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Geochemical baseline for chemical elements in top- and subsoil of Idrija

Geokemično ozadje kemičnih prvin v zgornjem in spodnjem sloju tal na območju Idrije

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Ključne besede: multi-elementna analiza, geokemija, urbano območje, korelacijska matrika, prostorska porazdelitev, Idrija

Abstract

This study is a continuation of our previous study (Bavec et al., 2015), where the geochemical baseline levels of potentially harmful elements (As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb and Zn) in Idrija top- and subsoil (0-10 cm and 10-20 cm) at 45 locations were reported. Here we summarise our previous work and present baseline levels of additional 33 elements (Ag, Al, Ba, Be, Bi, Ca, Ce, Cs, Fe, Ga, Hf, In, K, La, Li, Mg, Mn, Nb, P, Rb, S, Sb, Sc, Se, Sn, Sr, Th, Ti, Tl, U, V, Y and Zr) in order to round off the first systematic geochemical survey of soil in Idrija town and establish a data set of soil elements, which will serve as a baseline for monitoring future changes in the soil chemical composition of the studied area.

The baseline levels were determined after aqua regia digestion, their statistical distribution was examined and the medians were compared to the recently established European grazing land and Maribor urban soil medians. To investigate relationships between elements, a correlation-matrix-based hierarchical clustering method was performed and the spatial distribution of their highest levels was examined. The results showed that in general, the median levels of elements in Idrija soil are mostly similar or slightly higher than in European and Maribor soil, with exception of Hg. Elements Al, Bi, Ca, Ce, Co, Cr, Cs, Fe, Ga, Hf, La, Li, Mg, Mn, Nb, Ni, Rb, S, Sc, Th, Ti, Tl, V, Y and Zr are enriched in the rural surroundings, while elements Ag, Ba, Cu, Hg, P, Pb, Se, Sb, Sn and Zn are enriched only partly in the rural surroundings, but mostly in the urban part of the study area. It is assumed that elements, which are enriched only in the rural surroundings, are of natural origin, while elements, which are enriched also in the urban area, are to a certain extent influenced by anthropogenic activities.

Izvleček

Predstavljena študija je nadaljevanje preteklih raziskav (Bavec et al., 2015), kjer smo obravnavali vrednosti geokemičnega ozadja potencialno škodljivih elementov (As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb in Zn) v zgornjem in spodnjem (0-10 cm in 10-20 cm) sloju tal Idrije na 45. lokacijah. V članku povzemamo prejšnje preiskave in obravnavamo geokemična ozadja dodatnih 33 elementov (Ag, Al, Ba, Be, Bi, Ca, Ce, Cs, Fe, Ga, Hf, In, K, La, Li, Mg, Mn, Nb, P, Rb, S, Sb, Sc, Se, Sn, Sr, Th, Ti, Tl, U, V, Y in Zr) z namenom, da bi zaokrožili prve sistematične geokemične raziskave tal v mestu Idrija, ter da bi vzpostavili nabor podatkov o elementih v tleh, ki bodo služili kot osnova za spremljanje prihodnjih sprememb v kemijski sestavi tal na preiskovanem območju.

Vrednosti ozadja smo določili po razklopu z zlatotopko, preiskali njihovo statistično porazdelitev in primerjali ugotovljene mediane z medianami elementov v evropskih pašniških in mariborskih mestnih tleh, ki so bile vzpostavljene nedavno. Z namenom, da bi prepoznali povezave med elementi, smo uporabili metodo hierarhičnega razvrščanja na podlagi korelacijske matrike in ugotavljali prostorsko porazdelitev najvišjih vrednosti elementov. Rezultati so pokazali, da so na splošno mediane elementov v idrijskih tleh večinoma podobne ali nekoliko višje kot v evropskih in mariborskih tleh, z izjemo Hg. Elementi Al, Bi, Ca, Ce, Co, Cr, Cs, Fe, Ga, Hf, La, Li, Mg, Mn, Nb, Ni, Rb, S, Sc, Ti, Tl, V, Y in Zr so obogateni na ruralnem obrobju, medtem ko so elementi Ag, Ba, Cu, Hg, P, Pb, Se, Sb, Sn in Zn obogateni deloma na ruralnem obrobju ter v urbanem predelu preiskovanega območja. Predpostavljamo, da so elementi, ki so obogateni le na ruralnem obrobju, naravnega izvora, medtem ko so elementi, ki so obogateni tudi v urbanem predelu, v določeni meri antropogenega izvora.

Introduction

With regard to our previous study (Bavec et al., 2015), the geochemical baseline levels of 10 potentially harmful elements (As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb and Zn) in Idrija top- and subsoil (0-10 cm and 10-20 cm) at 45 locations were reported with intention to evaluate them according to the metal concentrations reported in other areas around the world and to the national guidelines. Current Slovenian legislation (Official Gazette RS, 1996) sets their limit, warning and critical soil levels. These levels are based on aqua regia digestion. However, the levels of 33 additional elements, which are not nationally considered as potentially harmful, were also established, which will be presented in this paper.

With regard to the European Thematic strategy on soil protection (COM(2006)231final)), anthropogenic activities (inadequate agricultural and forestry practices, industrial activities, tourism, urban and industrial sprawl and construction works) affect the soil negatively and prevent it from performing its broad range of functions and services to humans and ecosystems. As a consequence soil degradation problems (erosion, organic matter decline, compaction, salinization, landslides, contamination, sealing and biodiversity decline (SEC(2006)1165) arise. The problem of soil contamination reflects the use and presence of dangerous elements and substances in many production processes with respect to more than two hundred years of industrialisation.

In order to trace the anthropogenic contribution to soil element distribution, it is necessary to determine the baseline levels of elements in soils and monitor them through time. With the latter in mind, international, national and regional datasets on the 'actual' concentration and distribution of dozens of chemical elements in soils (Table 1) were established by many authors with the performance of multi-element geochemical baseline surveys. However, it is emphasized, that two different extraction methods (4-acid and aqua regia digestion) (Table 1) were used to determine the baseline levels, therefore the levels in Table 1 are not directly comparable between each other, except those determined after the same extraction.

For Europe (EU) the first geochemical baseline for topsoil (0-25 cm) was established by Salminen et al. (2005), when the levels of 64 elements were determined at up to 845 locations from 26 EU countries. Almost a decade later geochemical baselines (the levels of 52 elements) were established for grazing soil (0-10 cm) at 2023 locations and for agricultural soil (0-20 cm) at 2108 locations from 33 EU Countries (Reimann et al., 2014).

For Slovenia soil geochemical baselines were provided by the following authors. Šajn (2003) determined the levels of 42 elements in topsoil (0-5 cm) at 82 locations, which were situated in the rural area settlements without known industry and in six largest towns. With intention to monitor soil pollution on a national scale long-term, Zupan et al. (2008) determined the levels of 15 elements and 55 organic substances in Slovenian top- and subsoil (0-5 cm and 5-20 cm) at 376 locations covering the whole territory of Slovenia. Andjelov (2012) determined the levels of 24 elements in topsoil (0-10 cm) at 819 locations covering the whole territory of Slovenia. The mentioned studies provide fundamental background reference levels for distribution of elements in national soils.

Moreover regional geochemical baselines were established with intention to (1) provide reference element levels in soil at specific time and space that will be useful for monitoring future changes and (2) to detect pollution problems and pinpoint target areas, where adversities for its inhabitants threaten to become most pronounced. Šajn et al. (1998, 2011) determined the levels of 35 elements in Ljubljana topsoil (0-5 cm) at 477 locations. Žibret & Šajn (2008) determined the levels of 41 elements in the topsoil (0-5 cm) from Celje and near surroundings at 38 locations, Bavec et al. (2015) determined the levels of 10 elements in Idrija top- (0-10 cm) and subsoil (10-20 cm) at 45 locations. Gosar et al. (2016) determined the Hg levels in Slovenian topsoil (0-10 cm) at 817 locations. Gaberšek and Gosar (2017) determined the levels of 65 elements in Maribor topsoil (0-10 cm) at 118 locations.

The main objective of this paper is to summarise geochemical distribution of 10 elements (As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb and Zn) in Idrija soil from our previous study (Bavec et al., 2015) and to present geochemical distribution of 33 additional chemical elements (Ag, Al, Ba, Be, Bi, Ca, Ce, Cs, Fe, Ga, Hf, In, K, La, Li, Mg, Mn, Nb, P, Rb, S, Sb, Sc, Se, Sn, Sr, Th, Ti, Tl, U, V, Y and Zr) in Idrija soil. Furthermore statistical analyses (descriptive statistics and correlation-matrix-based hierarchical clustering

Table 1. Overview of some international, national and regional geochemical baselines of chemical elements, which are considered in this study (all levels are in mg/kg, except where otherwise stated).

