Contents and spatial distributions of chemical elements in soil at the ancient roasting site Pšenk (Idrija area, Slovenia)

Vsebnosti in prostorske razporeditve kemijskih prvin na območju nekdanje žgalnice živega srebra Pšenk (Idrijsko, Slovenija)

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Abstract

Analysis for 35 chemical elements (Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Th, Ti, Tl, U, V, W, Zn) was performed in soil and SOM (soil organic matter; 0–5 cm) at the ancient roasting site Pšenk in the surroundings of Idrija, which is highly contaminated with Hg. It was estimated that natural values of Al, Ba, Fe, K, Mn, Ni and Zn show normal distribution, while for the elements As, Au, Bi, Ca, Cd, Co, Cr, Cu, Ga, La, Mg, Mo, P, Pb, Sc, Se, Sr, Th, Tl, U in V the logarithms of elemental contents were considered normally distributed. Contents of the analyzed elements in the sampling material are mostly within the normal values for soils as also within Slovenian and European averages for soil. High contents of As were determined in soils from investigated roasting site, reaching as much as 122 mg/kg in the depth of 5–20 cm. Additionally Cd, Mo, Pb and U contents in the soil (5–20 cm) are higher compared to natural soils. Cd and Mo show somewhat increased contents also in SOM from studied roasting site.

Izvleček

Na nekdanjem žgalniškem območju Pšenk v bližini Idrije, ki je močno onesnaženo z živim srebrom, smo v vzorcih tal in SOM (vrhnji, z organsko snovjo bogat sloj tal; 0–5 cm) določali vsebnost 35 kemijskih prvin (Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Th, Ti, Tl, U, V, W, Zn). Ugotovljeno je bilo, da normalni porazdelitvi ustrezajo naravne vrednosti Al, Ba, Fe, K, Mn, Ni in Zn. Za ostale prvine (As, Au, Bi, Ca, Cd, Co, Cr, Cu, Ga, La, Mg, Mo, P, Pb, Sc, Se, Sr, Th, Tl, U in V) se logaritmirane vrednosti bolje prilegajo normalni porazdelitvi. Vsebnosti obravnavanih prvin so večinoma istega reda velikosti kot ocenjena slovenska in evropska povprečja za tla. V obravnavanih tleh smo določili visoke vsebnosti As, ki v globini 5–20 cm dosežejo vrednost 122 mg/kg. Povišane so tudi vsebnosti Cd, Mo, Pb in U v tleh (5–20 cm). Cd in Mo kažeta nekoliko povišane vsebnosti tudi v SOM iz obravnavanega območja.

Introduction

Pšenk is one out of 21 localities of ancient ore roasting sites in the woods surrounding Idrija, where mercury ore was roasted in the first 150 years (16th and first half of 17th century) of mercury production in Idrija (Čar & Terpin, 2005; Gosar & Čar, 2006; Kavčič, 2008). It is located about 2 km south-west from Idrija, on flattened surface at Lačna voda stream below Hleviše hill, above its confluence with the Padar ravine.

The detailed study on mercury contents in soils at the area of former roasting site and its surroundings, on approximately 210 x 180 m big area (Teršič & Gosar, 2009; Teršič, 2010), has shown that the ancient roasting site Pšenk and its surroundings are highly contaminated with Hg. The estab-lished median Hg content in soils (5–20 cm) of the investigated area is 70 mg/kg (5.5–8,600 mg/kg). In SOM (surface organic matter rich soil layer; 0–5 cm) the Hg contents ranged between 1.4 and 4,200 mg/kg with the median of 20 mg/kg. The highest Hg values were found in soil (5–20 cm) of supposed past roasting processes (approximately 40 x 50 m big area), where the determined median was 695 mg/kg (60–8,600 mg/kg). Spatial distri-butions of mercury in soil and SOM of the investi-gated area show the highest Hg concentrations in the central flat regions. On approximately 14 ha (37 % of studied area) the area is highly polluted (> 100 mg/kg Hg in soil). The contents decrease rapidly with the distance from this area although the anomaly in soil is continuing over the eastern margin of studied area. Extremely elevated Hg

concentrations in investigated soils are related to considerable losses of Hg during ore processing (spillages of liquid mercury and atmospheric emissions) and the possible presence of numerous Hg compounds in waste material (discarded roasting vessels and unroasted ore residues) (Teršič, 2010).

