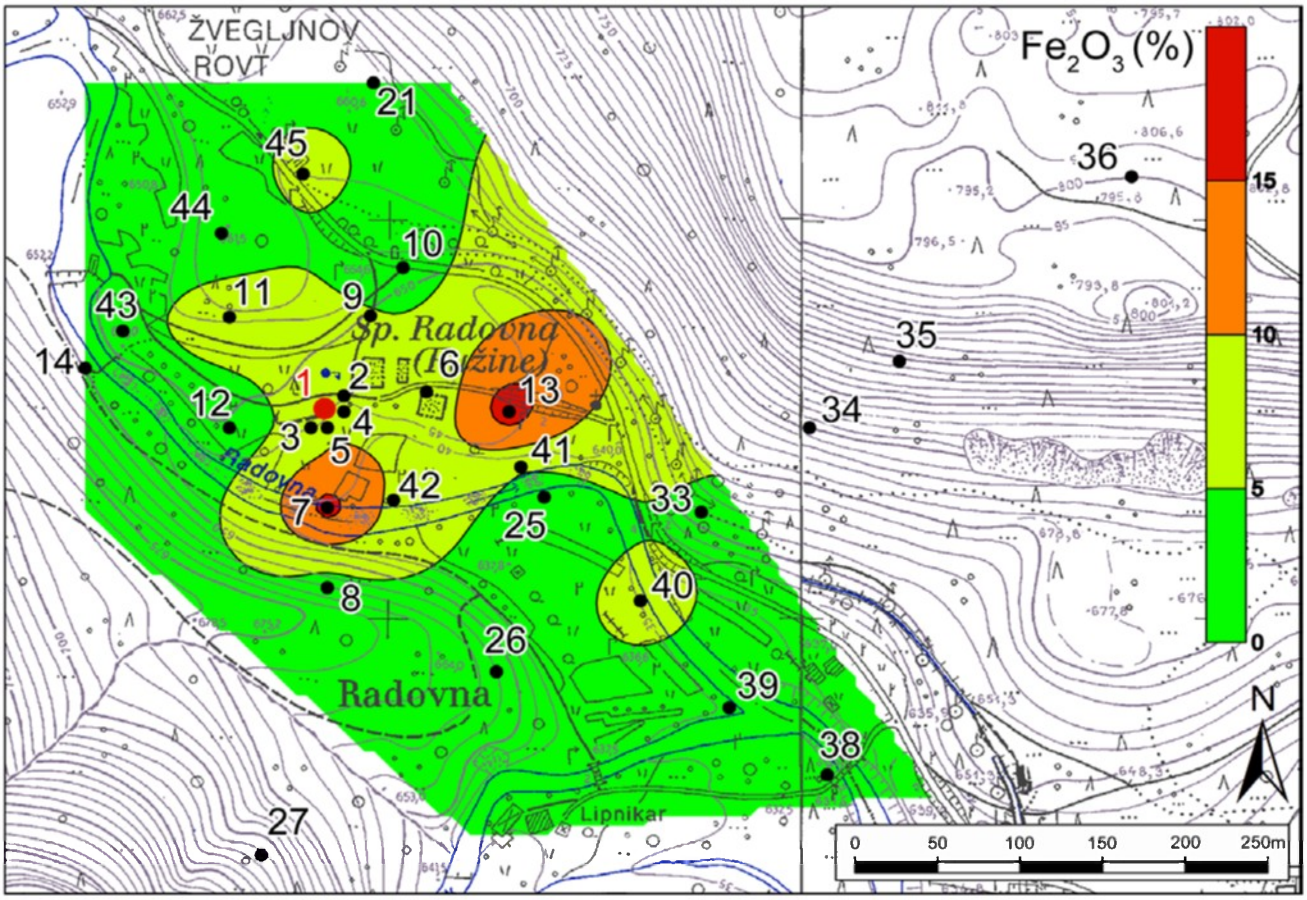

Fig. 16. Spatial distribution of Fe_2O_3 share in soil samples in the area of former ironworks in Spodnja Radovna