	Salminen et al. (2005)	Reimann et al. (2014)	Šajn (2003)	Šajn (2003)	Zupan et al. (2008)	Zupan et al. (2008)	Andjelov (2012)	Šajn et al. (1998, 2011)	Gaberšek & Gosar (2018)	Žibret & Šajn (2008)
Area	Europe	Europe	Slovenia rural areas	Slovenia urban areas	Slovenia	Slovenia	Slovenia	Ljubljana	Maribor	Celje
Depth	0-25 cm	0-10 cm	0-5 cm	0-5 cm	0-5 cm	5-20 cm	0-10 cm	0-5 cm	0-10 cm	0-5 cm
N	845	2026	59	23	135-288	124-253	819	477	118	37
Value	median	median	average	average	median	median	median	median	median	median
Extraction method	aqua regia	aqua regia	4-acid	4-acid	aqua regia	aqua regia	4-acid	4-acid	aqua regia	4-acid
Ag	0.27	0.04	/	/	/	/	/	/	0.093	0.1
Al (%)	11	1.07	6.8	4.7	/	/	6.92	5.55	1.64	5.7
As	6	5.6	15	12	10.2	12.5	/	/	10.1	15
Ba	65	63	355	459	/	/	360	333	96.5	408
Be	<2	0.51	/	/	/	/	/	/	0.7	/
Bi	<0.5	0.18	/	/	/	/	/	/	0.28	/
Ca (%)	0.922	0.31	/	/	/	/	0.78	3.88	1.1	3.5
Cd	0.145	0.2	0.52	1.3	0.62	0.48	/	0.6	0.32	2.2
Ce	48.2	27	/	/	/	/	/	/	28.1	51
Co	7	7.2	16	7.2	13.9	14.3	26	/	10.2	11
Cr	22	20	85	75	51	61	88	85	31	67
Cs	3.71	1.06	/	/	/	/	/	/	1.56	/
Cu	12	14.5	35	70	26.3	27	23	32	40.1	42
Fe (%)	1.96	1.7	3.5	2.6	/	/	3.8	2.94	2.58	3.1
Ga	13.5	3.4	/	/	/	/	/	/	4.45	/
Hf	5.55	0.0458	/	/	/	/	/	/	/	/
Hg	0.037	0.035	0.66	0.311	0.17	0.13	/	0.244	0.095	/
In	0.05	0.0177	/	/	/	/	/	/	/	/
K (%)	1.92	0.113	/	/	/	/	1.4	1.2	0.125	1.5
La	23.5	13.6	32	23	/	/	30	22	13.5	28
Li	/	11.3	/	/	/	/	/	/	18.95	37
Mg (%)	0.77	0.282	/	/	/	/	10.87	1.56	0.79	1.3
Mn	382	435	1090	802	862	871	902	753	612.5	714
Mo	0.62	0.42	1	2.4	1	1	/	/	0.85	1.2
Nb	9.68	0.52	8.4	5.3	/	/	/	/	0.685	7.1
Ni	14	14.4	47	36	29.2	32.5	47	29	27.5	32
P (%)	0.128	0.065	/	/	/	/	0.063	0.09	0.09	0.1
Pb	15	17.7	42	217	42	37	34	56	43.95	74
Rb	80	13.9	/	/	/	/	/	/	19.15	93
S (%)	227	0.03	/	/	/	/	/	/	0.04	0.1
Sb	0.6	0.28	1.1	3.9	/	/	/	/	0.86	1.1
Sc	8.21	2	12	9.4	/	/	13	9.5	3.1	10
Se	/	0.4	/	/	1.23	1.27	/	/	0.4	/
Sn	3	0.81	3.2	7.9	/	/	/	/	2.3	3.4
Sr	89	17.8	76	116	/	/	82	81	20.05	106
Th	7.24	2.5	11	7.8	/	/	11	6	2	9
Ti (%)	0.572	0.007	0.31	0.23	/	/	0.36	0.19	0.026	0.3
Tl	0.66	0.115	/	/	0.68	0.66	/	/	0.17	/
U	2	0.74	/	/	/	/	3.4	/	1.1	2.9
V	33	26	101	70	71	79	113	82	32	81
Y	21	6.5	16	16	/	/	15	16	8.9	14.1
Zn	48	46	124	465	99	95	104	25	130.5	314
Zr	231	1.6	39	23	/	/	46	40	0.3	36

method) were performed using the data of all 43 elements in order to investigate relationships between elements. The presented data will also serve as a baseline for monitoring future changes in the soil chemical composition.

Study site

The small town Idrija (Fig. 1) with 5,905 inhabitants reported in 2016 (STAT, 2017) is situated approximately 50 km west of Ljubljana, the capital of Slovenia. Along the Nikova and Idrijca rivers a small densely populated centre is developed, where residential apartment buildings as well as individual houses are located. The highly urbanized town centre quickly passes into steep, sparsely populated rural area, where mostly individual houses are situated. In the most urbanized parts, there are still several urban green spaces, such as parks and playgrounds. Two main roads follow the Idrijca and Nikova rivers, where traffic is heavy during rush hours, while on other streets and roads, traffic is light. Mercury mining and ore-processing presented the main reasons for urban and economic growth in the studied area. Mercury was discovered in 1490 and exploited for almost 500 years. The mine was closed in 1995. Idrija, one of the world's largest mercury mining site, was enlisted recently in the UNESCO World heritage list. After the mine closure, Kolektor, a commutator production company, that had started in the year 1963 as a small factory, developed into a successful global company (Kolektor, 2014). Its manufacturing facilities are located on both banks of the river Idrijca in the northern part of Idrija, where Hg ore roasting facilities were formerly located. The dominant wastes in the Kolektor's manufacturing process are plastic and nonferrous metals, primarily copper (Benčina, 2007).

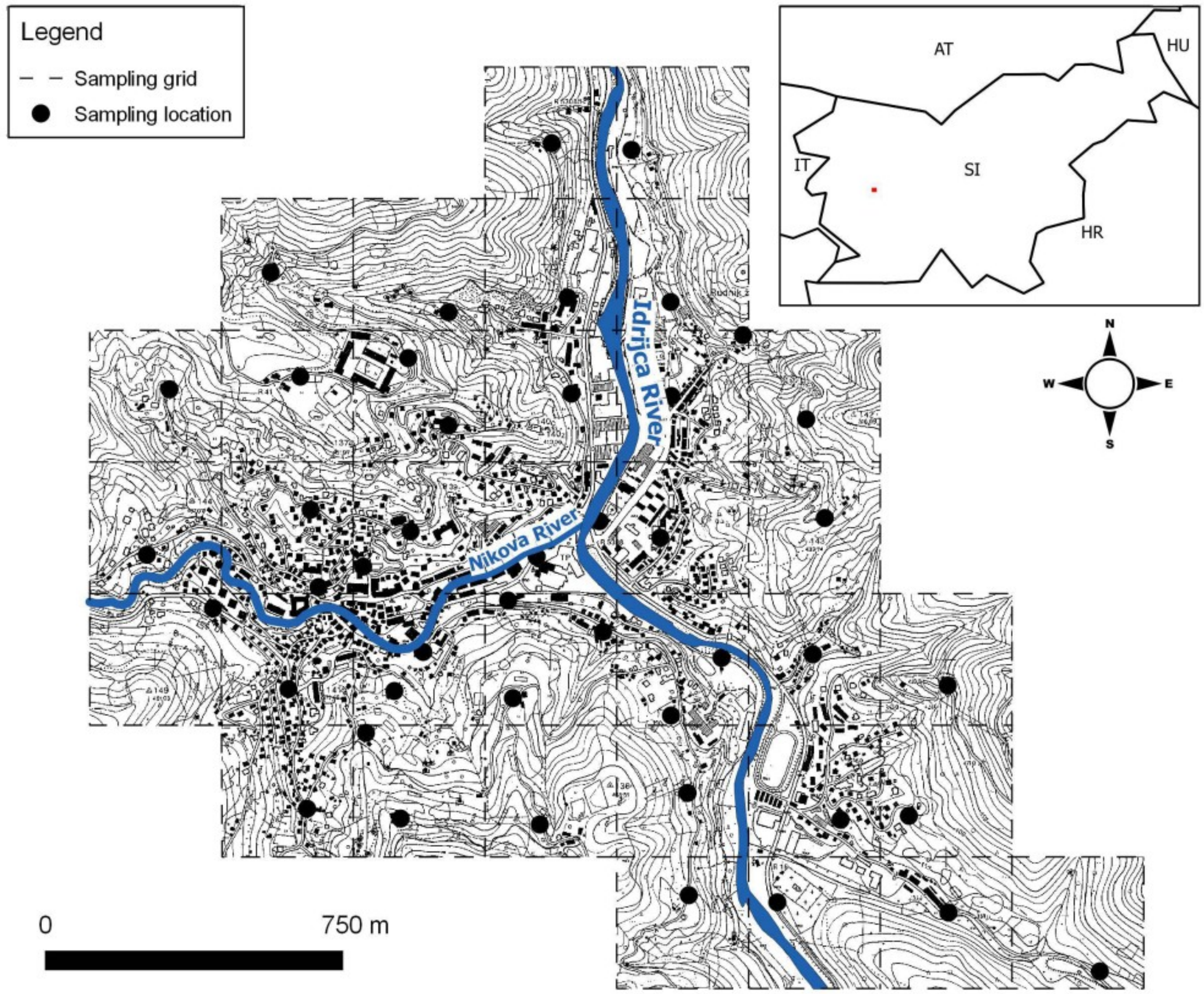

Fig. 1. Study area with sampling locations.