Beside extremely elevated Hg contents in soils of investigated areas, the contents of 35 other elements were also analyzed in order to define their contents and spatial distribution in soil (and SOM) in researched area and to establish increased values of any of these elements. In this paper results of multielement analyses and major soil characteristics at the area of ancient roasting site Pšenk are presented.

Materials and methods

Soil (5–20 cm) and SOM (0–5 cm) samples were collected from 73 sampling points on approximately 210 x 180 m big area. At the supposed roasting site area (40 x 50 m big area in the central part of investigated area) soil samples in two depths were taken (5–20 cm and 20–30 cm). Sampling locations (Fig. 1) and the distribution of Hg concentrations in soil and SOM are given in the preliminary geochemical study at the Pšenk roasting site (Teršič & Gosar, 2009).

Determination of soil and SOM pH

Soil pH is a measure of the acidity or alkalinity of the soil solution. It affects the health of microorganisms in the soil and controls the availability of nutrients and trace elements in the soil solution. A number of compounds contribute to the development of acidic and basic soil reactions. Inorganic acids and organic acids, produced by the decomposition of soil organic matter, are common soil constituents that may affect soil acidity. The H$^+$ ions may be present in soils as adsorbed H$^+$ ions on the surface of the colloidal complex, or as free H$^+$ ions in the soil solution. The portion of H$^+$ ions adsorbed by the clay complex becomes exchangeable H$^+$ ions. The exchangeable H$^+$ ions dissociate into free H$^+$ ions, and the amount adsorbed is usually in equilibrium with the amount free in solution. The types of H$^+$ ions and the degree of ionization and dissociation into the soil solution determine the nature of soil acidity. The adsorbed or exchangeable H$^+$ ions are the reason for the development of *potential*, *reserve* or *exchangeable acidity* that can be measured by addition of an excess of extracting cation such as K$^+$ or Ca^{2+}. The free H$^+$ ions create the *active acidity*. Taking together, the active and exchangeable acidity make up the total soil acidity (Tan, 1998).

Soil pH is the most important parameter influencing metal-solution and soil-surface chemistry. The number of negatively charged surface sites increases with pH. In general, heavy metal adsorption is small at low pH values. Adsorption then increases at intermediate pH from near zero to near complete adsorption over a relatively small pH range; this pH range is referred to as the pH-adsorption edge. At high pH values, the metal ions are completely removed (Bradl, 2005).

A standard measurement of soil pH in CaCl$_2$ is probably the most commonly used method to characterize soil pH. The use of CaCl$_2$ has some advantages for pH measurements (Swyngedouw & Lessard, 2007): (1) the pH is not affected within a range of the soil to solution ratios used, (2) the pH is almost independent of the soluble salt concentrations for non-saline soils, (3) because the suspension remains flocculated, errors due to the liquid junction potential are minimized, (4) no significant differences in soil pH determination are observed for moist or air-dried soil and (5) one year of storage of air-dried soil does not affect the pH.

The acidity of soil samples was determined electrometrically using pH meter MA 5735 after addition of 25 ml of 0.01 M CaCl$_2$ solution to 10 g of
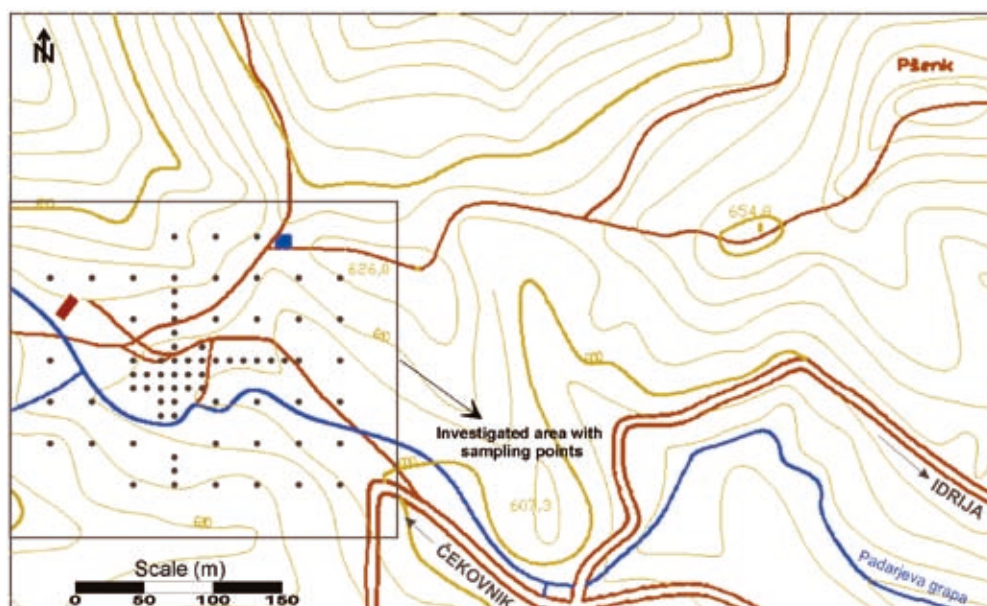

