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Comparison of elemental composition of surface and subsurface soils on national level and identification of potential natural and anthropogenic processes influencing its composition

Emil Pučko *, Gorazd Žibret, Klemen Teran

Geological Survey of Slovenia, Dimičeva 14, SI-1000 Ljubljana, Slovenia

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ABSTRACT

The elemental composition of soils is governed by geogenic processes and anthropogenic activities. A comprehensive soil study was conducted on a national level, in which the elemental composition of soils from two different layers was compared with the intention to differentiate between natural and anthropogenic sources of elemental enrichments. Topsoil (0–5 cm) and subsoil (20–30 cm) samples were collected from 249 different locations on a national scale (Slovenia). Elemental composition for 55 major, minor, and trace elements (ICP-MS, aqua regia digestion) was determined on the fraction <0.063 mm. By calculating the enrichment ratios in different lithological units, it was determined that levels of Ti are higher in soils overlying metamorphic and igneous rocks, Zr and Ca are more abundant over carbonates, while levels of Ni are higher in soils overlying marlstones. Elevated levels of Hg were detected in subsoils in the historical Hg mining area in Idrija, which indicates the presence of nearby orebodies as a potential source for the geochemical anomaly. Spatial distribution of elements showed that higher levels of Pb, Zn, Cu, and Hg were detected in topsoils of urban areas, indicating that anthropogenic sources could be the potential cause of soil contamination. Pb, Zn, Cu, and Hg levels were up to four times higher in topsoils compared to subsoils sampled at historical mining areas (e.g., Mežica, Idrija, Litija), which shows that historical mining left a significant environmental impact. Although mining and smelting activities ended a few decades ago, soils in some areas are still heavily enriched with various metals. Some other potential anthropogenic sources of elements were identified, such as farming and ironworks. Based on the results of this study, we can conclude that by comparing elemental compositions of soils from different layers, we can recognise the origin of elemental enrichments.

1. Introduction

Soil is a thin layer of Earth's crust consisting of loose mineral and organic material (Van Es, 2017). It is a complex ecosystem that homes different organisms and microorganisms and plays a vital role in food production. The composition of soils is affected by various factors, which can be of geogenic or anthropogenic origin (Soltani-Gerdefaramarzi et al., 2021). Among geogenic sources, the most crucial factor determining the soil's geochemical characteristics is the bedrock material on which soils develop (Zupančič et al., 2018). The influence of bedrock lithologies on the elemental composition of soils has been recognised by many researchers (Mehmood et al., 2018; Sterckeman et al., 2006; Wilson et al., 2022; Zupančič et al., 2018; and others). Apart from weathering of the surrounding bedrock, soils can also become enriched with trace elements from nearby mineral deposits (Xueqiu et al., 2016). Mineral deposits or other natural enrichments in various bedrock formations can produce geochemical anomalies in soils, which can also be traced outside the occurrences of deposits of lithological units because of particle transportation by gravitational processes, water, wind, or biological transport, producing regionally important enrichment of elements (Kabata-Pendias, 2010). The use of soil geochemistry is a common approach in mineral exploration. In several cases, pathfinding elements were used to help find new ore deposits. Such examples are the Panguna porphyry Cu-Au deposit on Bougainville Island in Papua New Guinea (Hope, 2011) and Yanacocha Gold Mine in Peru (Lewis and Alberto, 2011), where elements such as As and Sb were used to delineate mineralised zones, or Norilsk Nickel Deposits in Russia, where Cu and platinum group elements (PPGs) assisted in targeting ore bodies (Barnes

* Corresponding author.
E-mail address: emil.pucko@geo-zs.si (E. Pučko).

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et al., 2020). Previous studies show that underlying mineral deposits can affect the elemental composition of subsoil samples collected from depths 10 to 30 cm below the surface (e.g., Mann et al., 2005; Xueqiu et al., 2016). Besides geogenic processes, anthropogenic activities can also affect the elemental composition of soils. Some industrial operations, such as smelting, mining operations, power plants, and other facilities (Dietrich et al., 2019; Miler et al., 2022; Šajn et al., 2022; Žibret et al., 2013), traffic (Dietrich et al., 2021; Gaberšek et al., 2022; O'Shea et al., 2021; Teran et al., 2020), agriculture (Tóth et al., 2016), improper waste disposal and various environmental accidents can introduce numerous metals into soils. Levin et al. (2017) reported that the most concerning metals in urban soils are Pb, As, Ba, Cd, Cu, Hg, Ni, and Zn. Many researchers have reported elevated levels of metals, such as Cu, Zn, Pb, Ni, Sb, etc., in soils around mining and smelting areas (Miler and Gosar, 2010; Miler et al., 2022; Shen et al., 2017; Žibret et al., 2018; Wang et al., 2019), Pb, Cd, Ni, Zn, etc., in the vicinity of areas affected by heavy traffic (Gaberšek et al., 2022; Teran et al., 2020; Werkenthin et al., 2014), or Zn, Cu, Cd, etc., in soils proximal to agricultural activities (Adrees et al., 2015; Micó et al., 2006; Tóth et al., 2016).

Ex-situ materials can be either applied directly to soils as fertilizers, phytopharmaceuticals and waste disposal, or they can be transported by air or water. Similar to naturally occurring ones, anthropogenic anomalies can also be traced beyond the initially affected area and can produce locally or regionally important anomalies (Bland et al., 2022). For example, some metals, such as Pb, Cd, and Hg have been transported over long distances by air currents and deposited in the Artic region (Kozak et al., 2016).