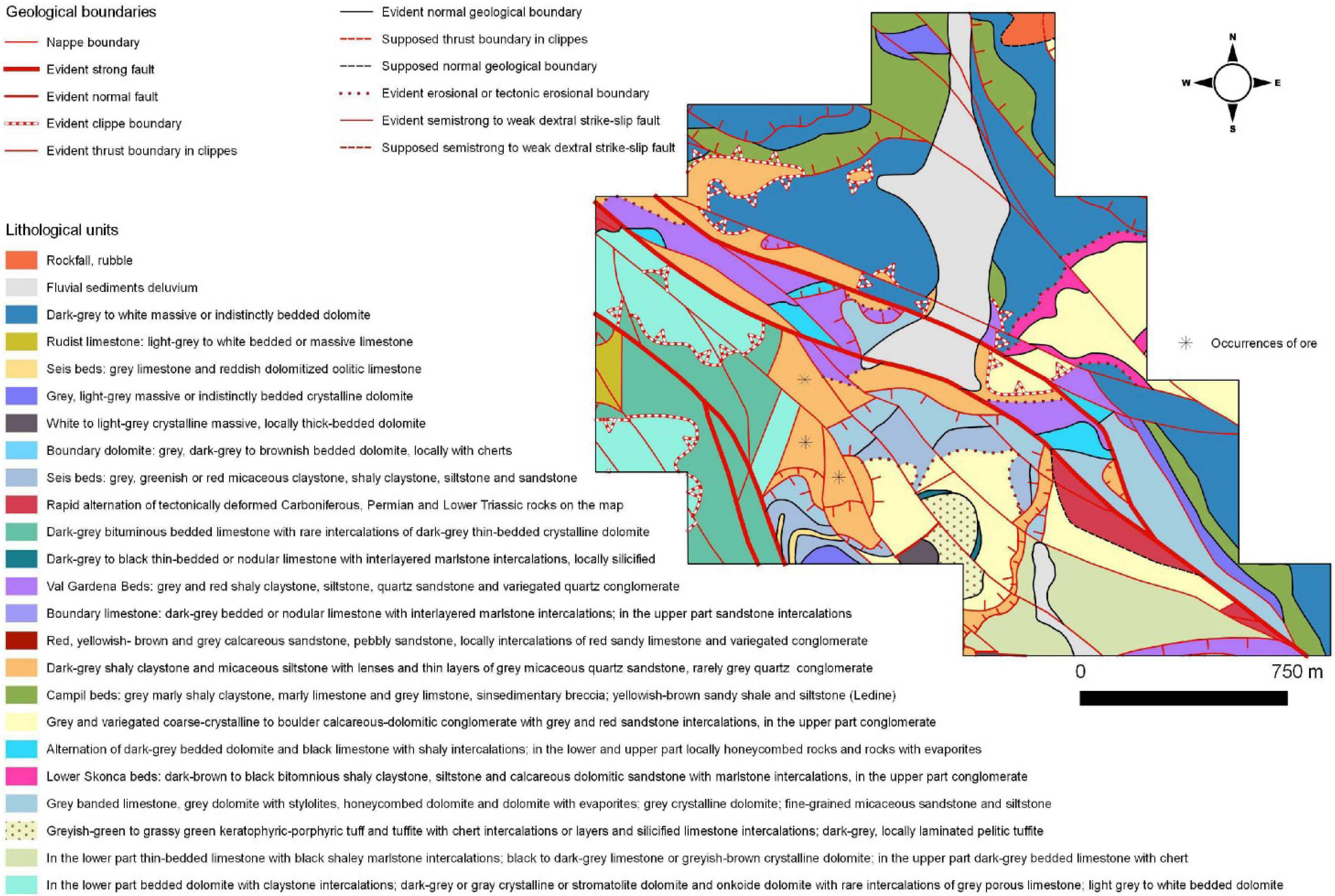

Fig. 2. Geological structure and lithological composition of the study area based on the data by Mlakar & Čar (2009, 2010)

A special characteristic of the town is that it is situated directly over the Idrija ore deposit. Ore deposit is monometallic, because mercury is the only mineral found in economically important quantities, while other ore elements occur only in traces or insignificant quantities (Čar, 1998). Several Hg sources were identified in the urbanised area, such as outcrops of rocks containing Hg ore, former ore roasting sites, ore residue dumps and mine ventilation shafts, which are discussed in detail by Bavec et al. (2014).

Geological properties

The detailed geological properties of the study area are presented in Fig. 2. The data were extracted out of the Geological map of the Idrija - Cerkljansko hills between Stopnik and Rovte 1:25000 and the associated explanatory book (Mlakar & Čar, 2009, 2010). In general about 70 % of the investigated territory consists of chemical sedimentary rocks (mainly different types of carbonate rocks - limestones and dolomites, rarely cherts), while about 30 % consists of detrital sedimentary rocks (breccias, conglomerates, sandstones, mudstones, claystones and shales). On the banks, along the Idrijca River, fluvial sediments deluvium occurs on the surface (Mlakar & Čar, 2009, 2010).

Pedological properties

With regard to the soil map of Slovenia (MKGP, 2017) (Fig. 3), the investigated territory in the urbanized area, along the Nikova and Idrijca rivers, consists of 100 % urban, water and non-fertile

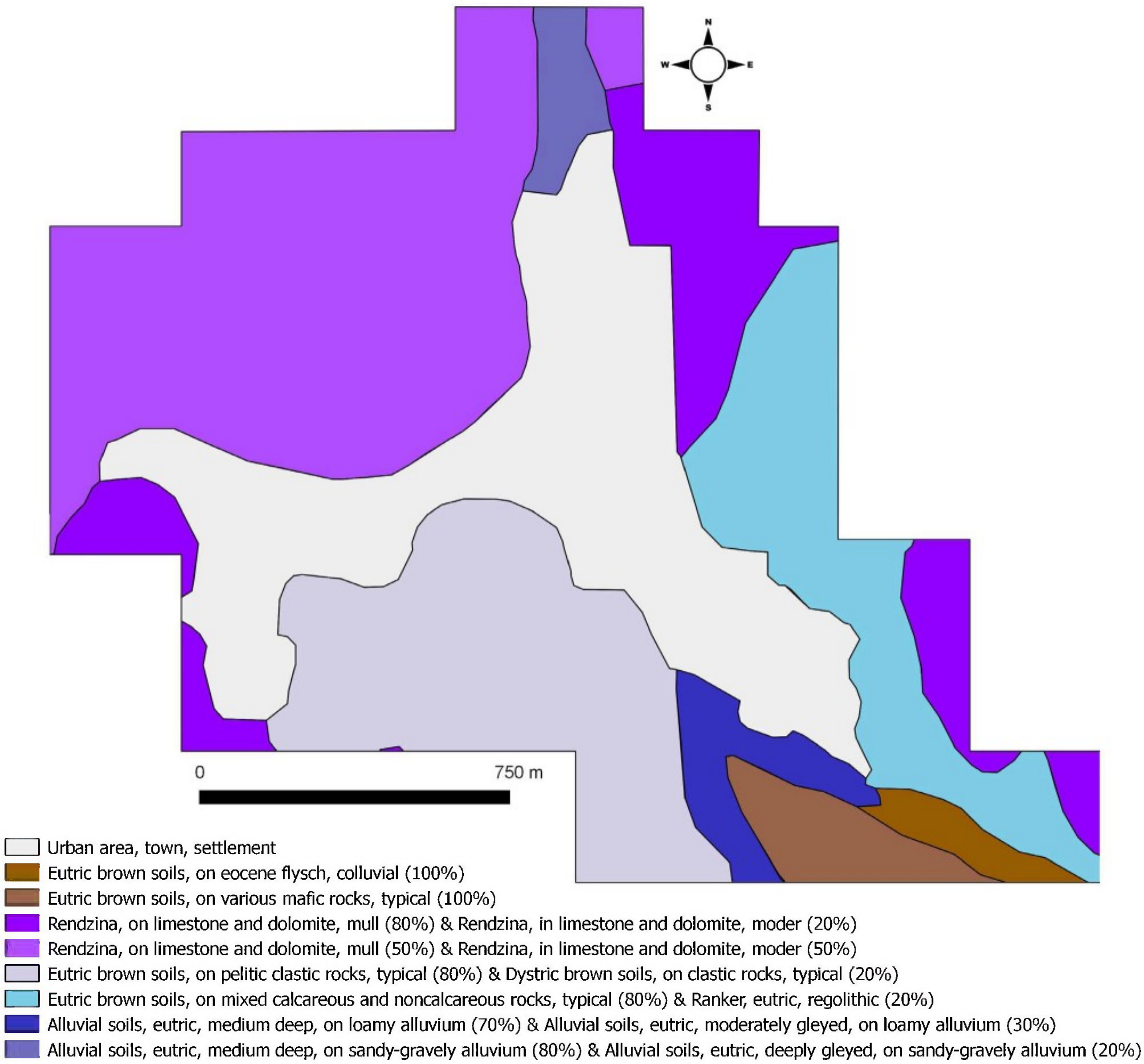

Fig. 3. Pedological composition of the study area based on the data by MKGP (2017).

surfaces. In the SW, NW and NE part rendzinas on limestone and dolomite with mull or moder humus are developed. In the SE eutric brown soils, on mixed carbonate rocks and regolithic eutric ranker with inclusions of eutric non-gleyic colluvial and deluvial soils are developed. In the S eutric brown soils on pelitic clastic rocks and dystric brown soils on clastic rocks are developed. In the E eutric brown soils on mixed calcareous and noncalcareous rocks and regolithic eutric ranker are developed. Along the Idrijca River at the SE part of the area eutric, medium deep or deeply gleeyed alluvial soils on sandy-gravely alluvium are developed. In the most SE part eutric brown soils on Eocene flysch or various mafic rocks are developed (MKGP, 2017).

Materials and Methods

The details of sampling, sample preparation, chemical analyses and quality control are described in Bavec et al. (2015) and are summarised below as follows:

Sampling and sample preparation

A total of 45 sampling locations were established following the sampling grid (Fig. 1). On each location, grassland topsoil (0–10 cm) and subsoil (10–20) samples were collected at urban area and nearby rural surroundings. Approximately 1 kg of each sample was collected and treated in the laboratory to determine aqua regia extractable concentrations of investigated elements. Samples were oven dried at below 30°C. Dry samples were gently crushed in a ceramic mortar, sieved through a 2 mm mesh sieve and homogenised in agate ball mill to the analytical fineness of <0.063 mm.