Fig.1. Location of Pšenk roasting site area with sampling locations

fresh sample. For SOM samples 125 ml of 0.01 M CaCl$_2$ solution was added to 10 g of fresh sample.

Multielemental analysis

The powdered soil samples were submitted for chemical analysis to ACME Analytical Laboratories in Vancouver (Canada) accredited under ISO 9001:2000. Analysis for 35 chemical elements (Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Th, Ti, Tl, U, V, W, Zn) was performed with inductively coupled plasma mass spectrometry (ICP-MS) after aqua regia digestion.

The accuracy and analytical precision of the analytical methods were verified against standard reference materials (standards GXR-2 (Park City, Summit Co., Utah), GXR-5 (Somerset Co., Maine), GXR-6 (Davidson Co., North Carolina) and SJS-1 (San Joaquin Soil) (Abbey, 1983; Epstein, 1990) and duplicate samples in each analytical set. The shipment of samples, duplicates (n=30) and geological standards (n=7) to the laboratory was carried out in a random succession to distribute evenly any errors due to laboratory performance. This procedure ensured an unbiased treatment of samples and a random distribution of possible drift of analytical conditions for all samples. Objectivity was assured through the use of neutral laboratory numbers.

Detection limits were 1 mg/kg for Ba, Cr, Ga, La, Mn, Sr and Zn, 0.5 mg/kg for As and Se, 0.1 mg/kg for Ag, Bi, Cd, Co, Cu, Mo, Ni, Pb, Sb, Sc, Th, Tl, U, and W, 0.01 % for Al, Ca, Fe, K and Mg, 0.05 % for S, 0.001 % for Na and P, 2 mg/kg for V, 20 mg/kg for B and 0.5 μg/kg for Au.

Accuracy (A) of the analytical method was estimated by calculating the absolute systematic error between the determined (X$_a$) and recommended values (X$_p$) of geological standards using equation:

$$A = \frac{\left| x_a - x_p \right|}{x_p} 100 \ [\%]$$

Most elements determined in standards differ on average by less than 15 % from their recommended values in the sample concentration range. Higher average deviations have only Au (16.1 %) and Cr (15.4 %).

Precision (P) was tested by relative differences between pairs of analytical determinations (x$_1$, x$_2$) of the same sample using equation:

$$P = \frac{2 \left| x_1 - x_2 \right|}{(x_1 + x_2)} 100 \ [\%]$$

The precision of analytical determinations is acceptable; repeatability is not so good only for Au, Cd, Cr, Cu, Se and Tl, at which P exceeds 20 %. The reliability of analytical procedures was considered adequate for using the determined elemental contents in further statistical analyses.

Statistical analysis

In order to better describe and interpret analytical results, descriptive statistics (mean, median, standard deviation, first and third quartile, maximum, minimum, frequency histogram and Kolmogorov and Lilliefors test for normality) were determined using Statistica 6.1 software to the database of soil and SOM samples results. Although 35 elements were analysed, only 29 were considered in the statistical analysis. The rest of variables (Ag, B, Na, S, Sb and W) were excluded for having more than 30 % of observations below the method's detection limit and for not being considered relevant for this study.

Statistical normality of elemental distribution was estimated with Kolmogorov and Lilliefors test for normality and visually with the examination of shapes of histograms of natural and logarithmic values, with tests of skewness and kurtosis, and with comparison of average and mean value with the median value.

Mapping/Kriging

Data analysis and production of maps were performed on a PC using the Statistica (ver. 6.1; StatSoft, Inc., USA), Autocad (ver. 2000) and Surfer (ver. 8.0; Golden Software, Inc., Colorado) software. The universal kriging with linear variogram interpolation method (Davis, 1986) was applied to construct the maps of areal distribution of Hg in SOM and soil (5–20 cm). For class limits the percentile values of the Hg distribution in investigated samples were chosen. Seven classes of the following percentile values were selected: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100.