When elemental analyses of soil samples show elevated levels of certain elements, the question arises about the true sources of these enrichments. Is the soils' elemental composition affected by anthropogenic activities, natural processes, or a combination of both? How to distinguish between natural and anthropogenic anomalies in soils? The way to answer this question is to compare the elemental composition of the uppermost soil layer, potentially influenced by anthropogenic sources, and the elemental composition of soils in lower layers, which might be influenced mainly by natural processes, assuming the soil profile was not altered by humans (i.e., construction, farming, etc.).

Standard methods for assessing enrichments in soils are, for example, the use of the geochemical index, enrichment factor, contamination factor, and integral pollution index, all of which are based on the relative ratio of the actual levels of each element in a soil sample compared to a local reference with a background value (Tume et al., 2018).

The aim of this article is to present a comparison of the results of elemental analyses of topsoil and subsoil samples on a national scale (Slovenia), where soil composition is affected by various natural and anthropogenic sources. In this study, the focus was mainly on the determination of the influence of lithology and various occurrences of mineral deposits, as well as the impact of anthropogenic activities on the soil composition, with a particular focus on potential pollutant transport by wind. Apart from identifying the origin of elemental enrichments, the purpose of the study was also to determine the connection between the lithological composition of the bedrock and the geochemical composition of the above-lying soils. Differentiation between anthropogenic and geogenic sources of elemental enrichment in soils has been undertaken by many researchers (e.g., Islam et al., 2019; Soltani-Gerdefaramarzi et al., 2021; Šajn and Gosar, 2007; Tume et al., 2018), by analysing and comparing soil elemental and isotope composition from different depths. However, these studies were mostly done in smaller and urbanised areas. On the other hand, the presented study was done on a large number of national samples covering various geological environments. The novelty of the presented study is also the categorization of samples according to the predominant bedrock type and a statistical analysis based on this grouping. The importance of such an approach was outlined already in previous research (e.g., Soltani-Gerdefaramarzi et al., 2021; Tume et al., 2018). The authors of this study are aware of the danger of collecting samples from allochthonous soils, which has been noticed by a few outliers. Consequently, outliers were taken into consideration during the interpretation of the results. The presented study was carried out as part of a more extensive research program in which various methods were tested with the intention to differentiate between natural and anthropogenic sources in a broader area and media, including top and subsoils, house dust, and street sediments.

2. Study area

The study was conducted on almost the entire territory of Slovenia. The country covers an area of 20.273 km^2 and is bordering Italy, Austria, Croatia, and Hungary. It is very heterogeneous in its lithological and pedogeographic characteristics and is located in an active tectonic region. The Periadriatic Lineament, which also runs across Slovenian territory, is a distinct fault system that divides African and Eurasian plates. Due to high tectonic actives, numerous active and inactive faults are present in this area, contributing to the formation of several rich mineral deposits (e.g., Mežica, Idrija, Litija).

2.1. Lithology

Slovenian territory is very diverse from a lithological point of view (Fig. 1). Sediments and sedimentary rocks are most abundant since they cover app. 93 % of the Slovenian surface area. The rest of the crustal cover consists of metamorphic, volcanoclastic, volcanic, and igneous rocks (Bavec et al., 2008; Komac, 2005). Among sedimentary rocks, carbonate rocks (limestone and dolomite) are representative of southern, south-west and northern and north-west parts of the country, while clastic rocks (claystone, siltstone, sandstone, and conglomerate) mainly outcrop in the central, eastern, and north-eastern part of Slovenia. Some minor outcrops of clastic rocks can also be found in the northern and southern parts of the country. Flysch, consisting of clastic and carbonate sedimentary rocks, builds western and south-western parts of Slovenia. Sediments (clay, silt, sand, and gravel) have been deposited in the central and north-eastern part of the Slovenian territory in younger sedimentary basins (Ljubljana, Celje, and Krško-Brežice basin) and the Drava and Mura plains. Igneous rocks and volcaniclastics are relatively rare in Slovenia and cover approximately 3 % of the total area. They outcrop mainly in the north-eastern and northern parts (Pohorje Mountain, around Črna na Korškem, Kozjak Mountain, and Karavanke Mountains). Small bands of igneous rocks can also be found in central Slovenia and around Goričko hills. A large granodiorite intrusion outcrops in the central part of the Pohorje mountain. Metamorphic rocks, including slate, phyllite, mica schist, gneiss, amphibolite, and eclogite, are the oldest rocks in Slovenia and build approximately 4 % of the territory. They are found in the north-eastern and northern parts of Slovenia on Pohorje, Kozjak, Strojna, and around Črna na Koroškem.

2.2. Pedogeographic soil types

Slovenia, with its diverse geology and geomorphology, also has various soil types, which can be generally divided into carbonate and non-carbonate soils (Vrščaj et al., 2017). Based on pedo-geographic characteristics, there are three main soil groups in Slovenia: soils of plains and valleys (mostly occurring up to 400 m in elevation), soils of hills and mountains, and soils developed on top of karst plains and plateaus (mostly occurring above 400 m in elevation) (Zorn et al., 2020). Lithosols and shallow rendzinas are developed on steep slopes in mountainous terrains, whereas in areas with gentle slopes, rendzinas and brown soils on limestone and dolomite are present. Rendzinas are also common on clastic carbonate sediments such as gravel and sand in river valleys and dystric rankers. Dystric brown soils and leached soils were developed over other noncarbonate clastic rocks and on top of most metamorphic and igneous rocks. Rendzinas and eutric brown soils were also developed on carbonate flysch and marlstones in the eastern part of Slovenia (Vidic et al., 2015).

