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Distribution pattern of mercury in the Slovenian soil: Geochemical mapping based on multiple geochemical datasets

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ABSTRACT

A regional geochemical survey was conducted, covering the entire territory of Slovenia. Medium-density soil sampling was performed in a 5 × 5 km grid, mercury concentrations were analysed and a map of mercury spatial distribution was constructed. The determined mercury concentrations revealed an important difference between the western and the eastern parts of the country. A huge anomaly in the western part is the consequence of environmental contamination due to the 500-year history of mining and ore processing in the Idrija mercury mine and partly due to Hg containing rocks on outcrops. Slightly elevated Hg concentrations revealed in the Ljubljana-Kranj and Celje basins indicate urban pollution due to industry, traffic and the use of mercury-containing products. It was established that, besides anthropogenic impacts, lithological and climatic characteristics that determine the type of soil also influence the distribution of mercury in soils. The data were compared to a previously conducted low-density geochemical survey (sampling grid 25 × 25 km, $n = 54$) and to the regional geochemical data set supplemented by local high-density sampling data (irregular grid, $n = 2835$). Comparing high-, medium- and low-sample density surveys, it was shown that higher sampling density allows the identification and characterization of anthropogenic influences on a local scale, while medium- and low-density sampling reveal general trends in the mercury spatial distribution, but are not appropriate for identifying local contamination in industrial regions and urban areas.

1. Introduction

Mercury is a trace element naturally present in the environment, from both natural and anthropogenic sources, and is highly toxic (Clarkson and Magos, 2006; Harada, 1995; Nance et al., 2012). In Europe, a EU mercury strategy was launched in 2005 (ec.europa.eu/environment/chemicals/mercury) and it includes 20 measures to reduce mercury emissions, cut supply and demand, and protect against exposure, especially to the methylmercury found in fish. In October 2013, the Minamata Convention on Mercury was signed, with the main goal to reduce human exposure to mercury (UNEP, 2013).

1.1. Hg sources

Natural sources of mercury include the weathering of mercury-containing rocks, volcanic eruptions and geothermal activity. Anthropogenic emissions include mercury that is released from fuels, raw materials or uses in products or industrial processes. Globally, small-scale gold mining is the largest source of anthropogenic mercury emissions, followed closely by coal combustion. Other large sources of emissions are the production of non-ferrous metals and cement (UNEP, 2013). Currently, about 30% of annual emissions of mercury to air come from anthropogenic sources and 10% from natural geological sources. The rest (60%) is from reemissions of previously released mercury that has built up over decades and centuries in surface soils and oceans. Current mercury emissions from anthropogenic sources are estimated to be 1960 tonnes annually, while annual re-emissions of mercury are 4000–6300 tonnes (Mason et al., 2012; UNEP, 2013).

In Europe, coal-fired power plants (CFPP) are the largest stationary anthropogenic source of mercury emissions (Weem, 2011). Mercury is volatilized during combustion and released in its elemental form Hg(0). Subsequent cooling of the flue gas and interaction of Hg(0) with other flue-gas constituents, such as chlorine and unburned carbon, will result in the partial transformation of Hg(0) to oxidized forms of mercury Hg(2+), and a proportion of the mercury will be adsorbed onto fly ash particles Hg(P). As a result, coal-combustion flue gas contains varying percentages of Hg(P), Hg(2+), and Hg(0) (Gharebaghi et al., 2011; Weem, 2011).

Another important source of Hg pollution is the use of mercury in agriculture. Although the use of mercury as seed dressing (antimicrobial and fungicidal chemicals applied prior to planting) was prohibited many years ago, pesticides, fertilizers, sewage sludge and irrigation water remain a source of mercury pollution (Hseu et al., 2010). Sources

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of mercury also include industrial processes and consumer products. Due to its special properties, including high density and a high rate of thermal expansion, mercury is often used in barometers and thermometers. It can also be combined with other metals to create special alloys called amalgams. Gold and silver amalgams have been used in dentistry for fillings, and tin amalgams are commonly used in production of mirrors. Mercury can be found in many different lamps, including 'black lights,' and is used in the industrial production of chlorine and sodium hydroxide (Environment Canada, http://www.ec.gc.ca/mercure-mercury/).

1.2. Main Hg sources in Slovenia

Low density soil and sediment geochemical survey in Slovenia was presented by Pirc et al. (1994). Geochemical maps show in both media an extended anthropogenic halo around Idrija mercury mine and indications of a differing Hg backgrounds between the western and the eastern part of the country, and indications of man-made anomalies were also observed through the country (Pirc et al., 1994). The Idrija area is strongly enriched with mercury due to mineralized rocks and mining and ore processing, and was the focus of many detailed investigations over the last decades (Bavec, 2015; Bavec and Gosar, 2016; Bavec et al., 2014, 2015, 2016; Biester et al., 1999, 2000; Covelli et al., 1999, 2001; Gosar, 2004; Gosar and Šajn, 2001, 2003; Gosar et al., 1997, 2002, 2006; Grönlund et al., 2005; Hess, 1993; Hines et al., 2006; Horvat et al., 1999, 2003; Kocman and Horvat, 2011; Kocman et al., 2004, 2011; Teršič, 2010, 2011; Teršič and Gosar, 2013; Teršič et al., 2011a, 2011b, 2014; Žibret and Gosar, 2005). During 500 years of mercury production in Idrija, approximately 40,000 tonnes of Hg were released into the environment (Cigale, 2006; Miklavčič, 1999; Mlakar, 1974). Non-point source mercury emissions occurring over one year from the Idrijca River catchment were estimated by Kocman and Horvat (2011). The results of modelling revealed that, annually, approximately 51 kg of mercury are emitted from contaminated surfaces into the Idrijca river catchment (640 km^2). In addition, it was estimated that at least additional 17–34 kg of mercury are emitted annually from the most important point source of mercury (the ancient roasting complex) into the atmosphere (Kocman and Horvat, 2011). Other sources of mercury for 2001 were identified by Svetina et al. (2002) and included: coal-fired power plants, dental amalgams, products of the electric industry (batteries, lamps, measuring devices as thermometers, manometers, barometers), chemicals, the cement industry, incineration and waste treatment. The main sources of mercury were divided into the following categories: the use of mercury in industrial processes (the chemical industry, the electrical industry, cement production), consumer products containing mercury, waste incineration, cremation and hazardous waste disposal. Annual emission of Hg in Slovenia into the environment from these sources was estimated to be 1620 kg in 2001; 900 kg was deposited as waste, 630 kg escaped into the air and 90 kg into the water (Svetina et al., 2002). Pirc and Budkovič (1996) also recognized the use of explosives containing Hg fulminate during the First World War as a Hg source in the area of Soča (Isonzo) front (west Slovenia).

In the present study mercury concentrations and regional distribution of mercury in the topsoil across the whole territory of Slovenia were estimated and a geochemical map of mercury distribution was elaborated. The data from Slovenia were compared to data from the whole of Europe. The main purpose of this study was to define a geochemical baseline for mercury in Slovenia, so that it will serve as a timeline for monitoring future changes. In addition, the objectives of the study were to identify the regional differences caused by and the environmental implications of anthropogenic activities, to establish whether the mercury geochemical anomaly caused by the Idrija mine is also reflected in the regional mercury distribution and to determine whether any geochemical anomalies exist at other known mercury sources.