Results and discussion

Soil characteristics

The prevailing soil types are Cambisols with typical A-B-C/R layers sequence. Visibly observed, soils are generally rich in organic matter to the depth of 30–40 cm; deeper the clayey loam prevails. Soils are variable in depth; depth to the parent material is mainly about 50 cm, but tongues extend to depths of 1 meter and more. At the surface there is a loose leafy litter resting on a brown granular horizon containing numerous earthworms. Boundaries between A and B horizon are mostly gradual and irregular. B horizon changes horizontally from location to location from dark brown loose and sandy to light brown firmly and loamy. These changes are observed also with depth in soil profile. In places A horizon is greyish brown mixture of organic and mineral material; this changes into a grey brown sandy layer, followed by a sharp change into a brown blocky or prismatic horizon with a high content of clay, then there is gradation to unaltered material. Soils are also characterized by the presence of many rock frag-

ments, from fine pebbles to stones, and by densely developed root-system, which aggravated digging and collecting of soil samples, especially deeper soil layers. Rock fragments are mostly sandstone, interchanging with dolomite. At the central investigated area soils are developed on waste material (pottery fragments and pieces of unroasted ore fragments).

pH in soil and SOM

The determined pH values in SOM samples from investigated area Pšenk range from 3.0 to 6.8 with the average of 4.7. At the roasting site area the average pH in SOM is 3.9 (range 3.3–6.5). In soils the pH values range between 3.1 and 7.1 with the average of 5.3 at the total investigated area and between 3.1 and 6.9 with the average of 4.8 at the supposed roasting site area. In soil samples of the narrow roasting site area the average pH of 4.5 (range 3.1–6.8) was determined in the depth of 5–20 cm, and 5.1 (3.4–6.9) in the depth of 20–30 cm (Table 1). Generally, pH on certain location is the lowest in SOM and it increases with depth in soil profile. Regarding the whole investigated area, pH values are lower in SOM and soils of the supposed roasting site area.

Table 1. pH values in SOM and soils of the investigated area at Pšenk locality

Area	Depth (cm)		n	Mean	Md	Min	Max
				pH (CaCl$_2$)			
total investigated area	SOM		67	4.7	4.4	3.0	6.8
	soil	5–30*	89	5.3	5.5	3.1	7.1
		5–20	73	5.3	5.7	3.1	7.1
roasting site area	SOM		20	3.9	3.7	3.3	6.5
	soil	5–30*	38	4.8	4.3	3.1	6.9
		5–20	22	4.5	3.8	3.1	6.8
		20–30	16	5.1	5.0	3.4	6.9

Md = median, min = minimum, max = maximum
* all soil samples

The spatial distributions of pH in SOM and soil of the investigated area (Figs. 2 and 3) are quite similar. They both show the lowest values in the central lowland part of the investigated area, while higher values prevail on the northern and southern elevated regions.

Elemental contents in soils and SOM

The univariate statistical results for analysed elements in soils and SOM of studied roasting sites Pšenk are given in Table 2.
On the basis of the results of normality tests and visual inspection of distribution histograms for all elements in soil and SOM, as also with comparison of average and mean values with the median values it was estimated that natural values of the following elements show normal distribution: Al, Ba, Fe, K, Mn, Ni and Zn. For all the rest elements
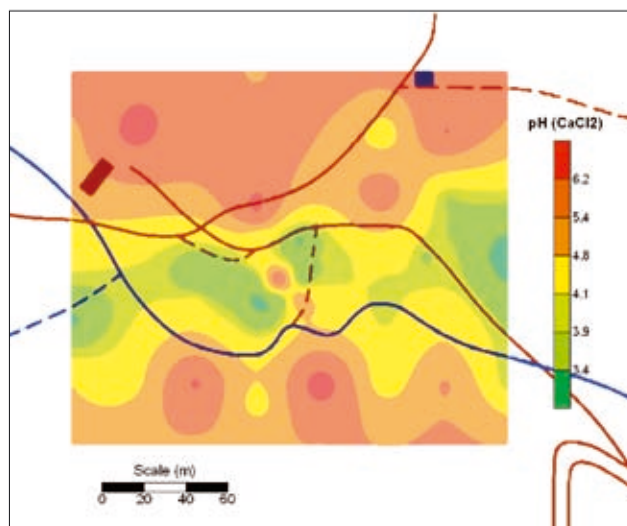