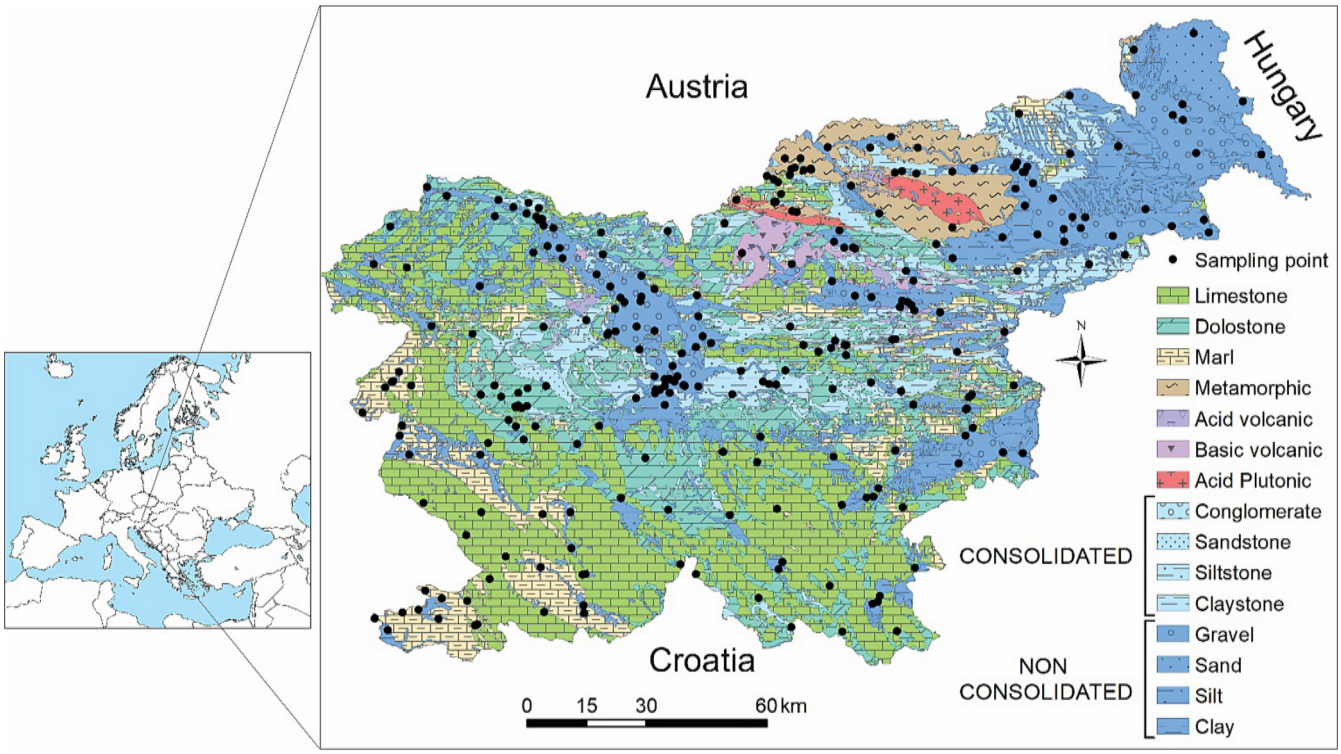

Fig. 1. Schematized lithological map after Bavec et al. (2008) and sampling locations. Selected lithological units were composed of the following units on the map: limestone (Limestone), dolomite (Dolomite), metamorphic (Metamorphic rocks), marlstone (Marlstone), alluvial (Conglomerate, Sandstone, Siltstone, Claystone, Gravel, Sand, Silt and Clay).

3. Methods

3.1. Sampling and sample preparation

Soils were sampled from 249 locations around Slovenia (Fig. 1). At each sampling location, a sample of topsoil (depth of 0–5 cm) and subsoil (depth of 20–30 cm) was collected as part of a sampling program in 2016 (Teran et al., 2020). Soil samples were processed in granulometric laboratories at the Geological Survey of Slovenia, where they were first dried in the oven at 303 K. Plant remains and coarse material were removed, and particle aggregates were gently crushed in a ceramic mortar, so skeletal particles remained intact. The dry screening was afterward carried out to obtain a pulp that contained 5 g of fraction <0.063 mm, which was later sent to the Bureau Veritas Mineral Commodities Laboratories, Vancouver, Canada, for multi-elemental analyses. Analysis of major, minor, and trace elements was performed by inductively coupled plasma mass spectrometry (ICP-MS) after a modified aqua regia digestion method (HCl:HNO_3:H_2O, 1:1:1) at 95 °C. 0.5 g per soil sample was used.

3.2. Quality control

The accuracy of the results was verified by mixing different certified reference materials (CRMs) with the original samples. In the sample batch of topsoil samples, the following standards were added: ERM-CC141 (4×), BCR-320R (2×), and BCR-176R (2×). The laboratory also added the following CRMs: DS10 (10×) and OREAS45EA (10×). The sample batch of subsoil samples included OREAS 45d (8×) and OREAS 45e (10×) CRMs, and the laboratory added BVGEO01 (4×), DS11 (5×) and OREAS262 (9×) CRMs.