To evaluate the differences in determined Hg geochemical anomalies between low- and medium-density sampling, the data for Hg concentrations in soils from this medium-density geochemical survey (sampling grid 5 × 5 km) were compared to a previously performed low-density geochemical survey (sampling grid 25 × 25 km, Šajn, 1999) and to the regional geochemical data set supplemented by local high-density sampling data (irregular grid, $n = 2835$). In addition, geochemical maps of non-transformed data were compared to the maps of data normalized by Box–Cox transformation (Box and Cox, 1964). Since many statistical techniques are sensitive to non-normally distributed data, the Box–Cox transformation was performed. The Box—Cox transformation improves this feature, especially for the skewness and level of normality of the data sets.

1.3. The study area

Slovenia is situated in Central Europe (Fig. 1) and covers an area of 20,273 km^2. In Slovenia, 4 geographical units meet: the Alps, the Pannonian Basin, the Dinarides and the Mediterranean; this fact is reflected in the great diversity of its geology, climate, relief, vegetation and pedological characteristics (Repe, 2004). The interaction of three major climate systems (Continental, Alpine and sub-Mediterranean) in the territory of Slovenia strongly influences the country's precipitation regime. The average density of the watercourses in Slovenia is 1.33 km per square km, among the highest density found in Europe. In Slovenia, the average annual precipitation is 1570 mm (Hrvatin, 2004). The spatial variability of the precipitation is high—the annual precipitation sum varies from 800 mm in the northeastern part of the country to >3500 mm in the northwest (www.arso.gov.si). Because of its diversity and distinct variation over short distances, bedrock is the most important pedogenetic factor in Slovenia (Repe, 2004). Divided by lithological type, 49.25% of Slovenian territory is composed of clastic rocks, 39.31% of carbonate rocks, and 4.27% of a mixture of the two. Metamorphic rocks comprise 3.9% of Slovenian territory, pyroclastic rocks 1.78% and the smallest area (1.49%) is occupied by igneous rocks (Komac, 2005). Slovenia is characterized by carbonate rock and the corresponding karst surfaces. In the highest parts of Slovenia (alpine and subalpine Slovenia) poorly developed regolith, shallow rendzina on carbonate rock or ranker on a silicate bedrock occur. Rendzinas, thin soils with A–C or A–R profiles, which form on limestone and dolomites, are the most widespread soil type, covering 24% of the territory. Older type soils with a developed cambic B-horizon; these are brown soils overlying hard carbonate rocks and terra rossa (both Chromic Cambisols according to FAO classification), which cover 14% of the Slovenian territory, eutric brown soils (Eutric Cambisols, 14%) and distric brown soils (Distric Cambisols, 16%). Eutric brown soils are developed in the valleys and basins of central Slovenia (Ljubljana basin, Celje basin) and compose the most fertile Slovenian agricultural land (Vrščaj et al., 2005). Various types of leptosols (lithic, umbric, rendzic), cambisols, luvisols, fluvisols, and histosols are found in alpine and subalpine Slovenia, according to the international FAO classification. In Sub-Mediterranean Slovenia mainly shallow rendzina, brown forest soil, and—in the Kras region as a special form—a distinctly red terra rossa soil type is developed (Vrščaj et al., 2005). Due to the abundance of surface waters and the relatively flat surface, the most gleyed and pseudogleyed soils in Slovenia are found in northeastern Slovenia. As a result of the flat surface, this is the most important agricultural area of Slovenia (Repe, 2004).

For the purpose of our study, Slovenia was divided into several natural units based on the units defined by Poljak (1987) by the geographical and geological characteristics of the Slovenian territory. The following 6 natural units were used in this study for the interpretation of statistical results and Hg distribution: Alps, Western Prealps, Eastern Prealps, Dinarides, Interior basins and Pannonian basin (Fig. 2). The description of natural units that follows is summarized after Poljak (1987). The **Alps** occupy the northern part of Slovenia and consist of several

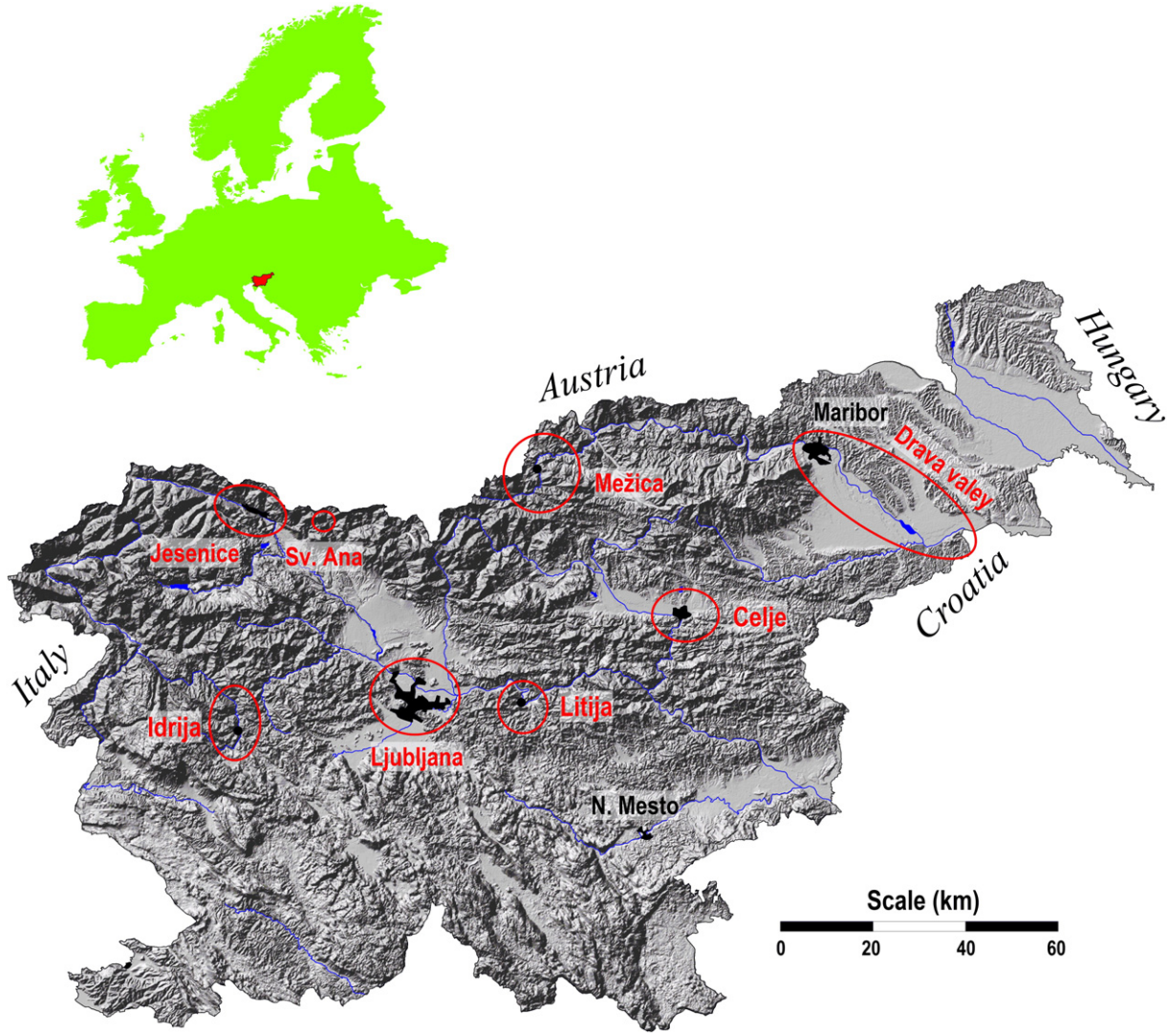

Fig. 1. Location of studied areas.