Fig. 2. Spatial distribution of pH (CaCl$_2$) in SOM at the roasting site Pšenk
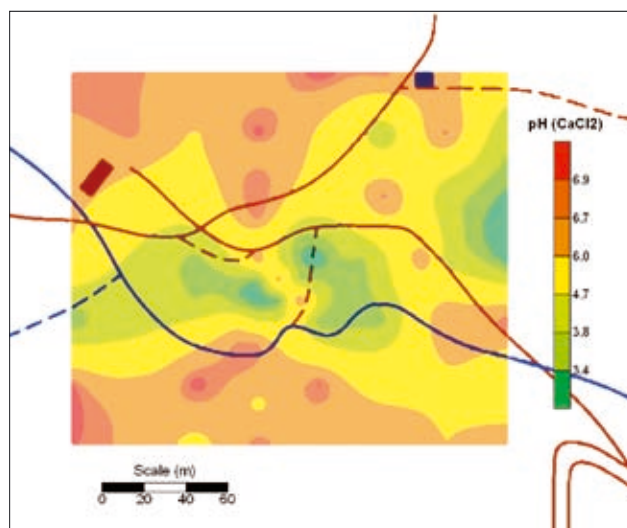

Fig. 3. Spatial distribution of pH (CaCl$_2$) in soil (5–20 cm) at the roasting site Pšenk

(As, Au, Bi, Ca, Cd, Co, Cr, Cu, Ga, La, Mg, Mo, P, Pb, Sc, Se, Sr, Th, Tl, U and V) the logarithms of elemental contents were considered normally distributed.

Contents of the above mentioned chemical elements in the sampling material are, with some exceptions, within the normal values for soils (URE & BERROW, 1982 in BIDOVEC et al., 1998) as also within Slovenian (ŠAJN, 2003) and European (SALMINEN et al., 2005) averages for soil (Table 3). However, certain elements exhibit elevated and highly elevated concentrations in analyzed media. High contents of As were determined in soils from investigated roasting site, reaching as much as 122 mg/kg in the depth of 5–20 cm. Additionally Cd, Mo, Pb and U contents in the soil (5–20 cm) are higher compared to natural soils. Cd and Mo show somewhat increased contents also in SOM from studied roasting site.

It is unknown why these elements express elevated concentrations. Idrija ore deposit is classified as a monometal deposit (MLAKAR & DROVENIK, 1971); mercury is the only metal found in the

Table 2. Statistical parameters of elemental concentrations in soils and SOM at the Pšenk locality