Chemical analyses and quality control

After aqua regia (1:1:1 $HCl:HNO_3:H_2O$) digestion, the levels of elements (N = 53; Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr, Pd and Pt) were determined at Bureau Veritas Minerals, Canada-Vancouver (accredited under ISO 9001:2008) with inductively coupled plasma (ICP) mass spectrometry (MS). The samples that contained Hg levels above the upper detection limit for ICP-MS (50 mg/kg) were analysed with ICP emission spectrometry (ES). To ensure quality control of the analysis (AOAC INTERNATIONAL, 2016) standard reference materials (SRMs) provided by Bureau Veritas Minerals (DS8 and OREAS45CA for ICP-MS run and GC-7 for ICP-ES run), blank spikes and sample replicates were used. Quality control is an integral part of any project in environmental geochemistry, because it enables the quantification of analytical recovery (accuracy) and relative standard deviation (precision), which clearly show whether the results of the multi-elemental analysis are trustworthy (Reimann et al., 2008). During the ICP-MS run additional SRMs, OREAS44P and NGU, which was provided by the urban geochemistry project (EGS, 2011, 2013, 2014, 2015, 2016), were used in order to independently check the quality control of analysis. SRM DS8 and OREAS45CA included referenced values for all investigated elements, except B and Ta, which were immediately excluded from the further analyses. SRM OREAS45PP included referenced values for As, Ba, Cu, Au, Pb, Mo, Ni, W and Zn and NGU for As, Pb, Cd, Cu, Cr, Hg, Ni and Zn. Elements (Au, Na, W, Te, Ge, Re, Pd and Pt), which had more than 20 % of measured values below the lower limit of detection (LDL), were also excluded from geochemical analyses with regard to Miesch (1976). With regard to AOAC INTERNATIONAL (2016) guidelines, analytical recoveries (RE) and relative standard deviations (RSD) were acceptable (80 % ≤ RE ≤ 120 %; 0 % ≤ RSD ≤ 20 %;) for studied elements (Table 2) with only few exceptions (Hg in SRM STD8 and OREAS45CA and Mo, Nb, Sb and Se in SRM OREAS45CA). However, analytical recoveries and relative standard deviations were good or acceptable at least in one SRMs tested for each investigated element, therefore the reliability of the chemical analysis was considered satisfactory for the purposes of this study and the results were used for further statistical and spatial analyses.

Statistical analyses

Analyses of statistical distribution (descriptive statistics) were performed using Excel 2010 software. Distribution of the data was examined with the use of box-plot diagrams, histograms and calculation of skewness and kurtosis. The majority of the elements is non-normally distributed, thus nonparametric Spearman correlations (r_s) were calculated and a correlation-matrix-based hierarchical clustering method was performed with the use of R 3.4.0. and R studio software in order to extract correlation patterns between elements in topsoil and display them

Table 2. Data set of quality control

			STD8				OREAS45CA				OREAS44P				NGU			
EL	**Unit**	**LDL**	**ME (N=4)**	**RV**	**RE (%)**	**RSD (%)**	**ME (N=7)**	**RV**	**RE (%)**	**RSD (%)**	**ME (N=4)**	**RV**	**RE (%)**	**RSD (%)**	**ME (N=4)**	**RV**	**RE (%)**	**RSD (%)**
Ag	µg/kg	2	1691.7	1690	100	5.8	259.6	275	94	6.6	610.5	/	/	0.9	47.8	47.5	101	2.7
Al	%	0.01	0.9	0.93	97	4.9	3.6	3.592	101	6.5	1.0	/	/	0.9	0.8	/	/	3.4
**As*	mg/kg	0.1	25.9	26	100	5.2	3.7	3.8	97	10.0	97.5	95	103	1.1	2.4	1.14	206	7.1
Ba	mg/kg	0.5	281.1	279	101	3.8	157.7	164	96	5.2	169.8	167	102	1.8	31.8	/	/	3.0
Be	mg/kg	0.1	5.5	5.2	105	6.2	0.6	/	/	20.3	1.7	/	/	12.4	0.1	/	/	34.6
Bi	mg/kg	0.02	6.3	6.67	94	5.7	0.2	0.19	91	13.7	8.2	/	/	3.6	0.1	/	/	6.9
Ca	%	0.01	0.7	0.7	100	4.1	0.4	0.427	93	3.1	0.3	/	/	2.6	0.3	/	/	2.0
**Cd*	mg/kg	0.01	2.4	2.38	101	5.0	0.1	0.1	104	8.7	0.4	/	/	6.4	0.1	0.103	97	12.2
Ce	mg/kg	0.1	26.0	29.8	87	9.7	34.2	35	98	5.2	37.1	/	/	2.4	27.4	/	/	4.8
**Co*	mg/kg	0.1	7.3	7.5	97	4.5	85.4	92	93	2.8	57.8	/	/	1.9	7.9	/	/	4.7
**Cr*	mg/kg	0.5	115.0	115	100	2.2	681.3	709	96	6.3	437.9	/	/	4.1	38.6	58.4	66	6.2
Cs	mg/kg	0.02	2.4	2.48	95	4.7	1.1	1.03	105	8.9	1.3	/	/	4.6	0.8	/	/	4.2
**Cu*	mg/kg	0.01	106.4	110	97	4.3	489.3	494	99	3.8	404.9	410	99	0.6	19.2	17	113	5.0
Fe	%	0.01	2.4	2.46	99	3.8	15.2	15.69	97	4.3	24.0	/	/	2.5	1.4	/	/	3.4
Ga	mg/kg	0.1	4.7	4.7	99	4.8	18.1	18.4	99	6.8	2.6	/	/	2.8	2.6	/	/	3.8
Hf	mg/kg	0.02	0.1	0.08	79	7.4	0.5	0.5	103	9.4	0.1	/	/	17.9	0.1	/	/	16.1
**Hg*	µg/kg	5	216.8	192	113	25.7	42.9	30	143	35.5	97.5	/	/	21.4	63.8	66	96.59	7.6
In	mg/kg	0.02	2.2	2.19	99	7.5	0.1	0.09	102	7.0	0.1	/	/	18.6	/	/	/	/
K	%	0.01	0.4	0.41	100	4.0	0.1	0.072	98	7.6	0.2	/	/	2.6	0.1	/	/	0.0
La	mg/kg	0.5	15.1	14.6	103	12.0	16.5	15.9	104	8.4	18.1	/	/	2.2	13.6	/	/	5.5
Li	mg/kg	0.1	26.9	26.34	102	5.8	7.7	6.2	124	11.1	7.1	/	/	1.9	9.2	/	/	6.1
Mg	%	0.01	0.6	0.605	100	3.9	0.2	0.139	111	9.7	0.3	/	/	1.2	0.6	/	/	2.9
Mn	mg/kg	1	605.2	615	98	2.9	902.7	943	96	3.8	714.8	/	/	2.2	269.0	/	/	4.4
**Mo*	mg/kg	0.01	12.6	13.44	94	5.7	0.7	1	71	19.9	354.0	407	87	0.5	0.3	/	/	6.9
Nb	mg/kg	0.02	0.7	1.1	63	13.5	0.1	0.22	68	23.7	0.03	/	/	14.1	0.5	/	/	6.0
**Ni*	mg/kg	0.1	36.3	38.1	95	4.3	243.2	240	101	4.3	460.8	401	115	0.2	25.4	27.8	91	4.7
P	%	0	0.1	0.08	100	6.9	0.04	0.039	101	2.5	0.03	/	/	2.3	0.05	/	/	5.0
**Pb*	mg/kg	0.01	121.8	123	99	6.4	20.1	20	101	8.8	182.5	183	100	1.2	8.4	8.29	101	3.9
Rb	mg/kg	0.1	37.1	39	95	6.7	8.9	8.2	108	10.4	11.5	/	/	3.2	12.3	/	/	2.9
S	%	0.02	0.2	0.168	95	3.6	0.0	0.021	107	19.2	/	/	/	/	/	/	/	/
Sb	mg/kg	0.02	3.8	4.8	78	11.6	0.1	0.13	56	36.5	2.4	/	/	19.0	0.1	/	/	20.0
Sc	mg/kg	0.1	2.1	2.3	93	6.4	38.5	39.7	97	6.0	4.1	/	/	2.9	2.0	/	/	5.4
Se	mg/kg	0.1	5.2	5.23	99	4.3	0.6	0.5	123	20.3	0.3	/	/	21.1	0.3	/	/	30.2
Sn	mg/kg	0.1	6.7	6.7	100	4.1	1.9	1.8	106	4.4	1.1	/	/	0.0	0.5	/	/	8.2
Sr	mg/kg	0.5	66.6	67.7	98	6.2	15.8	15	105	5.6	17.8	/	/	1.6	12.0	/	/	3.4
Th	mg/kg	0.1	6.3	6.89	91	10.7	6.8	7	97	10.8	6.0	/	/	0.6	2.8	/	/	3.9
Ti	%	0	0.1	0.113	94	3.9	0.1	0.128	97	6.3	0.0	/	/	14.9	0.1	/	/	1.5
Tl	mg/kg	0.02	5.3	5.4	97	4.9	0.1	0.07	108	23.3	0.3	/	/	2.4	0.1	/	/	4.4
U	mg/kg	0.1	2.6	2.8	93	12.9	1.1	1.2	94	11.3	2.6	/	/	1.8	0.6	/	/	0.0
V	mg/kg	2	39.8	41.1	97	4.9	200.6	215	93	2.8	25.8	/	/	1.5	22.8	/	/	1.9
Y	mg/kg	0.01	5.6	6.1	91	7.9	8.1	7.84	104	6.2	6.9	/	/	0.7	6.5	/	/	1.4
**Zn*	mg/kg	0.1	314.3	312	101	3.8	60.3	60	101	5.3	585.0	579	101	1.4	40.1	/	/	4.2
Zr	mg/kg	0.1	1.7	2.1	80	10.5	20.7	21.6	96	7.3	4.1	/	/	20.9	2.9	/	/	6.5

LDL = lower detection limit, ME = median, RV = referenced value, RE = Analytical recovery, RSD = relative standard deviation,

*after Bavec et al. (2015)

graphically (WEI & SIMKO, 2016). It was qualitatively assumed that correlations at statistically high significance ($p < 0.001$) reveal a strong association between elements. Correlation network model (EPSKAMP, 2014) was produced to visualize correlation patterns between elements in topsoil. With the use of Surfer 13 software, the universal kriging with linear variogram interpolation method (DAVIS, 1986) was applied for the construction of surface grid models showing the spatial distribution of elements in topsoil. For a graphical display of spatial distribution the maps with percentile distribution, where different colours represent different concentration arrangements, were produced with the use of QGIS 2.18.7 software. The seven classes of following percentile values were applied: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100. The rest of the maps in this study were produced with the use of QGIS 2.18.7 software.