The accuracy of the elemental analyses was checked by calculating the average percentage difference (%R) (results in Appendix 1) using Eq. (1), where $\overline{x}$ represents the average measured level of an element in the CRM and x_r represents the known (reference) level of an element in the CRM:

$$\%R = 1 + \frac{\overline{x} - x_r}{x_r} * 100\ [\%] \quad (1)$$

%R values between 90 % and 110 % were considered good, while elements with recovery rates ranging from 75 % to 90 % and between 110 % and 125 % were considered acceptable.

The precision of the elemental analyses was confirmed by inserting duplicate samples into the sampling batches. The batch containing topsoil samples included 28 duplicate samples and 11 duplicate samples were added to the batch of subsoil samples. Additionally, the laboratory added 12 duplicated samples to the topsoil samples and 9 to the subsoil samples. During the elemental analyses, the cross-contamination between samples was checked by inserting ten blank samples into the batch with topsoil samples and 9 with subsoil samples.

To test the analyses' precision, the relative percent difference (RPD) was calculated from duplicates, which were inserted in the field and in the laboratory. The equation used for calculating the RPD (Eq. (2)):

$$RPD = \frac{|x_1 - x_2|}{\overline{x}} * 100\ [\%] \quad (2)$$

in which x_1 is the level of an element in the first sample, x_2 represents the level of the same element in the repeated sample, and the $\overline{x}$ the average of both measurements. All the results of RPD calculations are shown in Appendix 1. Elements with RPD values higher than 30 % were excluded from further analysis (Appendix 2).

3.3. Data processing

Elements with >20 % of the measurement values below the detection limit were excluded from further data processing (Darnley et al., 1995). The following elements were excluded for both topsoil and subsoil samples: B, Ge, Pd, Pt, Re, Ta, and W. For all other elements, the values below the detection limit were replaced by the value of 50 % of the

detection limit, which is common practice in geochemical investigations (Hewett and Ganser, 2007; Reimann et al., 2014). Where duplicate samples were analysed for the precision test, the actual level was assumed to be an average value of both analyses.

To evaluate how the lithological composition of the bedrock influences soils' chemical characteristics, the entire sampling area was divided into different units based on the lithology of the bedrock (Fig. 1). The classification was based on the lithological map (Bavec et al., 2008) and was generalised into six groups with similar geochemical characteristics, to keep the number of groups manageable. The generalised groups include dolomites, limestones, various clastic rocks (sandstone, claystone, siltstone, flysch, or similar), igneous and metamorphic rocks, quaternary deposits of central Slovenia (carbonate rich sediments), and quaternary deposits of NE Slovenia (silicate rich sediments). To calculate how levels of certain elements are affected by the bedrock lithology enrichment ratio ER_{lith} (Eq. (3)) was calculated where MD_{elem_lith} is the median value of elemental levels of soils from a certain lithology and MD_{elem_all} is the median value of elemental levels from soils from all lithologies.

$$ER_{lith} = \frac{MD_{elem\_lith}}{MD_{elem\_all}} \quad (3)$$

For elements with the highest ER_{lith} values Box plot diagrams were prepared for each lithological type. Statistical treatment of data was conducted using STATISTICA 13.5 software. Descriptive statistical analyses were calculated (Table 1). Visual examination of histograms, and calculations of kurtosis and skewness (results are not presented in this paper) revealed that distributions for analysed elements for both, topsoil and subsoil samples were not normal, and non-parametric statistical tools (Mann Whitney *U* test) were used to compare medians of the elemental levels in top and subsoil for each of the element separately.

The enrichment ratio $ER_{top\text{-}sub}$ (Eq. (4)) was calculated for each of the sampling points to determine spatial variations of changes in elemental compositions of topsoil and subsoil samples. To identify areas with elevated $ER_{top\text{-}sub}$ values on a Slovenian-wide area, grid maps were created using the program Surfer version 22.3.185 (Golden Software Inc., Golden, Colorado, USA) by using a natural neighbour interpolation algorithm. The enrichment ratio $ER_{top\text{-}sub}$, which compares the level in the topsoil sample (c_{top}) and the level in the subsoil sample (c_{sub}) can potentially indicate if the geochemical anomaly is due to anthropogenic activities, is of geogenic origin, or possibly both.

$$ER_{top-sub} = \frac{c_{top}}{c_{sub}} \quad (4)$$

Further data processing included preparing scaling diagrams with Microsoft Excel and generating spatial distribution maps using GS Surfer.

4. Results

Table 1 shows non-parametric statistical parameters of elemental analyses of all collected topsoil and subsoil samples (this study) and the European grazing land soil median for reference (Reimann et al., 2009). Due to unsatisfactory QAQC results U, V, Tl, Te, Hf, and Au (Appendix 1) were excluded from further analyses. The results in Table 1 show that the predominant elements in both topsoils and subsoils are Fe and Al with the medians above 1 %. The K, Mg, and Ca medians in both sets of soil samples exceed 0.1 %, while the P median also exceeded 0.1 % in topsoil samples. Median levels of other elements are below 0.1 %. Data in Table 1 shows that the median values of most elements in the collected topsoil samples are comparable with the European grazing land soil median (Reimann et al., 2009). The biggest discrepancies have been observed for Hg, Pb, Zn, Cu, Sn, Ni, Mg, and Ca with median values approximately two to four times higher than the European grazing land soil median (Reimann et al., 2009). The results are also comparable with the results of a study by Gosar et al. (2019), in which Slovenian topsoil

Table 1
Statistic parameters for samples from topsoils and subsoils and the European grazing land soil median.