	SOM (n=67)					soil (5-20 cm) (n=73)					soil (20-30 cm) (n=16)				
	Mean	Median	Min	Max	St.D.	Mean	Median	Min	Max	St.D.	Mean	Median	Min	Max	St.D.
Al	0.72	0.72	0.16	1.42	0.31	1.82	1.77	0.72	3.36	0.54	1.75	1.88	0.71	2.45	0.56
As	14.95	11.50	2.00	53.80	12.02	44.30	37.80	2.10	122.20	34.51	5.14	5.30	1.05	10.20	3.48
Au	28.65	3.10	0.50	299.80	64.69	27.85	2.00	0.30	667.40	105.72	31.99	14.30	1.00	117.35	40.78
Ba	32.98	31.50	11.00	62.00	10.83	38.95	40.75	11.00	85.00	16.00	25.17	19.00	2.00	64.00	20.60
Bi	0.39	0.30	0.10	3.60	0.43	0.55	0.50	0.20	1.20	0.19	0.47	0.35	0.10	2.00	0.44
Ca	1.17	0.89	0.20	5.25	0.93	2.38	0.83	0.01	11.96	3.07	1.53	0.51	0.02	8.63	2.71
Cd	0.70	0.70	0.20	1.50	0.27	1.06	1.00	0.10	4.00	0.74	1.32	0.55	0.20	9.10	2.22
Co	2.92	2.70	0.20	7.40	1.71	8.66	7.80	1.70	28.50	4.94	6.14	5.90	2.50	11.80	2.60
Cr	9.78	9.00	3.00	25.00	4.82	18.89	16.00	3.00	44.00	10.23	12.25	11.50	4.00	27.00	5.62
Cu	16.43	15.00	9.00	48.00	6.12	15.48	14.75	0.30	45.40	7.13	12.54	11.60	3.70	26.60	6.72
Fe	0.85	0.78	0.20	1.57	0.37	2.17	1.97	0.25	5.31	0.88	1.89	1.95	1.08	2.40	0.38
Ga	2.45	2.00	1.00	6.00	1.08	5.90	5.50	2.00	24.00	3.24	6.25	5.00	3.00	21.00	4.17
K	0.15	0.14	0.08	0.34	0.05	0.19	0.17	0.07	0.48	0.09	0.15	0.15	0.08	0.26	0.06
La	8.16	8.00	1.00	19.00	3.73	23.30	22.00	5.00	44.00	7.48	23.75	22.00	17.00	36.00	6.48
Mg	0.42	0.30	0.09	2.20	0.38	1.44	0.68	0.19	6.84	1.64	1.04	0.56	0.24	5.28	1.37
Mn	396.41	339.00	47.00	1025.00	228.27	757.26	712.00	48.00	2219.00	466.53	626.78	408.00	92.00	2348.00	581.44
Mo	9.88	4.30	0.60	74.25	13.79	23.69	10.00	1.10	170.50	33.01	11.89	4.70	1.20	79.40	19.71
Ni	9.36	8.80	2.70	17.90	3.88	18.83	16.30	3.80	39.20	10.42	10.14	9.15	4.70	19.70	4.50
P	0.07	0.07	0.05	0.12	0.01	0.04	0.04	0.01	0.10	0.02	0.03	0.03	0.02	0.06	0.01
Pb	65.56	59.80	21.60	427.40	48.31	57.47	56.90	3.30	112.70	16.69	39.78	41.50	25.40	56.10	9.06
Sb	1.46	1.30	0.40	4.40	0.68	1.66	1.30	0.35	9.70	1.44	0.69	0.60	0.20	1.50	0.38
Sc	1.22	1.05	0.10	4.70	0.88	2.65	2.40	0.60	5.10	1.23	2.26	1.55	1.00	5.00	1.44
Se	2.48	1.08	0.50	35.10	4.77	6.08	1.65	0.50	100.00	14.59	12.78	7.35	0.70	81.30	20.09
Sr	16.96	16.00	9.00	36.00	5.01	18.05	12.00	1.00	57.00	15.14	9.88	8.00	3.00	34.00	8.71
Th	1.41	1.43	0.20	3.70	0.73	4.47	4.50	1.15	9.20	1.51	4.42	4.50	1.80	6.40	1.31
Tl	0.44	0.30	0.10	4.00	0.53	0.77	0.70	0.20	4.30	0.56	0.69	0.50	0.20	3.20	0.72
U	2.87	1.30	0.10	24.75	5.42	7.33	3.75	0.90	69.90	11.85	6.52	1.83	1.00	39.10	11.26
V	39.16	28.50	5.00	159.00	32.80	118.18	66.00	2.00	2397.00	292.80	88.88	53.50	8.00	571.00	132.53
Zn	71.04	75.00	33.00	109.00	17.87	68.69	70.75	18.00	116.00	25.01	46.03	46.50	13.00	80.00	18.09

– Al, Ca, Fe, K, Mg, Na, P and Ti in %, Au in μg/kg, all the others elements in mg/kg
– Md = median, min = minimum, max = maximum, St.D. = standard deviation

Table 3. Slovenian averages of chemical elements in soil, overbank sediment and stream sediment and world averages for mudstone, limestone and soil