Results and discussion

Descriptive statistics of analysed elements (n = 43) in the Idrija top- and subsoil are given in Table 3 together with limit/ warning/ critical soil levels from current Slovenian legislation (OFFICIAL GAZETTE RS, 1996), indicative/ intervention levels for severe contamination from the International guidelines (SOIL REMEDIATION CIRCULAR, 2013) and correlation coefficients of elements between top- and subsoil. The statistical distribution of elements in top- and subsoil is presented with boxplots (Fig. 4, 5, 6, 7 and 8) together with European grazing land soil medians (REIMANN et al., 2014; European medians in further text) and Maribor urban soil medians (GABERŠEK & GOSAR, 2017; Maribor medians in further text), which were also determined after aqua regia digestion.

Potentially harmful elements (PHE; Ag, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Ni, Sb, Se, Sn, Pb, Th, V and Zn)

First, attention is drawn to the 10 elements (As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb and Zn), which are recognized as the most hazardous for ecosystems and human health in the national legislative regulations (OFFICIAL GAZETTE RS, 1996). The comparison of the 10 elements to legislative levels was already established by BAVEC et al. (2015), where it was found that 82 out of the 90 investigated soil samples exceeded the value for Hg of 10 mg/kg (OFFICIAL GAZETTE RS, 1996), while other elements were below the national guidelines, with few exceptions; critical level for Cu (300 mg/kg) was exceeded in a single topsoil sample and critical level for As (55 mg/kg) in 2 topsoil and its subsoil pair samples. The 10 dangerous element median levels were also compared to median levels in soil of different urban areas around the world and the comparison showed only Hg is significantly enriched (several hundred or even thousand times) in Idrija top- and subsoil, while other elements were below, within or slightly above the reported metal concentrations in worldwide studies (BAVEC et al., 2015). High Hg values, that were already discussed by BAVEC et al. (2015), are in good agreement with other studies (GOSAR et al., 2006; TERŠIČ et al. 2011a, 2011b; BAVEC et al. 2016; BAPTISTA-SALAZAR et al., 2017), which showed mercury enrichment in Idrija soil due to the 500 years of mining and processing of mercury ore.

In addition to the above 10 elements, the international guidelines (SOIL REMEDIATION CIRCULAR, 2013) include intervention values for 2 elements, Ba and Sb, and indicative levels for severe contamination for six elements (Ag, Be, Se, Sn, Th,

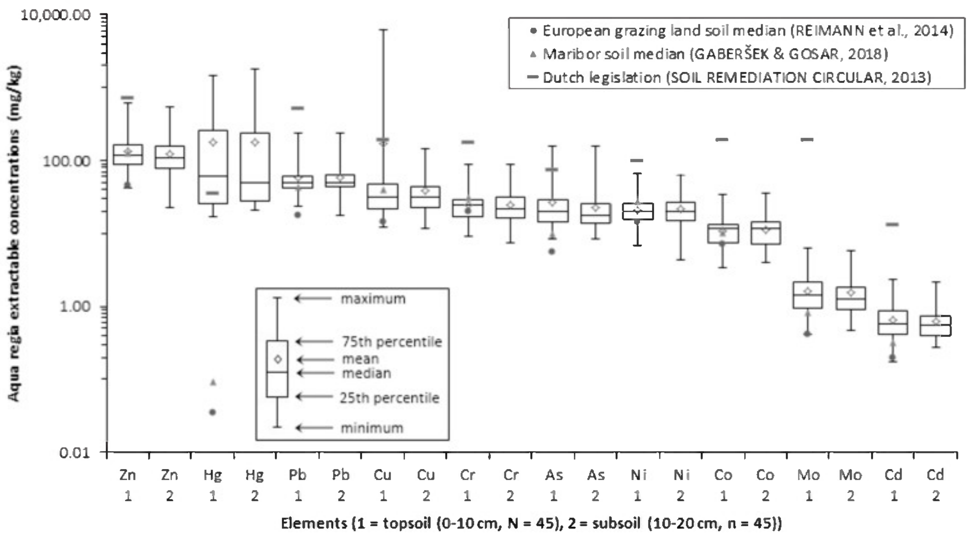

Fig. 4. Statistical distribution of PHE in Idrija topsoil and subsoil (the figure was modified after Bavec et al., 2015) together with European grazing land soil medians (REIMANN et al., 2014), Maribor urban soil medians (GABERŠEK & GOSAR, 2018) and Dutch legislation values (SOIL REMEDIATION CIRCULAR, 2013).

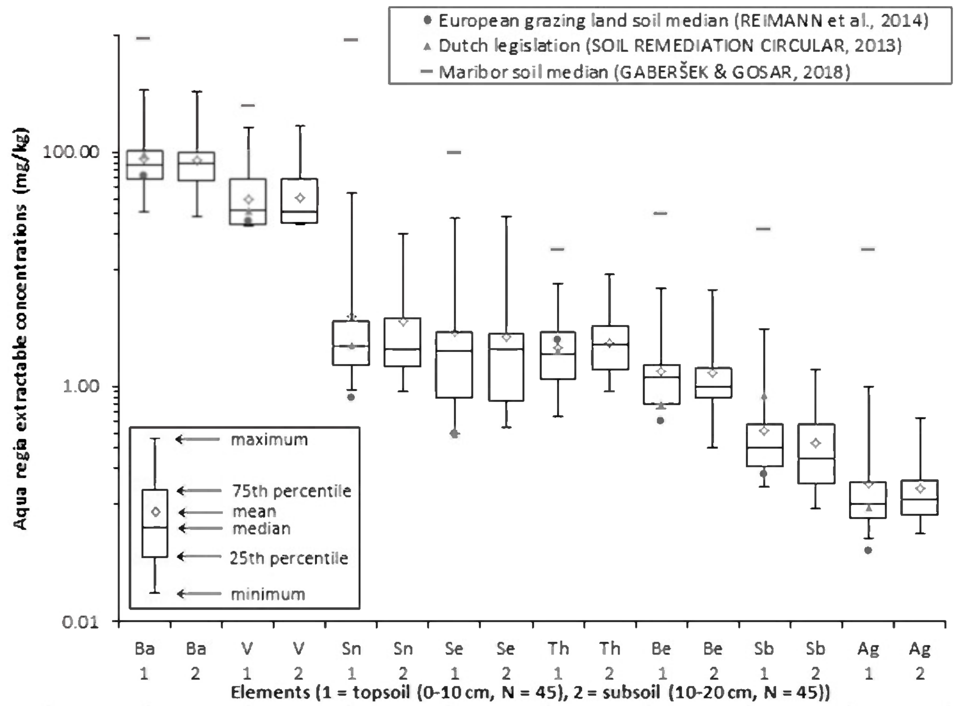

Fig. 5. Statistical distribution of PHE in Idrija topsoil and subsoil together with European grazing land soil medians (Reimann et al., 2014), Maribor urban soil medians (Gaberšek & Gosar, 2018) and Dutch legislation values (Soil Remediation Circular, 2013).

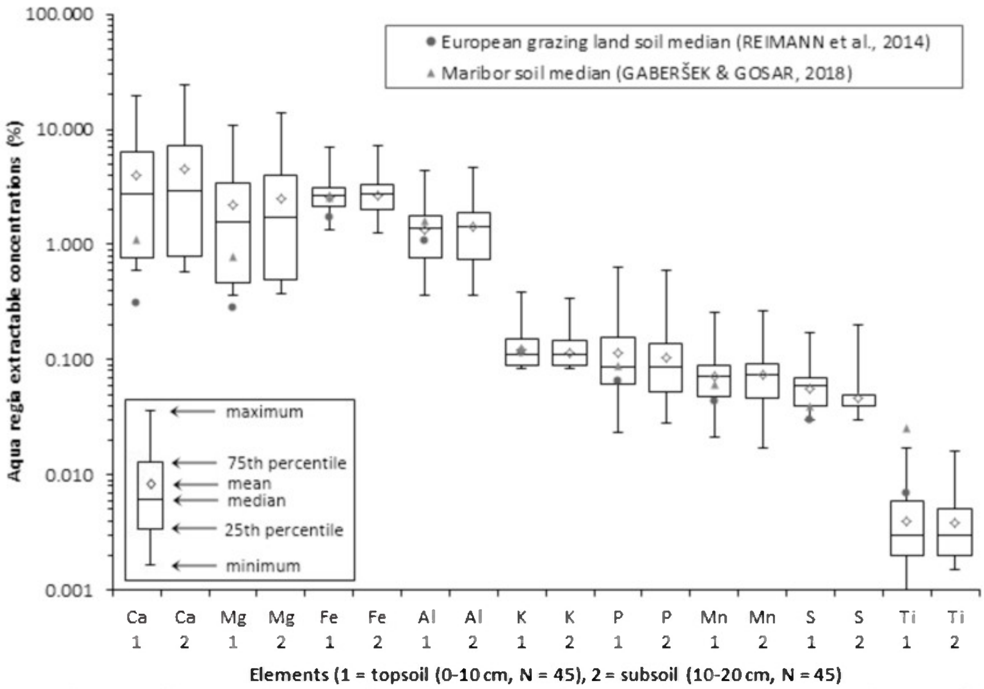

Fig. 6. Statistical distribution of major elements in Idrija topsoil and subsoil together with European grazing land soil medians (Reimann et al., 2014) and Maribor urban soil medians (Gaberšek & Gosar, 2018).