geographical and geological units (the Julian Alps, Karavanke, Kamnik Alps and Pohorje, which is part of the Central Alps). The Julian and Kamnik Alps are characterized by high plateaus with deep valleys and contain some of the highest peaks of Slovenia. The relief here is glacially determined and subject to recent karst type erosion. The highest parts are without vegetation; only in the lower parts are there some rare coniferous trees and meadows. Karavanke represent a long mountain ridge from the Italian and Austrian border across the whole northern part of Slovenia. Pohorje is a large massif in northeastern part of Slovenia, which is relatively sharply distinguished from other terrains. Because of the abundance of water, it is covered with lush vegetation. Geologically, the Julian and Kamnik Alps consist mostly of carbonate rocks, while Pohorje consist of igneous and metamorphic rocks, on which rich soils are formed. The **Prealps** are a unit that lies in the central part of Slovenia. The **Eastern Prealps** are the Posavje hills, which represent a string of ridges (up to 1000 m high) and valleys extending in east-west direction. The area is dominated by mixed forest and meadows with considerable cultivated areas. The **Western Prealps** consist of the Idrija-Žiri territory and the Polhov Gradec hills. The vegetation here is similar to that of the Eastern Prealps. Geologically, the Prealps consist mainly of sediments like claystones, marlstones and sandstones. This lithological composition significantly affects erosion, hydrogeological characteristics and vegetation cover. The **Dinarides**, which extend in southern Slovenia, consist of long mountain ridges and valleys oriented in a northwest-southeast direction. In the south there are also broader valleys (Vipava valley, Brkini) and a plateau (Kras). In the southwestern region, there is a strong Mediterranean influence. Geologically, the Dinarides consist of limestones and dolomites, while along the coast there are larger areas of flysch deposits. The relief is determined by the lithological composition and represents the so-called 'Dinaric karst'. The **Interior basins** lie within the described areas. The largest are the Ljubljana-Kranj basin and the Celje basin. Both represent flat lowlands, densely populated and cultivated. They consist of gravel, sand and clay of glacial, riverine-glacial and lake-glacial origin. The **Pannonian basin** consists of wide planes and lower mountain areas. The plains are wide river valleys, filled with alluvial deposits like gravel, sand and clay. Higher areas mainly consist of clastic sediments like sandstone and marl. Lithological characteristics, erosion type and climate determine the formation of deep fertile soils in Pannonian basin. The land here is intensively cultivated, especially the Mura valley and the Drava-Ptuj field (Poljak, 1987).

2. Materials and methods

2.1. Sampling and sample preparation

A regional radiometric and geochemical survey was performed at the Geological survey of Slovenia during the period 1990–1993,

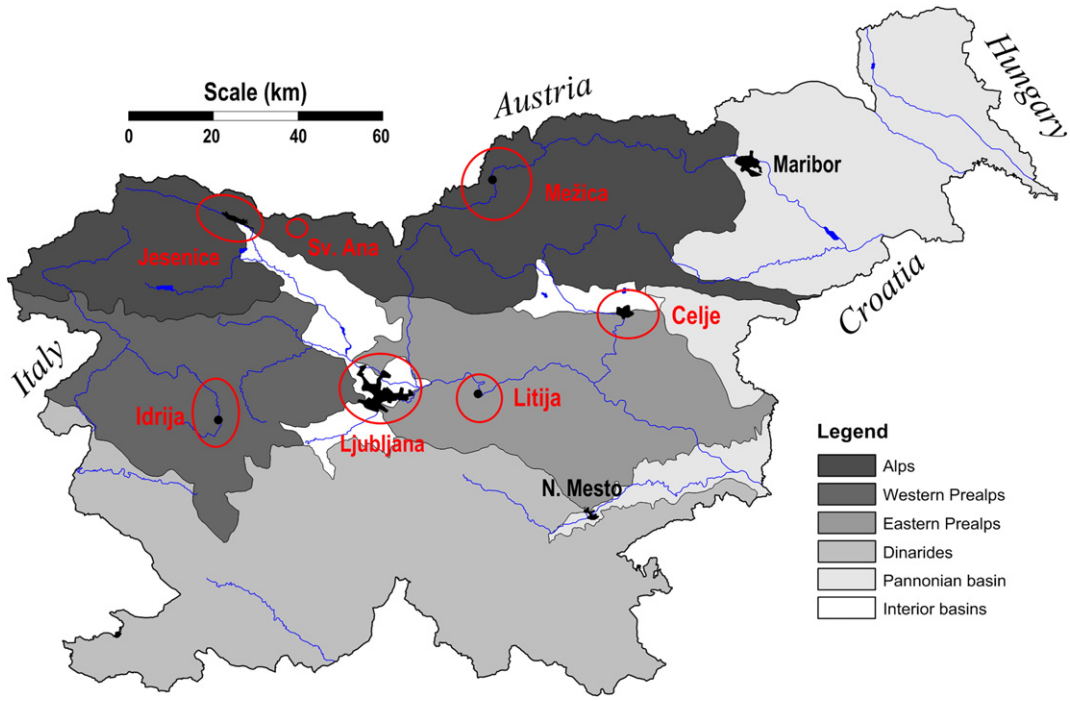

Fig. 2. The map of natural units in Slovenia (Poljak, 1987).

covering the entire territory of Slovenia. Soil sampling was performed in a 5 × 5 km grid with a randomly selected starting point to ensure systematic sampling (Andjelov, 1994). A total of 817 topsoil (0–10 cm) samples were collected and analysed for a wide array of elements but not Hg as reported Andjelov (1994). Besides air dried samples were gently disaggregated in a ceramic mortar, sieved through a 2 mm sieve and stored. The samples were deposited airtight in cool storeroom. According to studies in Idrija area mentioned in previous chapter cool storing of air dry samples did not considerably influence the total mercury concentrations. In 2012 the stored soil samples were taken out of the depot at the Geological Survey of Slovenia, pulverised in an agate mill to a fine-grain size (<0.075 mm) and submitted to chemical analysis.

2.2. Hg analysis

Mercury concentrations were analysed at AcmeLabs, Vancouver, Canada (accredited under ISO 9001:2008) with inductively coupled plasma (ICP) mass spectrometry (MS) after digestion of an aliquot of 15 g sample material with aqua regia (1:1:1 $HCl:HNO_3:H_2O$) for 3 h at 160 °C. The analytical set included routine soil samples, analytical soil replicates and the certified reference material (CRM) for quality control purposes. Objectivity was assured through the use of neutral laboratory numbers. The lower limit of determination for Hg was 0.01 mg/kg. Accuracy of the analytical method was estimated by calculation of the relative systematic error between the determined and recommended values of geological standard URGE_STD_N ($n = 4$, min = 40; max = 48; mean = 45.5, median referenced value is 0.51 mg/mg). The means of Hg in the analyses of standard generally differed 10.8% in range 3.9%–21.6% of the recommended values. Additionally accuracy was estimated by calculation of the relative systematic error between the determined and recommended values of geological standard DS-8 included by ACME ($n = 20$, referenced value 0.19 mg/mg (Acmelab, 2011; Bavec and Gosar, 2016)). The means of Hg in the standards generally differed 9.1% in range 0.1–18.8% of the recommended values. Precision was controlled by the relative differences between pairs of analytical determinations of the same sample ($n = 29$). Average precision 8.7% in range 5.2–13.0% was also considered sufficient. The reliability of the analytical procedures was considered adequate for using the determined elemental contents in further statistical analyses.