Element	Slovenia			Europe			World		
	Soil (0–5 cm)	Overbank sediment (n=142)	Stream sediment (n=129)	Soil (0–25 cm)	Overbank sediment	Stream sediment	Mudstone	Limestone	Soil
	(Šajn, 2003)	(Bidovec, 1998)	(Sotlar, 1995)	(Salminen et al., 2005)			(Turekian & Wedepohl, 1961)	(Bowen, 1979)	*(Ure & Berrow, 1982)
Al	6.9	5.18	6.62	11.1	10.4	10.4	8	0.7	6.7
Ca	0.7	5.82	1.98	0.922	2.07	2.44	2.2	34	2
Fe	3.5	2.77	3.04	1.69	3.33	3.57	4.7	1.7	3.2
K	1.6	1.17	1.48	1.92	2	2.01	2.7	0.3	1.8
Mg	0.7	2.31	0.83	0.77	1.2	1.2	1.5	0.6	0.8
Na	0.5	0.72	0.72	0.8	0.8	0.8	1	0.1	1.1
P	0.1	0.053	0.04	0.128	0.11	0.13	0.07	0.07	0.08
Ti	0.3	0.27	0.29	0.572	0.48	0.634	0.5	0.03	0.5
As	/	6.8	7	7.03	6	6	13	1	11.3
Ba	358	281	271	375	397	370	580	90	568
Cd	0.4	0.4	0.4	0.145	0.3	0.29	0.22	0.03	0.6
Ce	61.3	/	/	48.2	50.2	65.1	/	/	/
Co	16	10	12	7.78	7	8	19	0.1	12
Cr	90.9	60	66	60	59	64	90	11	84
Cu	30.6	19	23	13	17	17	45	5.1	26
Hf	1.4	/	/	5.55	4.51	8.11	/	/	/
La	32.1	24	28	23.5	24.9	31.9	40	4.1	30
Li	50.1	/	/	/	22.5	20.8	/	/	/
Mn	1054	606	695	650	710	770	850	620	760
Mo	0.8	/	/	0.62	0.62	0.6	/	/	/
Nb	8.3	5	7	20.8	21.3	27.6	18	0.3	15
Ni	49.5	32	37	18	22	23	68	7	34
Pb	41.7	21	22	22.6	22	21	20	5.7	29
Rb	107	/	/	80	71	70	/	/	/
Sb	1.1	0.4	0.4	0.6	0.74	0.64	1.5	0.3	1.7
Sc	12	10	13	8.21	/	/	13	1	10
Sr	77	104	98	89	131	124	140	610	278
Ta	0.6	/	/	0.68	0.83	1.01	/	/	/
Th	10.6	9	9	7.24	8	10	12	1.7	13
U	/	/	/	2	2	2	/	/	/
V	102	69	72	60.4	56	62	130	45	108
Y	17.3	12	12	21	20.1	24.9	41	3.8	50
Zn	124	78	81	52	65	71	95	20	60
Zr	38.5	28	42	231	215	386	160	20	345

– Al, Ca, Fe, K, Mg, Na, P and Ti in %, remaining elements in mg/kg
– * After Bidovec et al., 1998

Idrija ore deposit in economically important quantities, while other elements appear only in traces or insignificant quantities. Therefore high contents of above mentioned elements in studied soils are probably not the consequence of historical ore roasting, with the exception of uranium, whose increased concentrations might be the result of roasting extremely rich cinnabar ore from Skonca beds, which contain on average up to 7 times the average quantity of radioactive elements such as uranium, radium, thorium and potassium, and also radon as a consequence of radioactive decay (MLAKAR & DROVENIK, 1971).

Spatial distribution of chemical elements in soils and SOM

Contents of As and U in soil of studied roasting sites show interesting distribution patterns. Spatial distributions of these elements in SOM and soil (5–20 cm) are shown on Figures 4 to 7.

Spatial distributions of As in SOM and soil (5–20 cm) from studied roasting site are very similar (Figs. 4 and 5). They both show the highest concentration at the northern and southern parts of investigated area, while the lowest values prevail in the central part, just the opposite from spatial distributions of Hg in SOM and soil (5–20 cm) from this area (TERŠIČ & GOSAR, 2009). High As concentrations in SOM (above 30.5 mg/kg) are continuing across NW margin and in soil (above 93.8 mg/kg) across NW and SW margins of investigated area.