V). In Fig. 4 and 5 it is shown that PHE are not exceeded in Idrija soils with regard to the international guidelines, except Hg, as expected. It is also shown that top- and subsoil samples have similar statistical distribution of PHE, and that Idrija top- and subsoil medians are similar to Maribor soil medians and slightly higher than European soil medians, with exception of Hg and Se median. Mercury and Se median are much higher in comparison with both, Maribor and European median, especially Hg.

Major elements
(Al, Ca, Fe, K, Mg, Mn, P, S and Ti)

Top- and subsoil samples have similar statistical distribution of major elements (Fig. 6). Calcium and Mg median levels in Idrija soil are slightly higher than in Maribor and European soil. Iron, Al, K, P, Mn and S median levels are similar to European and Maribor medians, while median level of Ti is lower.

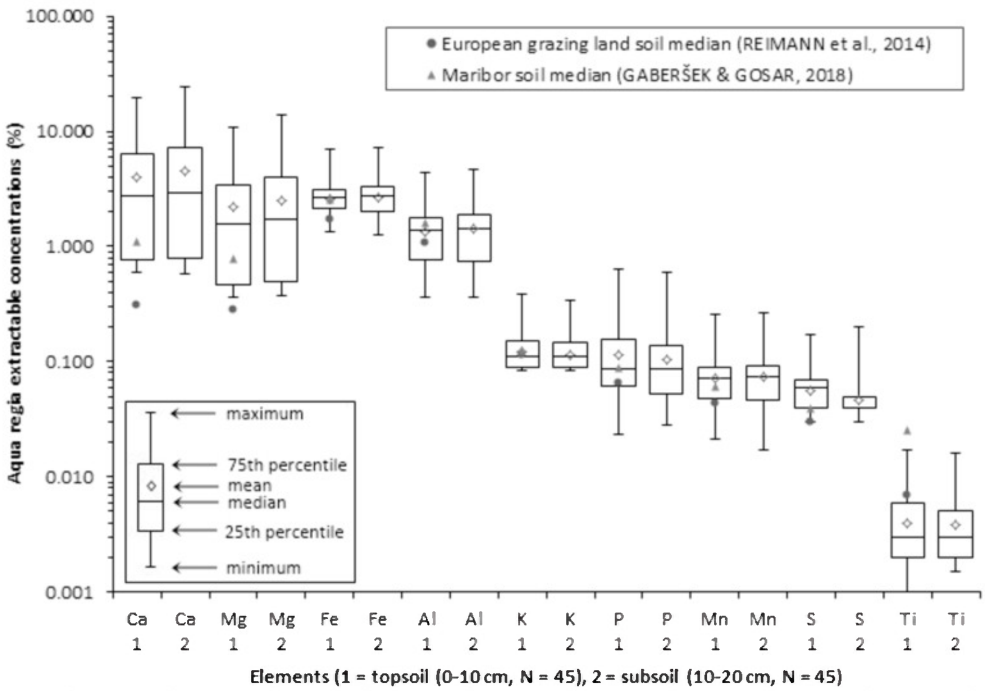

Fig. 7. Statistical distribution of REE in Idrija topsoil and subsoil together with European grazing land soil medians (Reimann et al., 2014) and Maribor urban soil medians (Gaberšek & Gosar, 2018).

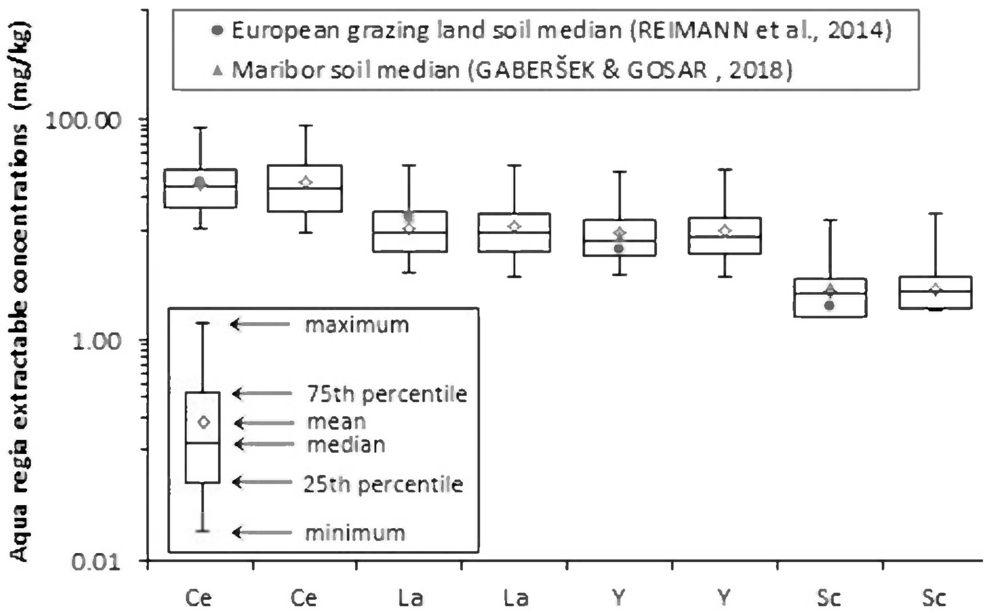

Fig. 8. Statistical distribution of other elements in Idrija topsoil and subsoil together with European grazing land soil medians (Reimann et al., 2014) and Maribor urban soil medians (Gaberšek & Gosar, 2018).

Rare earth elements (REE; Ce, La, Y and Sc) and other elements (Sr, Rb, Li, Ga, Zr, U, Cs, Nb, Bi, Tl, Hf and In)

Top- and subsoil samples have similar statistical distribution of REE (Fig. 7) and other elements (Fig. 8). Median levels of REE and other elements are similar to European and Maribor medians, with exception of Hf and In. Hafnium median in Idrija soil is lower in comparison with European and Maribor soil. Indium median in Idrija soil is higher in comparison with European soil.

Correlations and spatial distribution

Spearman rank correlation test for 10 PHE between top- and subsoil was already performed by Bavec et al. (2015) who found out strong positive correlation of element concentrations between topsoil and subsoil. The rest of the elements presented in this study (Table 3) also show strong positive correlation between topsoil and subsoil, except Be. It was shown that element distribution in topsoil and subsoil is not statistically different.

Table 3. Mean, median, minimum and maximum levels of 43 elements in Idrijan top- (0-10 cm) and subsoil (10-20 cm) (all levels are in mg/kg, except where otherwise stated); Slovenian and Dutch legislation data (in mg/kg); correlation coefficients (r_s) of elements between top- and subsoil.