2.3. Map production and statistical methods

Statistical analyses were performed with Statistica software. The basic statistics calculated were the minimum, maximum, median and averages of natural, log-transformed and Box–Cox-transformed data. Normality was assessed on the basis of the results of normality tests (by skewness and kurtosis) and the visual inspection of the distribution histograms (Table 1).

Data analysis and map production were performed on a PC using the Statistica and Surfer softwares. The universal kriging with linear variogram interpolation method was applied to construct the maps of areal distribution of Hg in topsoil. The basic grid cell size for interpolation was 100 × 100 m. For class limits the percentile values of distribution of the interpolated values were chosen. Eight classes of the following percentile values were selected: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90, 90–99 and 99–100.

3. Results and discussion

3.1. Mercury concentrations and general distribution in Slovenian soils

In discussed medium scale geochemical survey ($n = 817$, 1 sampling site per 25 km^2) determined Hg concentrations ranged between 0.012 and 5.293 mg/kg with a median of 0.106 mg/kg. Data were divided into the western and the eastern parts of Slovenia and an important difference in basic statistics was realized. The Hg median for the western part was 0.151 mg/kg (0.016–5.293 mg/kg) and for the eastern part 0.083 mg/kg (0.012–3.936 mg/kg), which is only about half the value determined for the western part. The determined Hg medians for both parts were higher compared to the Hg medians for European soils (0.037 mg/kg; Salminen et al., 2005; 1 sample site per 5000 km^2), agricultural soils (0.03 mg/kg) and grazing land soils (0.035 mg/kg) (Table 3, Ottesen et al., 2013; 1 sample site per 2500 km^2).

The basic statistics regarding Hg concentrations and distribution maps in this study (designated as Level 2, $n = 817$, medium-density

Table 1
Basic statistics of Hg concentrations in mg/kg from different density geochemical surveys (n—number of samples, $\overline{x}$—mean, $\overline{x}g$—geometric mean, Md—median, Min—minimum, Max—maximum, P—percentile of the distribution, A—skewness, E—kurtosis, log—logarithmed data, bc—Box–Cox normalized data).

Level	n	$\overline{x}$	$\overline{x}g$	$\overline{x}$ (bc)	Md	Min	Max	P25	P75	A	E	A (log)	E (log)	A (bc)	E (bc)
1	54	8.435	0.098	0.077	0.075	0.010	448	0.050	0.133	7.348	53.999	3.727	20.028	−0.136	2.075
2	817	0.174	0.117	0.109	0.106	0.012	5.293	0.069	0.180	10.381	135.237	0.838	2.094	−0.042	0.741
3	2835	19.412	0.237	0.183	0.175	0.005	5944	0.100	0.385	16.842	293.535	2.526	10.764	−0.066	1.278

sampling, 1 sampling site per 25 km^2) were compared to statistics from a previously conducted low-density geochemical survey (1 sampling site per 625 km^2, Level 1, $n = 54$, Šajn, 1999) and to statistics from aforementioned geochemical data set (Level 2) supplemented by data sets of local study cases such as Ljubljana (Šajn et al., 2011a, 2011b), Celje (Šajn, 2005), Mežica (Šajn, 2006), Idrija (Gosar et al., 2006), Jesenice (Šajn et al., 1998b), Drava valley (Šajn et al., 2011a, 2011b), etc. The sampling grid in mentioned case studies is one sample per 1–4 km^2 (Level 3). This means that in total 2835 analyses of Hg were collected from the irregular sampling grid and used for the map construction. The sampling locations of different density surveys are shown in Fig. 3. In the low-density survey the determined median was lower (0.075 mg/kg) compared to that of the Level 2 survey, while for Level 3 the determined median was almost twice as high (0.175 mg/kg). The higher median value determined for Level 3 can be explained by the large number of samples taken in the area around the former Hg mining district in Idrija. These data, which mainly show elevated Hg concentrations, have undoubtedly influenced the overall median Hg concentration.

Different data transformations (log-normal and Box–Cox) were used to compare statistics and geochemical maps of transformed data to statistics and geochemical maps of untransformed data. It can be seen that the Box–Cox data transformation shows the lowest skewness and kurtosis and that the mean is very close to the median of the untransformed data (Table 1). This proves that the distribution of Box–Cox-transformed data is close to normal distribution.

Geochemical maps of Hg distribution of untransformed and Box–Cox-normalized data at 3 different sampling densities are presented in Figs. 4 and 5. In both Figures, map A is a low-sample density map (Level 1) and shows the overall Hg pattern on a national scale, while most of the local anomalies are not shown or provide inaccurate information. Figs. 4B and 5B are presenting map of medium-density geochemical survey (Level 2), while map C in both Figures represents regional geochemical data set supplemented by local high-density sampling data (Level 3). For all three densities the geochemical map of Box–Cox-normalized data shows more realistic conditions compared to the map of untransformed data because transformation optimally normalized very asymmetric Hg data. However, the revealed general pattern of Hg distribution in the soils of Slovenia is similar in all 3 density maps; all show higher Hg concentrations in the western part of Slovenia compared to the eastern part. A considerable Hg anomaly localized in the western region, where the world's second largest mercury mine deposit (Idrija) is situated, was revealed in the low as well as in medium-density mapping. Due to atmospheric emissions from the roasting plant, the influence of mining and ore processing in this area stretches considerably far. The obtained results prove the important, large-scale impacts of ore processing in the Idrija area.

Some other anthropogenic influences are observed in the Hg distribution map (Fig. 5B and C). As is typical for urban soils, Hg is enriched in the soils of the city of Ljubljana. The influence of a polymetallic mine in Litija is also clearly expressed, while some other anthropogenic sources like coal-fired power plants near Velenje and Trbovlje are disclosed only on the Level 3 map of Hg distribution (Figs. 4C and 5C).

The Hg medians for the Slovenian regional units presented in the previous chapter were calculated and are given in Table 2. The highest median in this study (Level 2; 0.270 mg/kg) was found in the Western Prealps, followed by the Interior basins (0.154 mg/kg), while the lowest Hg median was determined for the Pannonian basin (0.067 mg/kg). The same succession of median values was also calculated for Level 3, while for Level 1 (the low-density survey) the highest median was determined for the Interior basins, followed by the Western Prealps. The average Hg concentrations of log-normal and Box–Cox-transformed data