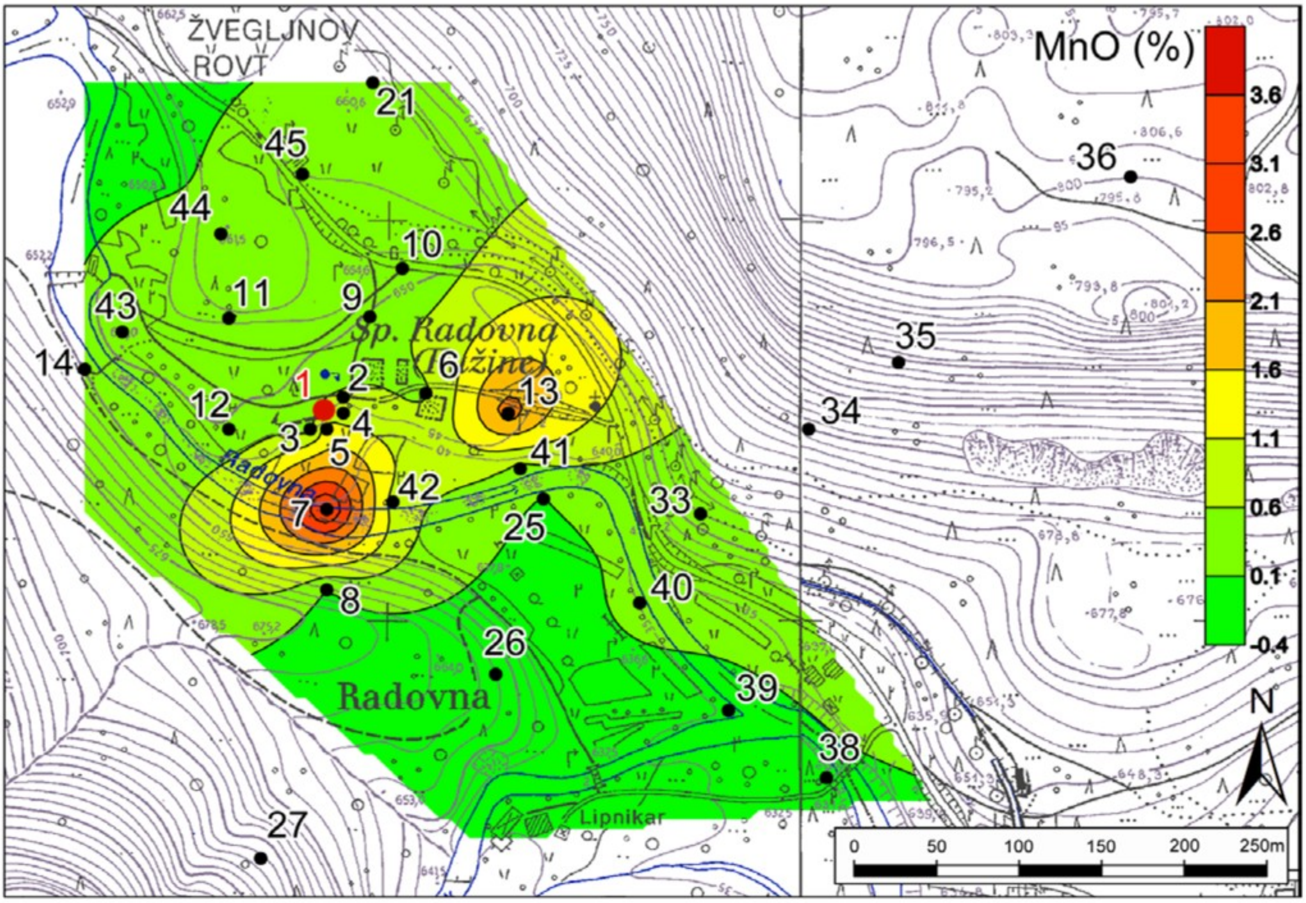

Fig. 17. Spatial distribution of MnO share in soil samples in the area of former ironworks in Spodnja Radovna

Table 2. Medians and ranges (in mg/kg) of heavy metal concentrations in Slovenia (Šajn, 2003) and investigated areas of Jesenice (Šajn & Gosar, 2004) and former ironworks in Spodnja Radovna.