Element	Unit	Subsoils minimum - 25th percentile - median - 75th percentile - maximum	Topsoils minimum - 25th percentile - median - 75th percentile - maximum	European grazing land soil median[a]
Ag	mg/kg	0.025 - 0.064 - 0.092 - 0.117 - 0.805	0.027 - 0.070 - 0.096 - 0.132 - 1.15	0.04
Al	%	0.27 - 1.68 - 2.03 - 2.54 - 4.49	0.42 - 1.48 - 1.82 - 2.19 - 3.61	1.07
As	mg/kg	2.7 - 9.5 - 12.4 - 16.5 - 73.9	2.5 - 8.5- 11.6 - 15.4 - 59.3	5.6
Ba	mg/kg	31.5 - 88.9 - 110 - 138 - 1970	30.5 - 83.8 - 104 - 135 - 1770	63
Be	mg/kg	0.1 - 0.8 - 1.0 - 1.3 - 3.3	0.3 - 0.8 - 1 - 1.3 - 3.1	0.51
Bi	mg/kg	0.11 - 0.28 - 0.35 - 0.43 - 2.83	0.18 - 0.3 - 0.385 - 0.46 - 2.63	0.18
Ca	%	0.06 - 0.32 - 0.965 - 3.83 - 18.5	0.16 - 0.46 - 0.86 - 2.65 - 16.9	0.31
Cd	mg/kg	0.05 - 0.33 - 0.545 - 1.04 - 12.4	0.10 - 0.38 - 0.605 - 1.02 - 11.4	0.2
Ce	mg/kg	4.1 - 28.6 - 37.4 - 48.9 - 111	5.1 - 25.9 - 34.7 - 42.3 - 93.2	27
Co	mg/kg	1.1 - 11.5 - 15.1 - 19.9 - 49.2	1.8 - 10.3 - 12.7 - 15.7 - 32.2	7.2
Cr	mg/kg	7.6 - 27 - 36 - 50.5 - 112	8.0 - 25.4 - 33.2 - 43.7 - 104	20
Cs	mg/kg	0.33 - 1.44 - 1.85 - 2.47 - 36.3	0.29 - 0.90 - 1.32 - 1.94 - 35.8	1.06
Cu	mg/kg	4.92 - 20.4 - 27.7 - 35.6 - 216	5.41 - 23.2 - 31.2 - 42.6 - 335	14.5
Fe	%	0.29 - 2.51 - 3.00 - 3.49 - 10.3	0.46 - 2.36 - 2.78 - 3.21 - 7.15	1.7
Ga	mg/kg	0.6 - 4.6 - 5.6 - 6.95 - 15.6	1.0 - 4.2 - 5.3 - 6.3 - 12.7	3.4
Hg	mg/kg	0.033 - 0.093 - 0.136 - 0.246 - 99.0	0.04 - 0.089 - 0.141 - 0.29 - 68.4	0.035
In	mg/kg	0.01 - 0.03 - 0.04 - 0.05 - 0.29	0.01 - 0.03 - 0.04 - 0.04 - 0.26	–
K	%	0.05 - 0.13 - 0.16 - 0.20 - 0.93	0.06 - 0.11 - 0.16 - 0.20 - 0.75	0.113
La	mg/kg	2.3 - 13.8 - 18.8 - 24.1- 92.6	2.3 - 12.3 - 16.5 - 20.8 - 72.4	13.6
Li	mg/kg	2.2 - 18.0 - 21.6 - 27.4 - 355	2.8 - 16.0 - 20.2 - 25.0 - 331	11.3
Mg	%	0.05 - 0.48 - 0.67 - 1.21 - 9.29	0.10 - 0.46 - 0.63 - 1.07 - 9.12	0.282
Mn	mg/kg	141 - 680 - 891- 1230 - 4740	203 - 602 - 779 - 1100 - 3240	435
Mo	mg/kg	0.16 - 0.57 - 0.88 - 1.42 - 28.8	0.20 - 0.64 - 0.93 - 1.50 - 23.0	0.42
Na	%	0.003 - 0.007 - 0.009 - 0.012 - 0.116	0.001 - 0.005 - 0.006 - 0.008 - 0.088	0.005
Nb	mg/kg	0.02 - 0.23 - 0.38 - 0.56 - 1.43	0.07 - 0.38 - 0.575 - 0.89 - 3.95	0.52
Ni	mg/kg	3.2 - 24.3 - 31.2 - 47.1 - 185	5.6 - 24.1 - 32.2 - 44.5 - 149	14.4
P	%	0.018 - 0.053 - 0.072 - 0.093 - 0.326	0.023 - 0.079 - 0.101 - 0.132 - 0.477	0.065
Pb	mg/kg	16.8 - 30.3 - 41.9 - 59.9 - 1030	14 - 29.9 - 43.0 - 61.0 - 1750	17.7
Rb	mg/kg	3.2 - 18.1 - 22.5 - 28.0 - 71.4	5.7 - 15.4 - 19.9 - 24.8 - 58.6	13.9
S	%	0.01 - 0.02 - 0.03 - 0.04 - 0.29	0.01 - 0.05 - 0.06 - 0.08 - 0.27	0.03
Sb	mg/kg	0.09 - 0.26 - 0.345 - 0.51 - 12.3	0.14 - 0.31 - 0.42 - 0.60 - 12.6	0.28
Sc	mg/kg	0.6 - 3.8 - 4.7 - 5.95 - 13.1	0.7 - 3.0 - 3.9 - 4.75 - 10.2	2
Se	mg/kg	0.1 - 0.2 - 0.4 - 0.5 - 1.7	0.1 - 0.3 - 0.5 - 0.6 - 1.2	0.4
Sn	mg/kg	0.4 - 1.1 - 1.5 - 2.2 - 20.3	0.6 - 1.35 - 1.9 - 2.5 - 13.7	0.81