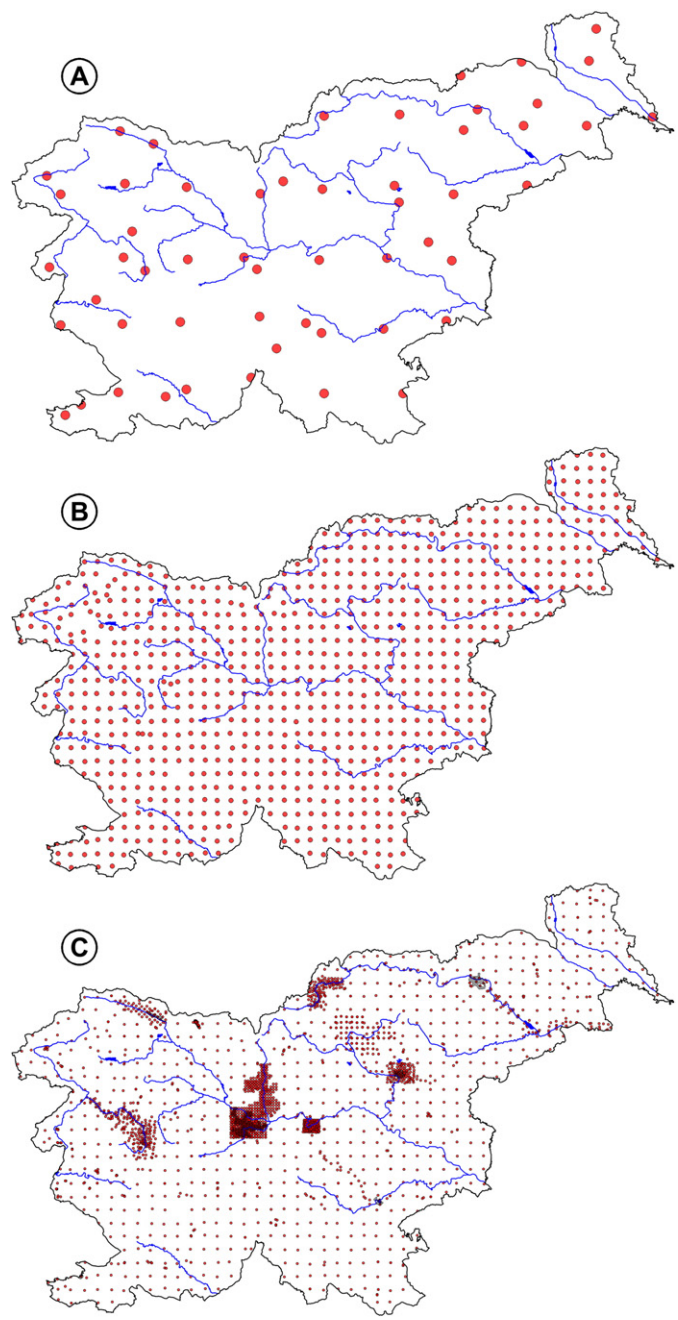

Fig. 3. Sampling locations of different density surveys; A is low sample density map (Level 1, $n = 54$), B is medium-density regional geochemical survey (Level 2, $n = 817$) and C is regional geochemical data set supplemented by local high-density sampling data (Level 3, $n = 2835$).

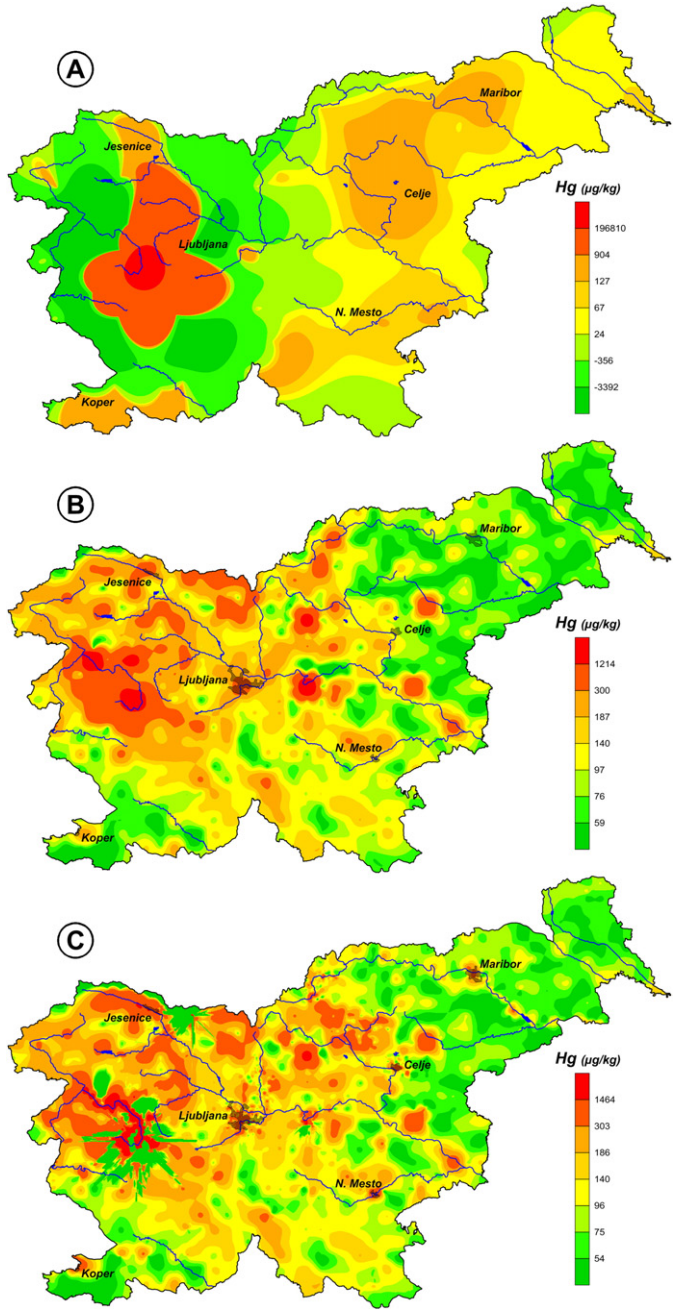

Fig. 4. Geochemical maps of spatial Hg distribution in Slovenia created by using natural, untransformed data at 3 different sampling densities (A is low sample density map (Level 1, $n = 54$), B is medium-density regional geochemical survey (Level 2, $n = 817$) and C is regional geochemical data set supplemented by local high-density sampling data (Level 3, $n = 2835$).

are both quite close to the median Hg concentrations, while the averages of untransformed data differentiate quite a bit from the medians, especially for the Western Prealps, due to some exceptionally high Hg concentrations determined in this area (Idrija area impact) (Table 2). The highest median for the Western Prealps is the consequence of environmental contamination because of the 500-year history of mining and ore processing in the Idrija Hg mine. The second-highest median determined for the Interior basin can be ascribed to urban pollution due to industry, traffic and the use of mercury-containing products. In addition, the Hg median for the Alps is slightly elevated; this may, on the one hand, be due to the igneous and metamorphic rocks in Karavanke, from which organic rich soils are formed. These soils tend to accumulate Hg by natural processes, as explained in Ottesen et al. (2013). On the other hand, elevated Hg concentrations might be due to the residual soils on limestone and dolomite. The lowest Hg concentrations were determined in the Pannonian basin and are probably related to the geological settings and soil type (alluvial deposits of gravel, sand and clay) in this area, although higher concentrations might have been expected due to intense agriculture which included the use of Hg containing pesticides and fungicides in the past.