Element	Slovenia	n=59	Jesenice	n=59	Radovna	n=45
	median	min - max	median	min - max	median	min - max
As	15	6.0 - 37	22	7.1 - 76	13.1	3.9 - 54.6
Cd	0.52	0.15 - 2.0	3.7	2.1 - 8.7	1.6	0.1 - 3.5
Co	16	5.5 - 33	/	/	6.3	1.2 – 17.4
Cu	35	18 - 165	51	26 - 96	24.4	7.9 - 83.1
Hg	0.066	0.010 - 0.25	1.3	0.42 - 2.5	0.21	0.02 - 1.2
Mo	0.92	0.30 - 12	/	/	0.8	0.3 – 1.7
Ni	47	10 - 131	40	12 - 85	12.2	5.8 - 32.9
Pb	42	20 - 87	655	328 - 1866	62.6	7.4 - 468.1
Zn	124	75 - 215	708	375 - 1480	84	17 - 221

Additionally, a spatial distribution of iron and manganese oxide contents in soils from the ironworks area was displayed as both are additional indicators of possible pollution in the area. Their distribution, with two obvious distinctions at locations of sampling points 7 and 13 (Figs. 16, 17) and somewhat lower values in the entire ironworks area, implies an anthropogenic source connected with former iron processing activity in the area.

Impact of former ironworks on the environment

The high concentration of heavy metals and additionally their spatial distributions confirm the impact of ore processing activities in the former ironworks on the environment. The element showing an increased concentration in the entire ironworks area is Cd, with concentrations exceeding the officially determined limit and in some cases also warning values. Apart from the described situation of areal pollution, locations

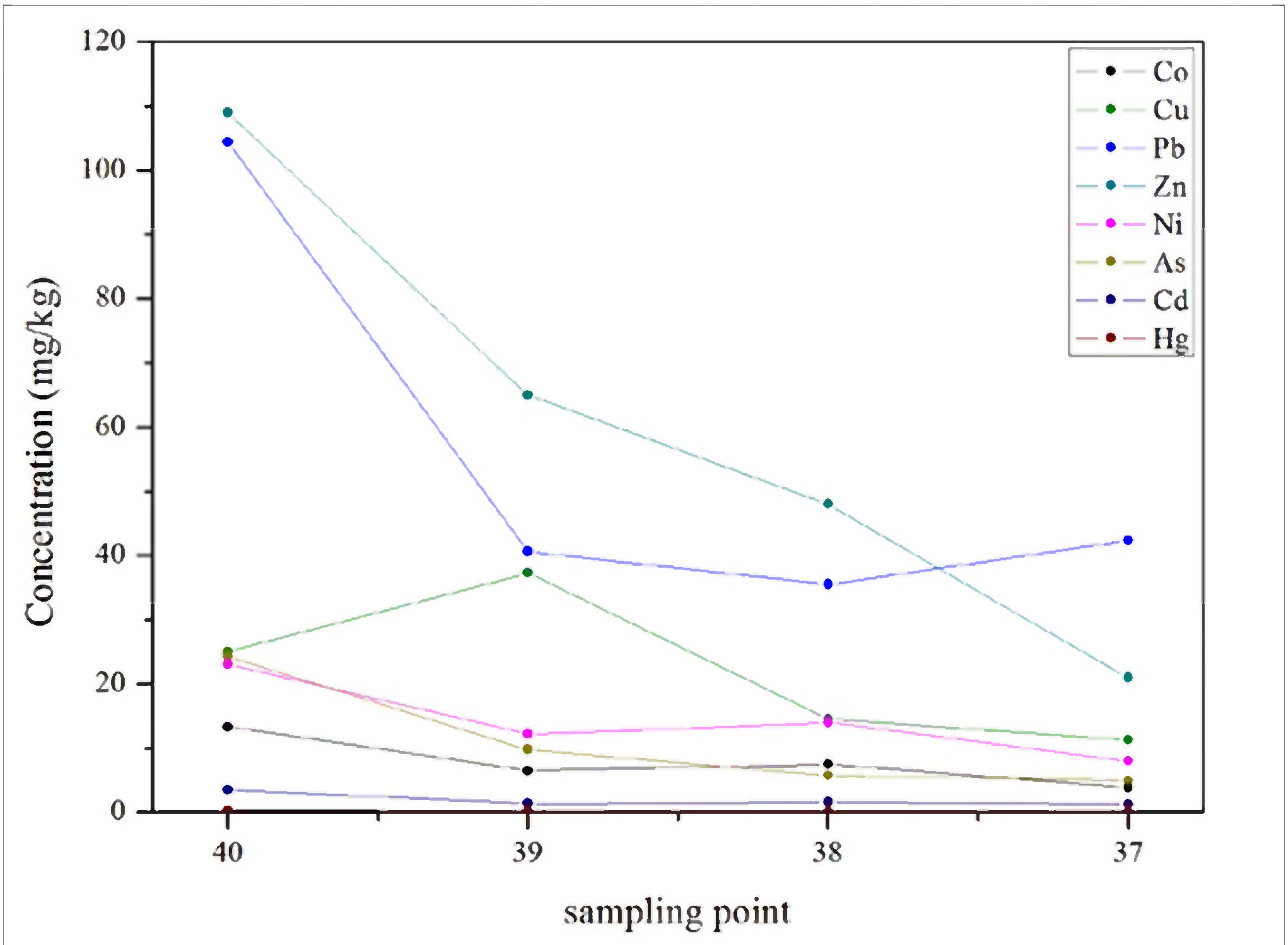

Fig. 18. Heavy metal concentration in downstream direction from the location of profile B-B' and blast furnace