(*continued on next page*)

Table 1 (*continued*)

Element	Unit	Subsoils minimum - 25th percentile - median - 75th percentile - maximum	Topsoils minimum - 25th percentile - median - 75th percentile - maximum	European grazing land soil median[a]
Sr	mg/kg	4.9 - 13.9 - 22.7 - 40.2 - 1640	5.3 - 14.0 - 20.0 - 31.1 - 1350	17.8
Th	mg/kg	0.4 - 3.1 - 4.3 - 5.7 - 15.0	0.2 - 2.0 - 2.6 - 3.4 - 7.1	2.5
Ti	%	0.0005 - 0.004 - 0.008 - 0.015 - 0.249	0.0005 - 0.004 - 0.008 - 0.015 - 0.225	0.007
Y	mg/kg	1.82 - 9.25 - 11.9 - 16.5 - 116	1.90 - 9.11 - 11.6 - 15.3 - 97.7	6.5
Zn	mg/kg	30.6 - 74.8 - 90.9 - 121 - 1610	31.4 - 84.7 - 105 - 140 - 1990	46
Zr	mg/kg	0.1 - 1.1 - 2.1 - 3.4 - 10.1	0.1 - 0.8 - 1.7 - 2.9 - 8.3	1.6

[a] European grazing land soil median (Reimann et al., 2009), aqua regia digestion methods.

background elemental levels were determined. It was noticed that some discrepancies have been observed for Cu, P, K, Sr, Pb, and Zn with median values in our study approximately one and a half to two times higher, and for Th with median values approximately one time lower in comparison to the Slovenian topsoil background elemental levels (Gosar et al., 2019).

A comparison between median values of elemental levels for topsoils and subsoils superimposed on a certain lithological unit and the median level of that element in all samples is shown in Fig. 2. The blue line ($ER_{lith} = 1$) indicates no difference between both medians, ER_{lith} values below 1 indicate that the lithology has lower, and ER_{lith} values above 1 higher median level of an element in comparison to the median elemental levels for all lithological units combined. As can be seen from Fig. 2, the biggest variations between the lithological units regarding the soils' elemental composition were noticed for elements Ti, Zr, Ca, and Ni for which Box and Whiskers diagrams were made and are shown in Fig. 3a to d. The median values of Ti (Fig. 3a) were approximately seven times higher in soils on top of metamorphic rocks and alluvial sediments from the NE part of Slovenia than in soils from other lithological units. The opposite trend can be seen for elements Zr and Ca (Fig. 3b and c) for which the median values were several times higher in soils on carbonate rocks, marlstones, and alluvial sediments from the SW part of Slovenia than in soils from metamorphic rocks and alluvial sediments from the NE part of Slovenia. Median levels of Ni (Fig. 3d) are higher on marlstones than other lithological units. Observations of spatial distribution of Ni in topsoils (Fig. 4a) and subsoils (Fig. 4b) identified, that elevated levels of Ni occur in the SW part of Slovenia where flysch sedimentary sequence predominantly occurs.

Mann Whitney *U* test (Fig. 5) was performed to assess the variations of elemental levels between the topsoil and subsoil samples. Wilcoxon Z values that are above 1.96 or below −1.96 show statistically significant differences (with $p = 0.05$). It was confirmed that the distribution of elemental levels in both sets of samples differs for 28 elements, with surface soils showing higher levels of S, P, Nb, Zn, Sb, Se, Sn, Cu, and Bi, while subsoil samples indicating higher levels of Cr, Tl, Hf, As, Ce, Zr, Ga, Mn, Li, Fe, La, Al, Rb, Co, Sc, Cs, Na, and Th. Topsoil samples contain higher levels of several urban polluting elements such as Zn, Cu and Sb, which were also historically exploited in several mines in Slovenia, whereas levels of elements that are commonly referred as 'geogenic' elements, like Al, Na, Mn or Fe, are higher in subsoils.

Pb, Zn, Cu, and Hg were recognised as elements that are not only present in various amounts in different rock formations but have also been strongly associated with past and present anthropogenic activities, such as mining, ore processing, agriculture, traffic, etc. in Slovenia (Gaberšek and Gosar, 2018; Šajn et al., 2012; Teran et al., 2020). In order to assess the difference between levels of these elements in topsoils and subsoils in different lithological units, all assayed values were plotted on graphs presented in Fig. 6a to d. Point values which lie above the blue line represent higher levels of a certain element in topsoils, and