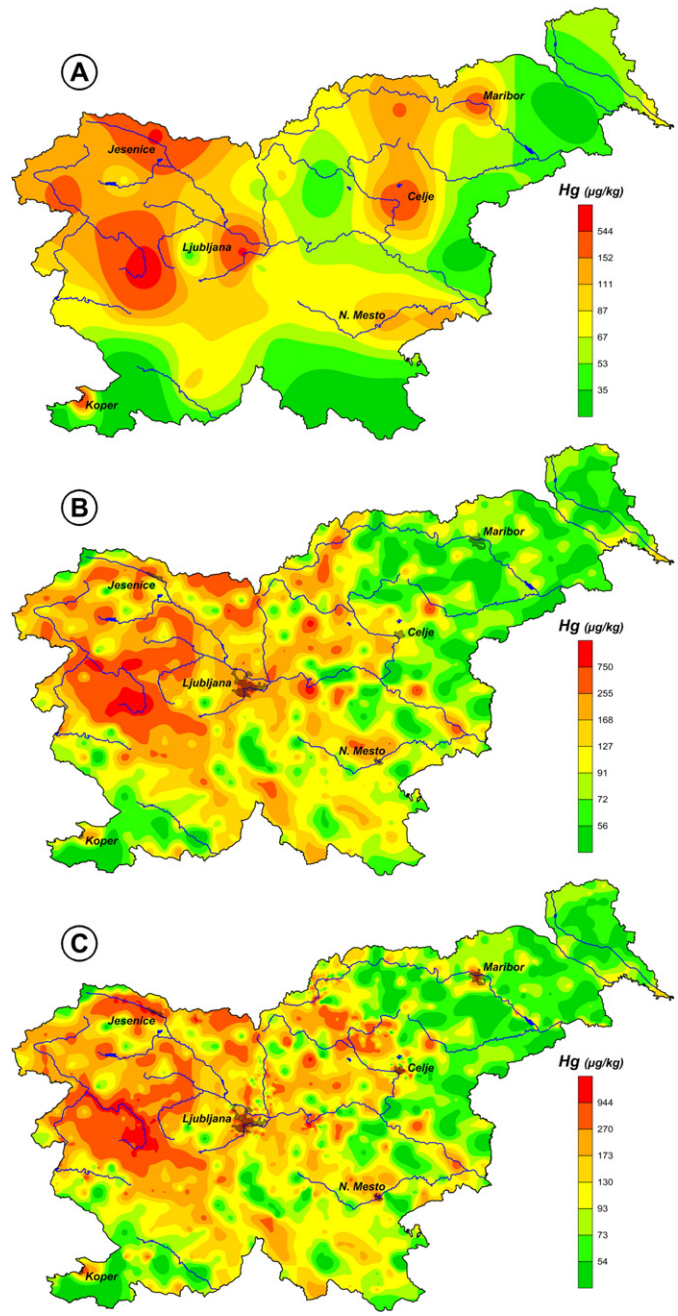

Fig. 5. Geochemical maps of spatial Hg distribution in Slovenia created by using **Box–Cox normalized data** at 3 different sampling densities (A is low sample density map (Level 1, $n = 54$), B is medium-density regional geochemical survey (Level 2, $n = 817$)) and C is regional geochemical data set supplemented by local high-density sampling data (Level 3, $n = 2835$).

Table 2
Median (Md) and means Hg concentrations in mg/kg for untransformed data ($\overline{x}$), logarithmed data ($\overline{x}g$) and Box–Cox transformed data $\overline{x}$(bc).

Natural unit	n	$\overline{x}$	Md	$\overline{x}g$	$\overline{x}$(bc)
Level 1					
Alps	10	0.173	0.110	0.116	0.104
Eastern Prealps	6	0.058	0.060	0.055	0.053
Western Prealps	6	74.828	0.223	0.520	0.196
Dinarides	17	0.109	0.075	0.066	0.057
Interior basins	3	0.549	0.490	0.384	0.325
Pannonian basin	12	0.081	0.055	0.063	0.059
Level 2 (this study)					
Alps	**184**	**0.184**	**0.118**	**0.125**	**0.114**
Eastern Prealps	**116**	**0.174**	**0.111**	**0.117**	**0.110**
Western Prealps	**98**	**0.435**	**0.270**	**0.276**	**0.253**
Dinarides	**228**	**0.122**	**0.103**	**0.105**	**0.101**
Interior basins	**38**	**0.169**	**0.154**	**0.153**	**0.149**
Pannonian basin	**152**	**0.075**	**0.067**	**0.068**	**0.067**
Level 3					
Alps	596	2.800	0.200	0.242	0.191
Eastern Prealps	611	0.347	0.170	0.192	0.171
Western Prealps	388	136.200	0.769	1.472	0.785
Dinarides	315	0.135	0.110	0.109	0.102
Interior basins	651	0.365	0.200	0.225	0.205
Pannonian basin	270	0.092	0.069	0.073	0.070

3.2. Main Hg anomalies in Slovenia

In this chapter we describe the main Hg anomalies revealed in presenting study (Level 2) in more detail. In addition, the data and results of local detailed investigations, included in the Level 3 statistical data and geochemical maps of Hg distribution, are summarized and discussed.

3.2.1. Idrija mercury mine area

The maximum Hg concentration in soil (5.293 mg/kg) was determined in the Idrijca River valley, between Slap ob Idrijci and Idrija pri Bači, about 35 km downstream from the town of Idrija, and is the consequence of the transportation of Hg-contaminated sediments via the Idrijca River and the consequent accumulation in the areas of slow riverflow. High Hg concentration in the river and overbank sediments of Idrijca were reported many times (Bavec, 2015; Bavec et al., 2014; Gosar, 2004, 2008; Gosar et al., 1997; Hines et al., 2006; Horvat et al., 1999, 2003; Kocman and Horvat, 2011; Kocman et al., 2004, 2011; Žibret and Gosar, 2005); thus, this high value was expected. The second-highest concentration (4.205 mg/kg) was determined about 3 km west from the town of Idrija at 780 m altitude, on Rejčev grič. This increased concentration is probably the consequence of atmospheric emissions from the Idrija mercury-ore roasting plant, as demonstrated by Gosar et al. (2006). The concentration could also be due to the historical small-scale ore-roasting sites that were spread throughout the forests around Idrija (Čar and Terpin, 2005; Gosar and Čar, 2006).

The area around the Idrija Hg mine in the western part of Slovenia is the most important district influenced by Hg mining and ore processing in Slovenia. Half a millennium of Hg production is reflected in the increased mercury contents of all of its environmental compartments. Systematic investigations of mercury contents in soil and its spatial distribution in the years 2000–2001 over an area of 160 km^2 around the Idrija mercury mine (Gosar and Šajn, 2001, 2003; Gosar et al., 2006) and in Idrija urban area (Bavec et al., 2015) showed very high values in the town of Idrija and along the Idrijca River near the pollution source (a smokestack). Hg concentrations decreased exponentially with the distance from Idrija. It was determined that the New Dutchlist action value for Hg (10 mg/kg; MHSPE, 1994) exceeded on an area of 19 km^2 (Gosar et al., 2006). The results of these soil surveys are included in the Level 3 geochemical map of Hg distribution (Fig. 5C).

Besides the main Hg contaminated area in the town of Idrija near the smokestack, other Hg sources also exist in the Idrija area. Extremely contaminated locations (Hg concentrations in soil samples of up to 19,900 mg/kg) of historical small-scale roasting sites were discovered in the area surrounding Idrija (Teršič and Gosar, 2009; Teršič et al., 2011a, 2011b, 2014). The unique method of small-scale ore processing at these sites has had an impact on the present extension and spatial distribution of Hg in the Idrija region. It was shown that the ancient roasting sites still remain important sources of Hg-contaminated material and one of the primary reservoir of persistent Hg release into the aquatic ecosystem (Gosar and Teršič, 2015).

Moreover, the systematic monitoring of Hg contents in sediments draining from the Idrija area have demonstrated that high waters have deposited Hg-rich material on the floodplains in the lower part of the Idrijca and Soča River valleys, thus producing a large accumulation of Hg in the soils of the floodplains along the Idrijca and Soča Rivers (Biester et al., 2000; Gosar, 2008; Gosar and Teršič, 2015; Gosar and Žibret, 2011; Gosar et al., 1997; Žibret and Gosar, 2006).

Hg distribution in soils shows that the influence of atmospheric emissions caused by the Idrija roasting plant has resulted in environmental impacts on a regional scale (Gosar et al., 2006). The relatively low Hg concentrations found in our study, compared to previous and ongoing local-scale investigations of the Idrija area, are due to the low density of sampling grid. In our medium-density regional geochemical survey, no sample was taken near Idrija or in the Idrijca River valley. Despite this the strong influence of Hg mining in Idrija was revealed in all 3 density maps (Figs. 4, 5).