Element	mean	median	min	max	mean	median	min	max	r_s	Slovenian legislation[1]	Dutch legislation[2]
Depth (cm)	0-10	0-10	0-10	0-10	10-20	10-20	10-20	10-20			
Ag	0.147	0.1	0.026	0.832	0.137	0.109	0.026	0.389	0.81	-	15**
Al (%)	1.3	1.4	0.4	2.7	1.4	1.4	0.4	2.8	0.96	-	-
As[3]	26.3	20.3	6.3	128.9	22.7	18.0	5.1	131.2	0.783	20/30/55	76*
Ba	86.6	77.0	27.7	241.0	84.9	80.5	29.7	230.3	0.93	-	920***
Be	1.3	1.2	0.1	5.3	1.3	1.0	0.5	5.3	0.37	-	30**
Bi	0.4	0.4	0.1	1.2	0.4	0.4	0.1	0.8	0.89	-	-
Ca (%)	4.0	2.7	0.2	13.5	4.6	3.0	0.2	17.3	0.98	-	-
Cd[3]	0.8	0.7	0.3	1.6	0.6	0.6	0.1	1.4	0.833	1.02.2012	13*
Ce	25.8	25.1	5.3	50.6	26.9	24.1	5.2	51.8	0.97	-	-
Co[3]	11.0	11.7	4.2	20.5	11.4	11.8	3.1	21.2	0.923	20/50/240	190*
Cr[3]	24.5	24.5	8.0	598.0	24.8	22.2	9.1	55.9	0.933	100/150/380	180/78*
Cs	0.7	0.6	0.1	2.1	0.9	0.7	0.2	2.2	0.97	-	-
Cu[3]	170.6	31.6	10.0	6067.8	38.0	31.1	10.7	98.1	0.863	60/100/300	190*
Fe (%)	2.6	2.7	0.8	3.8	2.7	2.7	0.7	4.0	0.92	-	-
Ga	3.8	3.9	1.3	7.2	3.8	4.0	1.1	7.4	0.96	-	-
Hf	0.08	0.07	0.01	0.22	0.08	0.08	0.01	0.20	0.53		
Hg[3]	1768.0	608	8.5	1210	178.8	50	6.9	1550.0	0.973	0.8/2/10	36/4*
In	0.06	0.04	0.01	0.40	0.05	0.04	0.01	0.21	0.53		
K (%)	0.12	0.11	0.01	0.23	0.11	0.11	0.01	0.20	0.88	-	-
La	10.4	9.3	2.4	24.0	10.6	9.5	2.7	23.9	0.96	-	-
Li	13.4	11.0	3.2	29.6	14.3	12.1	4.3	35.0	0.93	-	-
Mg (%)	2.2	1.6	0.1	7.4	2.5	1.7	0.1	9.9	0.98	-	-
Mn	722.8	725.0	264.0	1687.0	735.9	747.0	297.0	1715.0	0.95	-	-
Mo[3]	1.7	1.5	0.6	4.2	1.6	1.3	0.4	4.1	0.913	10/40/200	190*
Nb	0.5	0.5	0.0	1.5	0.5	0.4	0.1	1.3	0.92	-	-
Ni[3]	21.0	19.7	8.7	40.2	21.6	20.3	10.3	37.6	0.93	50/70/210	100*
P (%)	0.1	0.1	0.0	0.5	0.1	0.1	0.0	0.5	0.94	-	-
Pb[3]	59.5	49.5	19.2	174.5	59.1	50.1	25.5	170.4	0.923	85/100/530	530*
Rb	13.1	12.4	4.4	30.0	13.6	13.4	3.9	29.0	0.98	-	-
S (%)	0.06	0.06	0.01	0.10	0.05	0.05	0.01	0.15	0.67	-	-
Sb	0.42	0.30	0.07	2.66	0.33	0.24	0.06	0.93	0.89	-	22*
Sc	2.7	2.6	0.1	8.6	2.9	2.7	0.1	10.2	0.91	-	-
Se	2.9	2.0	0.4	24.7	2.7	2.1	0.3	25.2	0.76	-	100**
Sn	3.9	2.2	0.6	40.7	3.6	2.1	0.6	16.4	0.93	-	900**
Sr	29.0	25.9	5.2	71.7	32.5	29.3	4.8	98.4	0.97	-	-
Th	2.1	1.9	0.6	4.7	2.3	2.3	0.5	5.8	0.97	-	15**
Ti (%)	0.004	0.003	0.001	0.011	0.004	0.003	0.001	0.011	0.9	-	-
Tl	0.32	0.30	0.09	0.63	0.33	0.33	0.08	0.63	0.87	-	-
U	1.6	1.5	0.6	3.3	1.6	1.6	0.7	3.6	0.94	-	-
V	40.0	31.5	1.0	103.0	40.5	31.0	1.0	111.0	0.93	-	250**
Y	9.4	7.9	2.0	20.8	9.7	8.5	2.4	23.1	0.96	-	-
Zn[3]	133.4	119.6	45.7	464.3	123.9	109.3	54.7	391.1	0.943	200/300/720	720*
Zr	1.7	1.8	0.1	4.7	1.9	1.8	0.1	5.1	0.91	-	-

min = minimum; max = maximum, r_s = Spearman correlation coefficients of elements between top- and subsoil; [1]Official Gazette RS, 1996 (limit/warning/critical values), [2]Soil Remediation Circular, 2013 (*intervention value, **indicative level for severe contamination, *** intervention value for Ba has been temporarily repealed, that is former value), [3]Bavec et al. 2015 (aqua regia, n=45); r_s = correlation coefficient

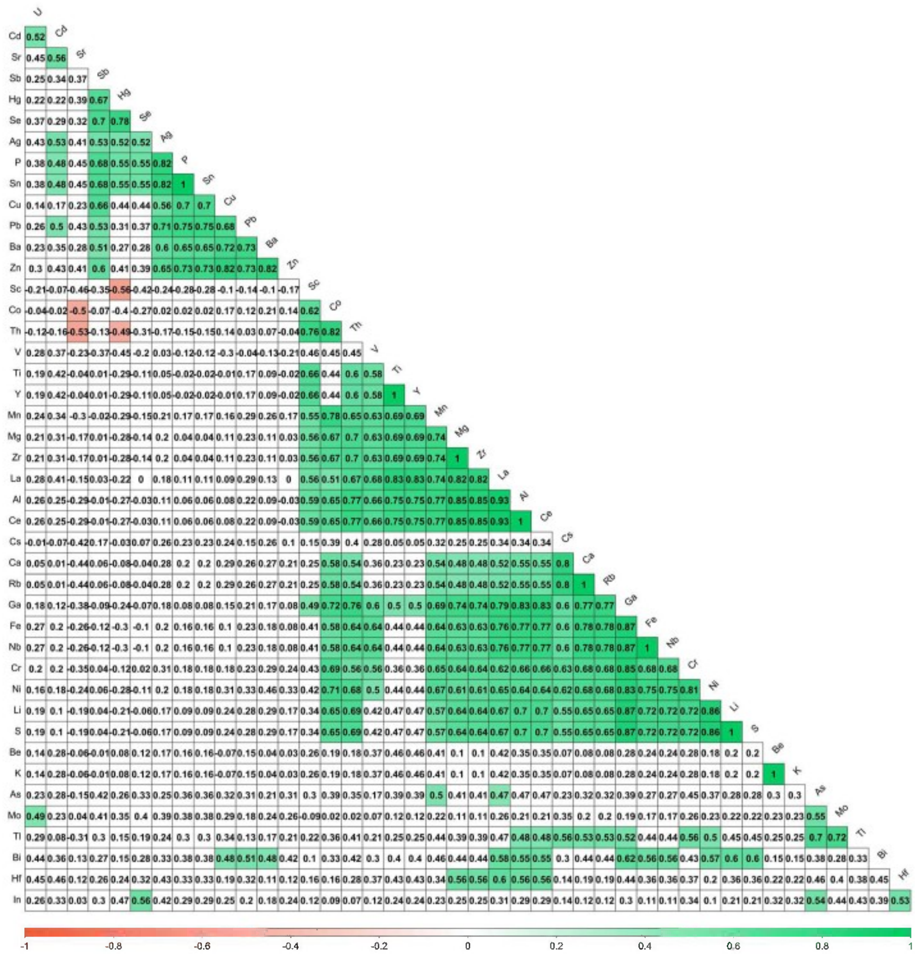

Fig. 9. Correlogram with correlation patterns between elements in topsoil; statisticaly significant positive (green) and negative (red) correlations at $p < 0.001$.

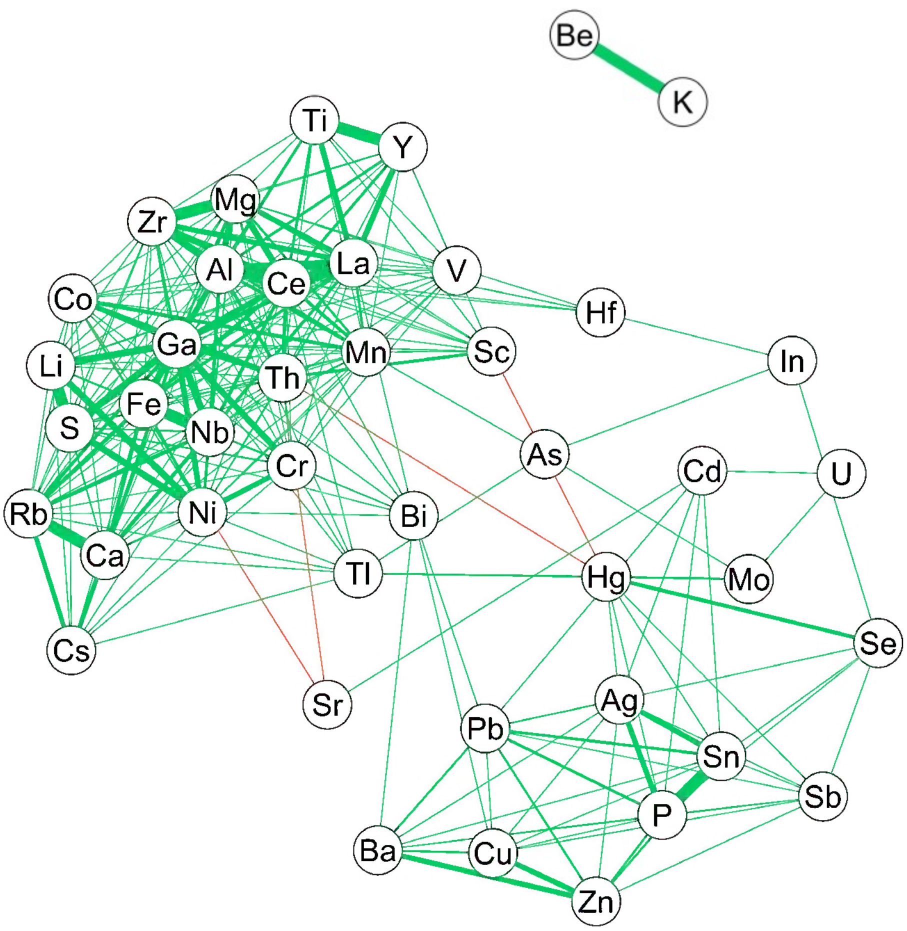

Fig. 10. Correlation network model between elements in topsoil; strong positive (green) and negative (red) coefficients ($p < 0.001$) are presented with proportional nodes.

Hierarchically ordered Spearman rank correlation coefficients between elements in topsoil (Fig. 9) and their network model (Fig. 10) indicated the following associations of elements, with regard to their significant positive correlations. A so called rural association of elements consisting of Al, Bi, Ca, Ce, Co, Cr, Cs, Fe, Ga, Hf, La, Li, Mg, Mn, Nb, Ni, Rb, S, Sc, Th, Ti, Tl, V, Y and Zr and rural-urban association of elements consisting of Ag, Ba, Cd, Cu, Hg, P, Pb, Se, Sb, Sn and Zn. In addition to rural and rural-urban associations, strong association was observed between Be-K. The associations of elements As, In, Mo, Sr and U are very limited compared to the above mentioned elements and these elements present an indirect links between rural and urban associations of elements. The association of elements with regard to their significant negative correlations (Co-Sr-Th and Sc-Hg-Th) (Fig. 9 and 10), are very limited as well.