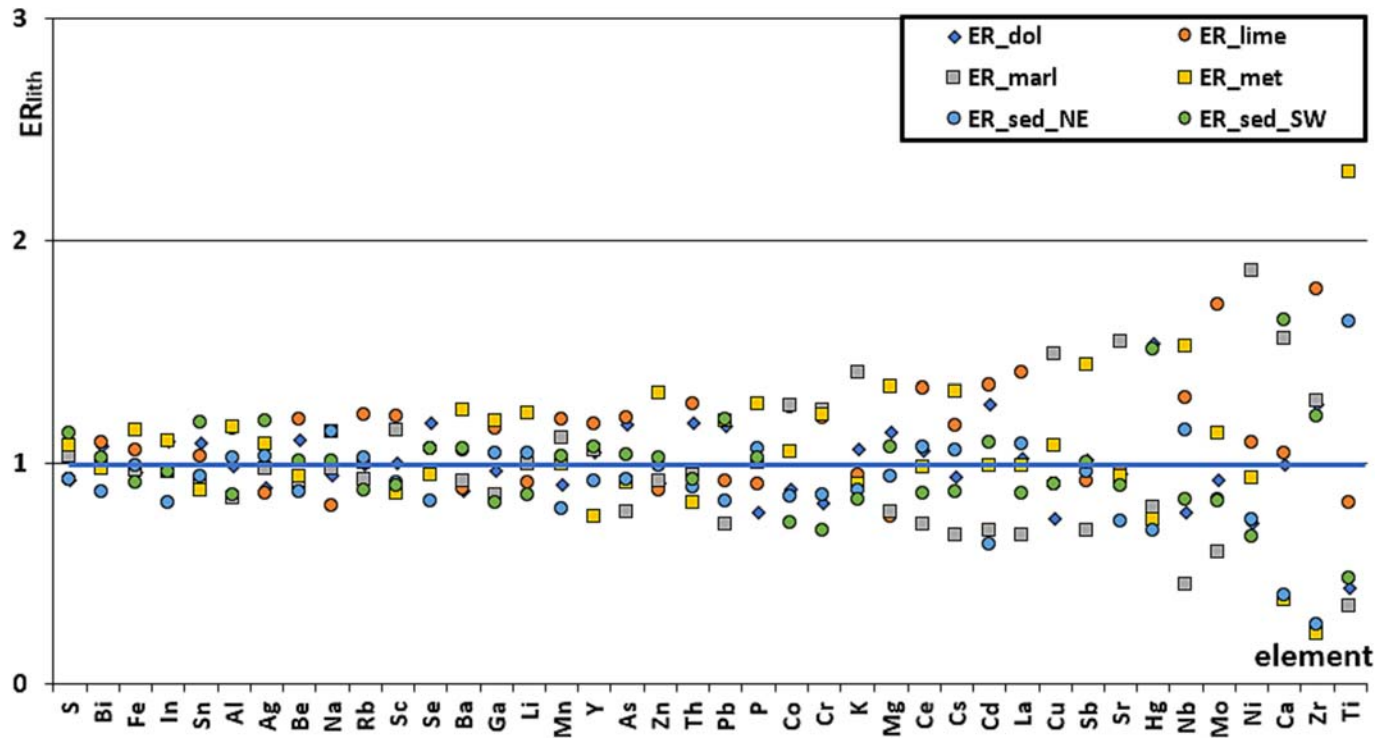

Fig. 2. Comparison between median values of elemental levels for soils superimposed on different lithologies. Key: ER_dol: Enrichment Ratio (ER) in dolomite; ER_marl: ER in marlstone; ER_sed_NE: ER in quarternary deposits of NE Slovenia; ER lime: ER in limestone; ER_met: ER in igneous and metamorphic rocks; ER_sed_SW: ER in quarternary deposits of central and SW Slovenia.