3.2.2. Litija polymetallic mine area

In the area of Litija in central Slovenia, the second-strongest Hg anomaly (3.936 mg/kg) was detected. The soil sample was sampled at a site of the systematic sampling grid located at the foot of Sitarjevec hill, near the location of former mine shafts. Undoubtedly the main reason for this geochemical anomaly is the mining and smelting of ore in the Litija mine. In this area mining has been performed throughout history. Lead, zinc, mercury, silver, iron and barite were mined and processed until 1965. During the entire period, 50,000 tonnes of Pb, 1000 kg of Ag, 42.5 tonnes of Hg and 30,000 tonnes of barite were produced from local ore, according to estimation by Drovenik et al. (1980).

A detailed soil geochemical survey across the wider area influenced by the polymetallic mining and smelting region of Litija was undertaken by Šajn and Gosar (2007, 2014). In an area of 30 km^2, the soil (0–5 cm and 15–30 cm) was systematically sampled in a 500 × 500 m grid (120 sampling sites) (Šajn and Gosar, 2007, 2014). A metal dispersion halo of increased contents of Sb, Pb, Hg, Sn, As and Mo has been detected in a wide circle around Litija and interpreted as the anthropogenic influence of former mining and smelting in the Litija area. These elements have typically high values in the upper soil horizon, and the values decrease with depth. The samples with the highest concentration of these elements were located in the Podsitarjevec mining area and in the area of the former smelter in Litija. The determined Hg concentrations in the Litija area ($n = 120$) ranged between 0.065 and 6.0 mg/kg with the median of 0.35 mg/kg in the topsoil, and between 0.080 and 6.0 mg/kg with the median of 0.22 in the bottom soil (Šajn and Gosar, 2007, 2014). The results of this survey are included in the Level 3 geochemical map of Hg distribution (Figs. 4C and 5C).

3.2.3. Jesenice ironworks area

In a town Jesenice, an area of about 20,000 inhabitants, the impact of centuries-long ironworks activities has been investigated. The map of Hg distribution shows an anomaly of increased Hg concentrations around Jesenice. The highest concentration in this area (0.708 mg/kg) was found on the hill of Planina pod Golico, north of the town of Jesenice, and is comparable to the average Hg concentration (0.795 mg/kg) in the bottom soil horizon ($n = 78$) determined in a detailed survey in the area around Jesenice by Šajn et al. (1998b) and is

higher than the average Hg concentration determined by Šajn et al. (1998b) for the topsoil horizon in this area (0.263 mg/kg; $n = 44$).

3.2.4. Ljubljana area

Elevated Hg concentrations were also found in and around the capital city of Ljubljana; one soil sample was taken at the foot of Castle Hill (0.602 mg/kg), situated in the center of Ljubljana, and the other sample with an increased Hg concentration (0.335 mg/kg) was taken northeast of Ljubljana, on the hill above the Dol pri Ljubljani. Hg is shown to be strongly enriched in urban soils across Europe; for example, a median Hg concentration for Berlin was determined to be 0.19 mg/kg (Birke et al., 2011). Hg anomalies (>0.1 mg/kg, Ottesen et al., 2013) were also observed at other European cities, namely London, Rotterdam and Paris. However, for all these anomalies, it is typical that Hg concentrations decline quickly with the distance from the source and reach the European median value (0.03 mg/kg) a few km from the city boundaries (Ottesen et al., 2013). This characteristic is also valid for the Hg anomaly in the Ljubljana area (Fig. 4B, C). The obtained results are comparable to previous investigations of the urban soil pollution in Ljubljana (Šajn et al., 2011a) from traffic, industry and households. In the study, which covered an area of 168 km^2, the determined Hg average for the soil in the surrounding Ljubljana area was 0.220 mg/kg, and in the town center, 0.250 mg/kg. The impact was shown to be the highest in the downtown area, with many high Hg values. Several samples with a high Hg concentration were collected near the Ljubljanica River. Hg anomalies were also found on the site of the ancient municipal-waste disposal site. Individual high values near arterial roads indicated that traffic is one source of mercury (Šajn et al., 1998a). The data of this study are included in the Level 3 geochemical map of Hg distribution (Figs. 3C, 4C).

3.2.5. Podljubelj mercury mine area

The map of Hg distribution in Slovenian soils shows an anomaly of increased Hg concentrations in an area between Podljubelj and Zg. Jezersko and north from this area, on the Karavanke range. One of the soil samples, with slightly elevated levels of Hg (0.535 mg/kg), was taken in Potočnikov graben, upstream of an abandoned mine and could be explained by the influences of atmospheric emissions from historical Hg ore processing.

The abandoned Podljubelj mercury mine is situated in the northwestern part of Slovenia, in a narrow alpine valley near the border with Austria. It was in operation from time to time in long period (1557 to 1902). The entire operating period yielded about 110,000 tonnes of ore, from which 360 tonnes of Hg were produced. A soil and stream sediment survey was conducted in the Podljubelj mine area by Teršič et al. (2005, 2009). The determined Hg concentrations in the soil varied between 0.17 and 719 mg/kg, with a mean of 3.0 mg/kg. It was established that in an area of about 9 ha, Hg content in soil exceeded The New Dutchlist action value for Hg (10 mg/kg; MHSPE, 1994).

3.2.6. Mežica Pb-Zn mine and Ravne ironworks areas

The upper part of the Meža river valley cuts through the Eastern Karavanke mountains. The narrow valley is wider in two places where two settlements, Črna and Mežica, have grown. Increased Hg concentrations were found in the Meža river valley where 300 years of Pb-Zn mining and ore processing, as well as the ironworks industry, have had a negative impact on the environment (Miler and Gosar, 2013). Elevated Hg concentrations were found in the town of Ravne na Koroškem (0.66 mg/kg) and in the hills southeast of Žerjav and Črna na Koroškem (0.673 mg/kg). In the Mežica area, no Hg anomalies could be determined in our investigation, probably because there were no sampling locations near the town or in the upper Meža River valley. The ironworks industry in the Meža River valley began in 1620 and in the 18th century, ironworks operated in Črna, Mežica and Ravne (Mohorič, 1954). Previous investigations of heavy metal pollution in the Meža River valley have shown that the environment in the upper Meža valley is highly polluted, due to 300 years of mining and smelting of Pb and Zn ore (Fux and Gosar, 2007; Šajn, 2002, 2006). In contrast with the distributions of other heavy metals, higher Hg concentrations were found only in the vicinity of the Pb smelter in Žerjav, near Mežica. The average Hg concentration determined in the Mežica area was 0.146 mg/kg, and for the Ravne area, 0.140 mg/kg (Šajn, 2002).

3.2.7. Celje area

In the area of Celje, a town with about 50,000 inhabitants, very high contents of heavy metals (toxic trace elements) were found, of which the source is the smelting of zinc ore between 1873 and 1970. In the Celje area, the regional geochemical survey does not show any increased Hg concentrations; however, local investigations revealed an Hg anomaly in the town (Fig. 3C). High Hg contents in the topsoil were identified, the source of which was the smelting of zinc ore. The average Hg content in the town center (0.258 mg/kg) is >2 times higher than the average content in the area around Celje (0.11 mg/kg) (Šajn, 2001, 2005).