The rural association of elements is closely related to their spatial distribution of higher concentrations. The higher concentrations of all the elements from the rural association, except Ca and Mg, are mostly found in the N, NE, NW, S and SW rural surroundings (see spatial distribution model of Mn as representative in Fig. 11), where limestone and dolomite bedrock predominate (Fig. 2). Therefore it is assumed that these elements reflect natural geological background levels that have been released during weathering processes of bedrock. Ca and Mg show very similar distribution (see spatial distribution model of Ca as representative in Fig. 11) and their higher concentrations occur, where dolomite bedrock (Fig. 2) prevails; that is in the central (urban) part of the studied area and in the SE surroundings (Fig. 2). However, higher concentrations of Ca and Mg could also originate from the material, which is underlying investigated soils in the urban area. During sampling it was observed that at urban green spaces, soil contained anthropogenic particles, such as plastic and brick particles, which indicated that the soil underlying material is embankment material. In the latter, Ca is found in residues of mortar, cement, gypsum and other components of building material. In addition, higher values can be due to the erosion of buildings and roads within the urban area.

With regard to the rural-urban association of elements, higher concentrations (see spatial distribution models of Cu, Pb and Zn as representative distributions in Fig. 11) were found in (1) N and SW rural surroundings, where limestone and dolomite bedrock prevail, (2) in the urban area at SW part, where ore containing clastic bedrock prevail and (3) along the Idrijca river, where fluvial sediments deluvium (Fig. 2) mixed with ore residue dumps (Čar, 1998) prevail. Drovenik et al. (1980) reported that Berce (1958) analysed 4 samples of mercury ore and 2 samples of cinnabar and determined Cu in all samples. Later analyses (Drovenik et al., 1980) also showed that Cu was detected in all samples in addition to Pb in 4 cinnabar samples and Zn in 2 samples (Table 4). Two samples of steel ore from Skonca beds contained organic substances and were especially enriched with Pb (Sample 6 and 7 in Table 4). Zn was especially high in metacinnabar sample (sample 10 in Table 4), which was explained as understandable, because Hg is often replaced by Zn in metacinnabar (Drovenik et al., 1980). The authors also em-

Table 4. Geochemical contents of elements (in mg/kg; - means undeterminable and blank not measured) in mercury ore from Idrija by Drovenik et al. (1980)

	5	6	7	8	9	10
Ag	-	4	-	/	/	/
Cu	1	200	16	100	11	5
Ga	-	13	10	3	-	-
Ge		3	10	7	-	-
Mn	5	5				
Ni	2.5	2.5				
Pb	32	1000	150	5	-	30
Tl		10	-	-	-	-
Zn	-	200	-	-	-	>1000
5 = Idrija (Grafenauer, 1969), 6-8 = Idrija, steel ore from Skonca beds, 7 = Idrija, steel ore from Upper Permian dolomite, 9 = Idrija, Cinnabar crystals from dolomite sheet, 10 = Idrija, metacinnabar aggregate from a fracture in Upper Sythian dolomite)						

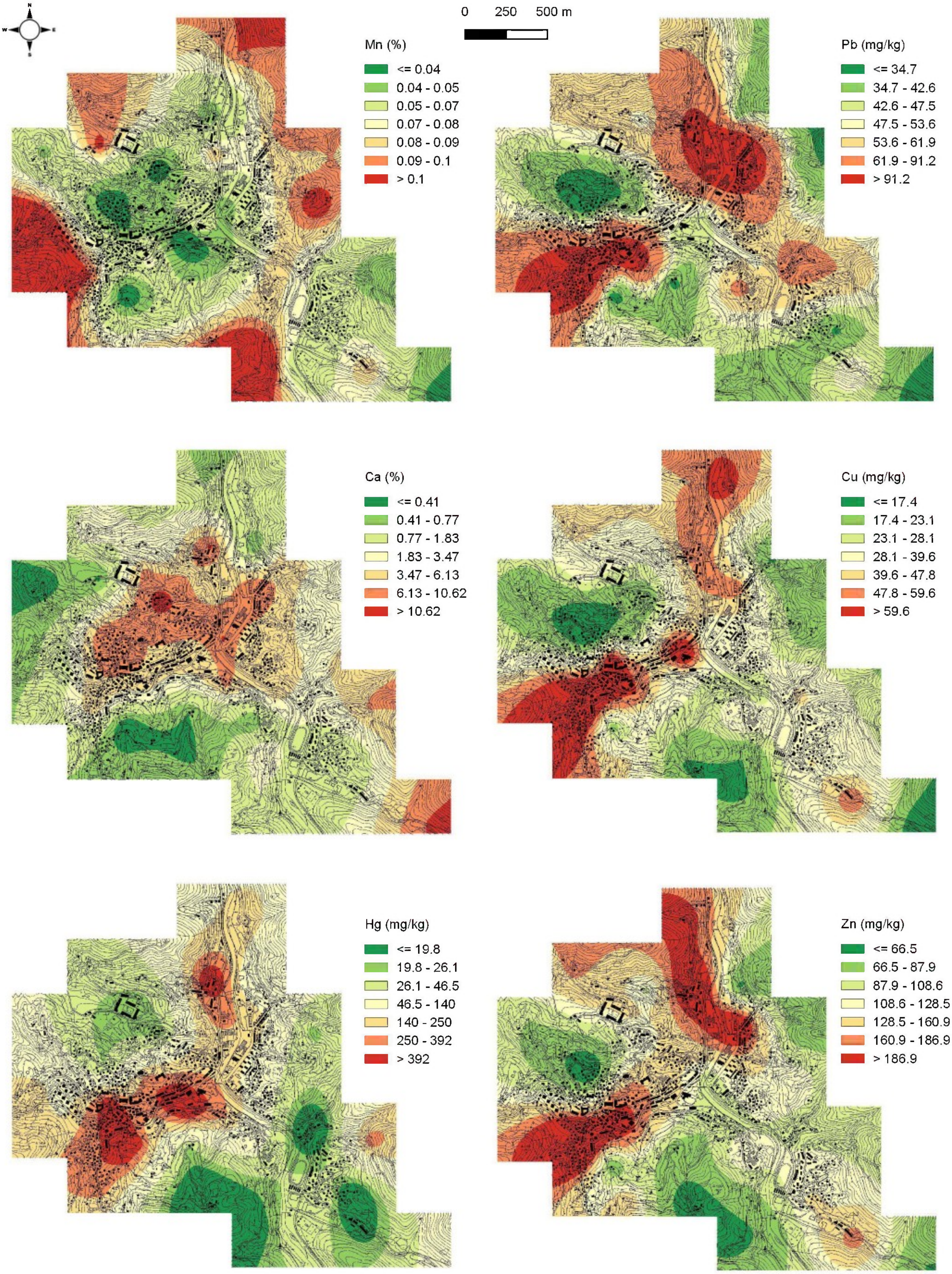

Fig. 11. Models of spatial distribution of selected elements in topsoil.

phasized that As and Sn were below the limit of detection in analysed samples. It is assumed that elements from rural-urban association reflect natural geological background levels, but are to a certain extent influenced by anthropogenic activities, such as traffic, industry (Kolektor's manufacturing process wastes are plastic and non-ferrous metals, primarily Cu), households, but also past mining activities; especially deposits of mercury ore residues along the Nikova and Idrijca river. If we compare Hg distribution with Cu, Pb and Zn (Fig. 11), it is shown that higher concentrations occur in general from the SW along the Nikova River, toward the N along the Idrijca River after the confluence with Nikova. Spatial distribution of high Hg concentrations (Fig. 11) was already discussed by Bavec et al (2015). They found out that high Hg concentrations occur in the urban area and form a certain pattern of contamination in the SW-NE direction. The authors showed that contamination was only to a small extent a consequence of natural origin; in the SW part of the area, where soils overlie rocks containing mercury ore. However the contamination is predominantly of anthropogenic origin, such as ore residue dumps, roasting sites and related emissions and ventilation shafts that are/ were situated in the urban area.

Conclusion

The Idrija town urban area along the Nikova and Idrijca River, where anthropogenic influence is high, quickly passes into steep, sparsely populated rural surroundings with individual houses and farms, where anthropogenic is influence low. In this study geochemical baseline data set of 43 elements in soil of Idrija town was established to enable monitoring of future changes in the soil chemical composition. The results of soil levels of 43 elements, their hierarchically ordered Spearman rank correlation coefficients and their spatial distribution of highest levels are presented. The determined Idrija soil element medians were also compared to European grazing land and Maribor urban soil element medians. The results indicated that elements Al, Bi, Ca, Ce, Co, Cr, Cs, Fe, Ga, Hf, La, Li, Mg, Mn, Nb, Ni, Rb, S, Sc, Th, Ti, Tl, V, Y and Zr are enriched in the rural surroundings, while elements Ag, Ba, Cd, Cu, Hg, P, Pb, Se, Sb, Sn and Zn are enriched partly in the rural surroundings, but mostly in the urban area. It is assumed that elements, which are enriched in the rural surroundings, are of natural origin, while elements, which are enriched also in the urban area, are to a certain extent influenced by anthropogenic sources (ore residue dumps, households, traffic and industry). The statistical distribution of elements in top- and subsoil and strong positive correlation of elements between top- and subsoil showed that soil element distribution in the two investigated layers is not statistically different. In general, the median levels of elements in Idrija soil are mostly similar or slightly higher than in European grazing land soil and Maribor urban soil, with exception of Hg.

Acknowledgement

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