of tailings deposition were identified. The location with the most extreme concentrations of As, Pb (both close to critical value), Cu (exceeded limit value) and additionally elevated Fe_3O_3 and MnO values, was sampling point 13, located 110 m from the blast furnace, in the southeastern part of the ironworks area. This area, stretching towards location 7 (Figs. 16, 17), was most probably the location intended for the deposition of tailings and now presents a source of point pollution. This was additionally confirmed by a comparison of cross-valley profiles A-A' and B-B, where in the valley bottom of the profile B-B' higher concentrations of As, Cd, Mo and Pb were detected. In the downstream direction from profile B-B' a rapid decrease in concentrations of heavy metals in soil is observed (Fig. 18). In the distance of around 200 m towards sampling point 37, concentrations of Zn decrease to around 20 % and of Pb to around 40 % from the initial concentration in sampling point 40.

Another distinctive location with elevated values of Cu, Hg and Zn is the location of blast furnace, where the concentrations of all elevated heavy metals exceed the official limit value. The analysis of heavy metal distribution in cross-valley profiles A-A' and B-B' revealed the presence of areas possibly affected by diffuse pollution. Slopes of the Mežakla plateau stretching in the northeastern direction from the ironworks area show higher concentrations of As, Co, Cu, Hg, Ni, Zn, while on the slopes of the Pokljuka plateau in the southwestern direction higher concentrations of Hg, Pb and Zn were detected. Pb concentrations in soil exceed the warning value of 100 mg/kg. A possible reason for elevated concentrations of analyzed heavy metals could be diffuse pollution taking place during iron ore processing activities in the ironworks, when air was the main transporter of pollution. Due to the quite steep slopes of the Mežakla plateau in comparison to Pokljuka, resulting in a more closed character of the valley in this area, air pollution had the greatest impact on soil composition in this part. However, the hinterland of Mežakla slopes as well as the Mežakla slopes on their own, represent locations with significant anthropogenic activity (residential facilities, local roads, forestry). The actual contribution to soil pollution due to activities in the ironworks is therefore hard to determine. Concentrations of Cu and Zn show even higher values on the slopes than in the valley bottom in the vicinity of the ironworks. There are some elevated concentrations of Cd, Co and Ni in profile A-A' (sampling points 19, 20) in the Pokljuka area, which are most probably of anthropogenic origin from a local contamination source and are not a consequence of ironworks activities.

Conclusions

The analysis of heavy metal distribution in soil in the area of former ironworks and its vicinity confirmed the influence of former smelting activities on the environment. Since the obtained concentrations of Co, Mo and Ni do not represent a threat to the environment, concentrations of Cd and Pb in the ironworks area and concentrations of As, Cu, Hg and Zn at point pollution sources exceed the officially allowed limit and warning values governed by the *Decree on limit values, alert thresholds and critical levels of dangerous substances into the soil* (Official Gazette of the RS no. 68/1996, 41/2004). In the slopes of Pokljuka (profile A-A'), elevated Pb concentrations in soil exceed the official warning values of 100 mg/kg.

The true impact of former iron ore processing activities in the area of ironworks is hard to determine. Higher concentrations of heavy metals, distinctive of iron industry and tailings, were detected in a quite narrow area around the ironworks. However, in the century from the closure of the foundry the area has undergone many changes, since diverse anthropogenic activities have taken place in the area. Residential buildings of the ironworks were, with breaks, inhabited long after closure, agricultural activities took place in the area, and traffic infrastructure has been developing, which could all contribute to the geochemical state of the environment. The most significant threat to the environment as a consequence of iron ore processing activities are therefore sources of point pollution (tailings locations).

Acknowledgements

Research work was conducted in the scope of research program Groundwater and Geochemistry (P1 – 0020) financed by the Slovenian Research Agency.

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