3.2.8. Sava River floodplains

The Sava River sediments have a high metal load, according to several authors (Frančišković Bilinski, 2008; Kotnik et al., 2003; Štern and Förstner, 1976). The largest and longest Slovenian river, the Sava, collects in Slovenia's water and sediments from an area measuring about 10,000 km^2. It is influenced by several anthropogenic factors, like influences from the town of Kranj and the capital Ljubljana. The main source of pollution is the longstanding iron and steel industry in the Jesenice area. In the past, iron ore was smelted in the area and by-products were deposited on a slag dump near the Moste water reservoir (in northwest Slovenia). The investigation made by Štern and Förstner (1976) proved the existence of a heavy pollution load, with Zn, Pb and increased Cd and Hg in the Sava River sediments taken from the Moste Dam reservoir (Štern and Förstner, 1976). In addition, Kotnik et al. (2003) and Frančišković Bilinski (2008) confirmed increased concentrations of Cd, Cr, Cu, Ni, Pb and Zn in the sediments of the Moste Dam.

In our study highly increased Hg concentrations along the Sava River have not been found, with the exception of one soil sample influenced by the Litija mining area and another, taken on the floodplain between Krško and Brežice, which had a slightly increased level of Hg (0.537 mg/kg). The anomaly in the latter could probably be attributed to the influence of contaminated sediments from the Sava River. Anomalies related to the Hrastnik chlor-alkali plant, which was identified as a cause of increased Hg concentrations in Sava River sediments (Kotnik et al., 2003), were not observed in our study.

3.2.9. Minor Hg anomalies

Hg is enriched in soil of western Slovenia in the World War 1 Soča (Isonzo) front area, which is due to the use of explosives during warfare (from 1915 to 1918), that contained about 15% of mercury fulminate in the mixture (Pirc and Budkovič, 1996). Some other minor Hg anomalies were determined and can be observed on the map of Hg distribution. Some of these would demand a closer look, but for the most part these anomalies are the consequence of elevated Hg concentration in just one soil sample, with no known Hg sources in the vicinity. These are, for example, Zabukovje nad Sevnico (1.021 mg/kg), the Kamniška Bistrica valley (0.565 mg/kg), the hills of Hom near Gornji Grad (2.633 mg/kg), Tolsti Vrh near Slovenske Konjice (0.955 mg/kg) and others (Fig. 4C). These anomalies cannot be attributed to mineralisation or contamination from mining or urban contamination. Therefore we presume that these elevated Hg concentrations are probably due to some local-point contamination, e.g. the spillage of mercury thermometers, disposal of mercury-containing wastes, etc.

Table 3
Comparison of statistical results of Hg concentrations in our study (Level 2) to statistical results of Hg concentrations in European soil (n—number of samples, Md—median, Min—minimum, Max—maximum, P—percentile of the distribution, Ap—agricultural soils, Gr—grazing land soils).

		n	Unit	Min	P2	P5	P10	P25	Md	P75	P90	P95	P98	Max
Slovenia		817	mg/kg	0.012	0.032	0.039	0.05	0.069	0.106	0.18	0.305	0.438	0.725	5.293
Europe, GEMAS project	Ap	2108	mg/kg	<0.003	0.0056	0.0085	0.012	0.018	0.03	0.048	0.076	0.1	0.19	1.6
Ottesen et al. (2013)	Gr	2024	mg/kg	<0.003	0.0072	0.0099	0.013	0.02	0.035	0.059	0.094	0.13	0.21	3.1

3.3. Comparison to Hg concentrations in European soil

Slovenia has also participated in the European GEMAS project, in which metal concentrations in European agricultural and grazing-land soils on a continental scale were established. The Hg concentrations found here align with results obtained in the GEMAS project (Ottesen et al., 2013; Reimann et al., 2014a, 2014b), in which distributions of 60 chemical elements, including Hg, were studied in European agricultural (Ap) and grazing land (Gr) soils. In Slovenia, 9 project sample sites are located, and Ap and Gr soil samples were taken at each location. The Hg median for Slovenia was 0.084 mg/kg for agricultural and 0.091 mg/kg for grazing-land soils (Ottesen et al., 2013), which is only slightly lower than the Hg median determined in this study (0.106 mg/kg). The Slovenian median Hg concentration reported in the GEMAS project is much higher than the median determined for European soils (0.03 mg/kg for agricultural and 0.035 mg/kg for grazing land soils) (Table 3) and is the highest among European countries. This probably indicates the strong influence of hundreds of years of Hg mining and related atmospheric emissions, and might also be due to a characteristic of residual soils that have developed in large parts of Slovenia.

3.4. Comparison of overlapping high- and low-sample density surveys

The resolution of the patterns generated at medium density-sampling survey (sample grid 5 × 5 km, Level 2) is much better compared to the low-density survey (Level 1), leading to identification of the patterns and local anomalies not revealed by the low-sample density survey. While low-density sampling still reveals some general trends in the Hg spatial distribution (for example, large regional differences), it is not appropriate for identifying local contamination in industrial regions and urban areas. Comparing Level 2 (Fig. 5B) and Level 3 (Fig. 5C) geochemical maps, we can see that the geochemical patterns produced are nearly the same. This proves that the regional geochemical survey with the sampling density used (1 site per 25 km^2) is very useful for determining regional or national Hg distribution. However, the higher sampling density allows for the identification and characterization of anthropogenic influences on a local scale. Closer examination of the Level 3 geochemical map reveals some Hg anomalies not observed on the Level 2 map, especially in the urban areas of Celje, Maribor and Novo mesto, and around the areas of Velenje and Šoštanj. In addition, anomalies around Jesenice are more clearly expressed and some elevated values along the Drava River can be observed. Other local anomalies, obtained through local-scale high-density sampling geochemical surveys, are highly consistent with the anomalies determined by the medium-density regional (Level 2) geochemical survey (Fig. 5B, C).

Birke et al. (2015) studied the differences between low- and high-density sampling in water and stream sediment surveys of Germany. They demonstrated that comparable analytical data of certain elements in different surveys with reduced sampling densities can produce the same patterns. In addition, the geochemical patterns produced from low-sample density surveys were very nearly the same as those from the high-sample density surveys, and could be related to natural processes. It was observed, however, that the anthropogenic influences associated with contamination and various land use can be better identified and characterized in the high-density mapping projects (Birke and Rauch, 1993; Birke et al., 2015).

4. Conclusion

The regional distribution of mercury in the topsoil of Slovenia revealed a distinct Hg anomaly around the Idrija area, the consequence of past mining and ore processing. As a consequence the Hg median for the western part of Slovenia is almost double the value for eastern Slovenia and exceeds the Hg median for European soil by a factor of 4. When viewed according to the natural geographic units of Slovenia, the highest median is located in the Western Prealps, where the Idrija mercury mine is situated, followed by the Interior basins, characterized by urban pollution. The lowest Hg median is located in the Pannonian basin, formed from young sediments. Besides Idrija area, increased Hg concentrations could also be observed around other mining areas (Litija, Podljubelj), the urban area of Ljubljana and areas with ironworks (Jesenice, Ravne). Medium-density regional geochemical mapping of Hg concentrations in Slovenian soils was presented and compared with a low-density national geochemical survey and with high-density local-scale geochemical surveys. The resolution of the pattern generated is the best when the high-density survey on a regional scale is supplemented with the geochemical data of the high-density surveys on a local scale. Anthropogenic impacts (pollution), as well as natural processes (mineralization), are registered on the maps of Hg distribution in the soils of Slovenia. The variability of the spatial distribution of Hg depends mainly on pollution, but also on the influence of lithology, weathering and organic-matter content, which can be observed on the high-density geochemical maps.

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