The highest concentrations of U in SOM and soil (5–20 cm) from Pšenk roasting site (Figs. 6 and 7) appear in the centre of investigated area, with the highest anomaly at the region similar to the highest anomaly of Hg (TERŠIČ & GOSAR, 2009). High concentrations are then continuing in the medi-
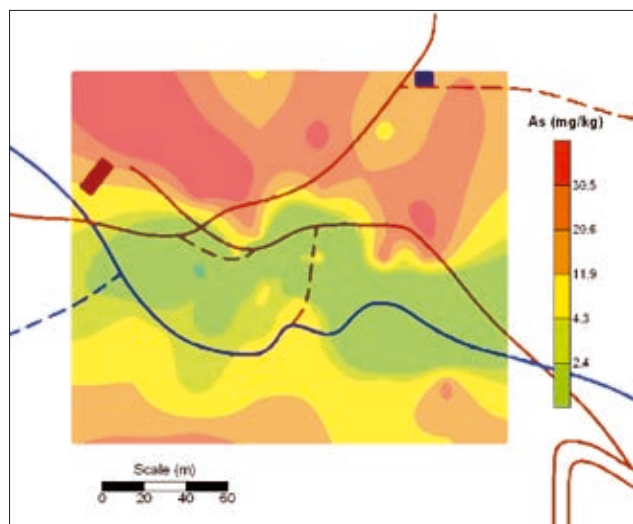
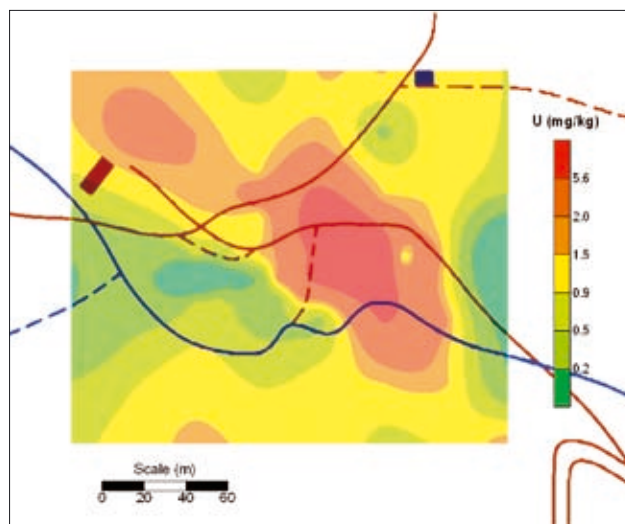Fig. 4. Spatial distribution of As in SOM at the roasting site Pšenk

Fig. 6. Spatial distribution of U in SOM at the roasting site Pšenk
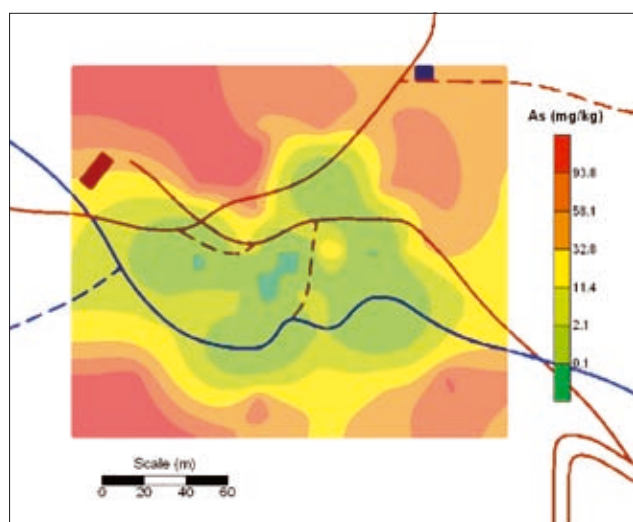

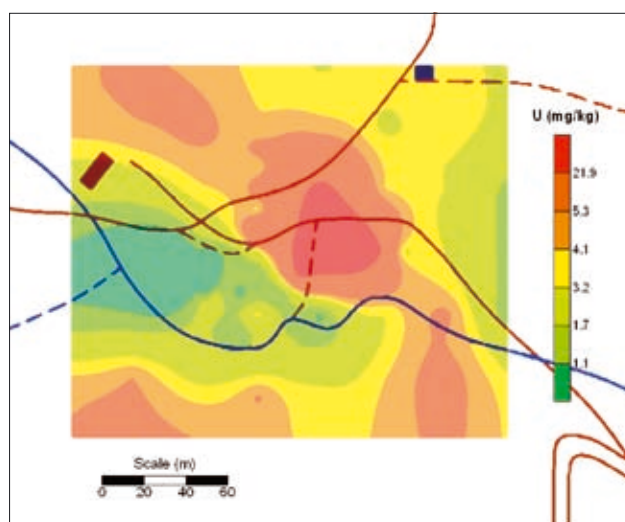Fig. 5. Spatial distribution of As in soil (5–20 cm) at the roasting site Pšenk

Fig. 7. Spatial distribution of U in soil (5–20 cm) at the roasting site Pšenk

um-sized zone towards the NW and SE. Interestingly, the lowest values prevail at the flat surface SE from the camper's cottage, where large amount of roasting vessels were found and highly elevated Hg contents were determined. This suggest that U is not linked only to roasting of ore from radioactive Skonca beds and that there might perhaps exist another source of elevated U in this area.

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