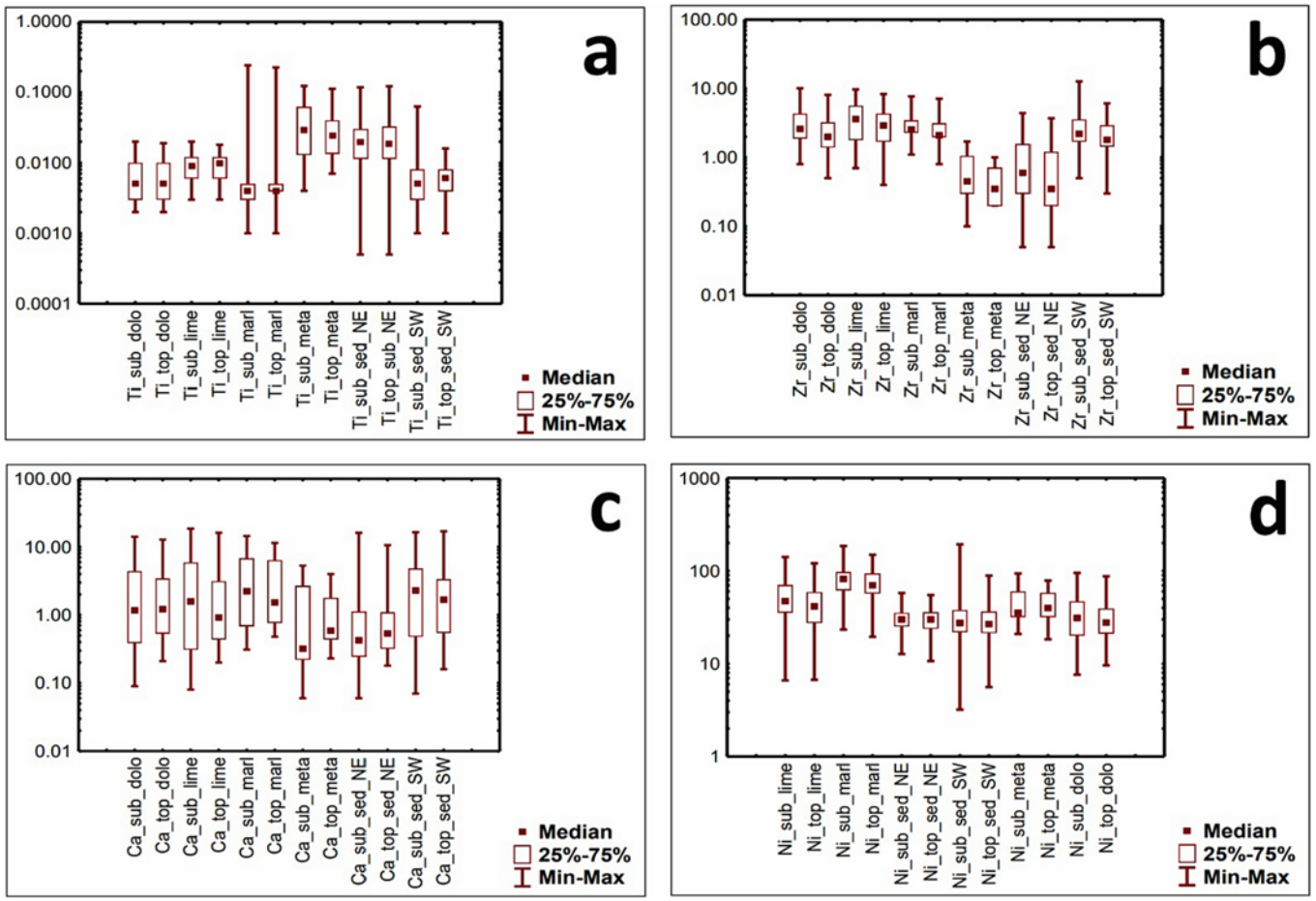

Fig. 3. Variations between the lithological units regarding the soils' elemental composition for Ti(a), Zr(b), Ca(c) and Ni(d); Key: Ti: titanium; Zr: zirconium; Ca – calcium; Ni: nickel; sub – subsoil; top – topsoil; dolo – dolomite; lime – limestone; marl – clastic rocks and flysch; meta – igneous and metamorphic rocks; sed_NE – quarternary deposits of NE Slovenia; SW – quarternary deposits of central and SW Slovenia.

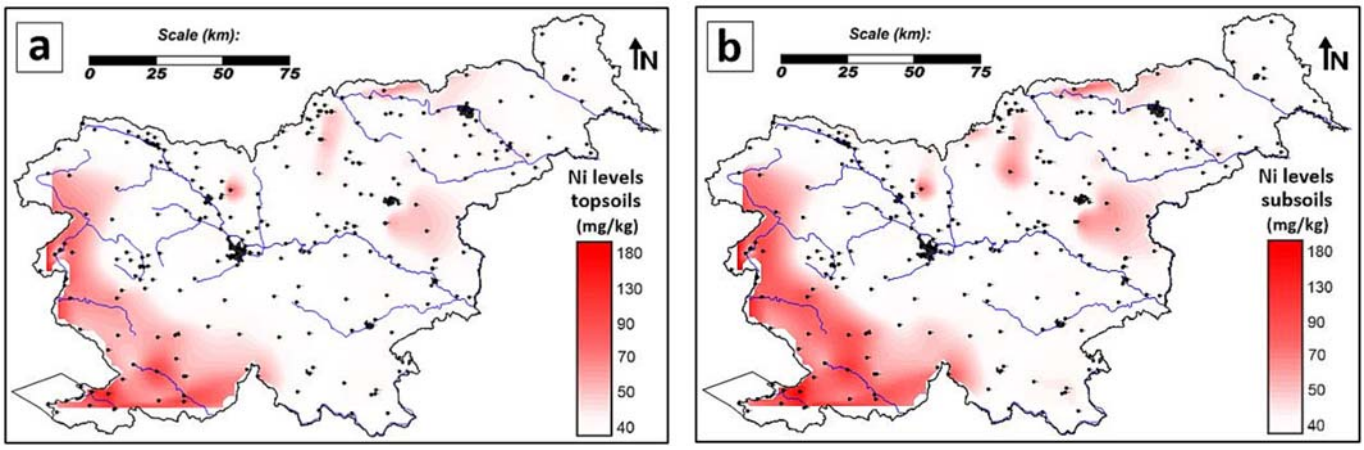

Fig. 4. Spatial distribution of Ni in topsoils (a) and in subsoils (b). The colour scale indicates elemental levels in mg/kg.

points below the blue line represent higher levels in subsoils.

As shown in Fig. 6a levels of Cu are mostly higher in topsoils compared to the subsoils overlaying all lithological units. The same is also true for Zn (Fig. 6b) indicating that the increased amounts of these two elements in topsoils could be the result of an anthropogenic enrichment on a regional scale. Elements Pb and Hg (Fig. 6c and d) are evenly distributed in both layers in most lithologies except in metamorphic rocks in which higher levels have been noted in topsoils compared to subsoils. Fig. 7 presents the spatial distribution of Cu, Zn, Pb, and Hg levels in the topsoil layer, in which areas of increased elemental levels are marked by red colour, and Fig. 8 shows the spatial distribution of ER factors across the study area for these elements and indicates areas of enrichments. Fig. 8a and b confirm that Cu and Zn values are overall mostly higher in topsoils in comparison to subsoils in all lithological units. Elevated levels of Zn in topsoil samples in relation to the subsoils have especially been noticed in the area around the steel

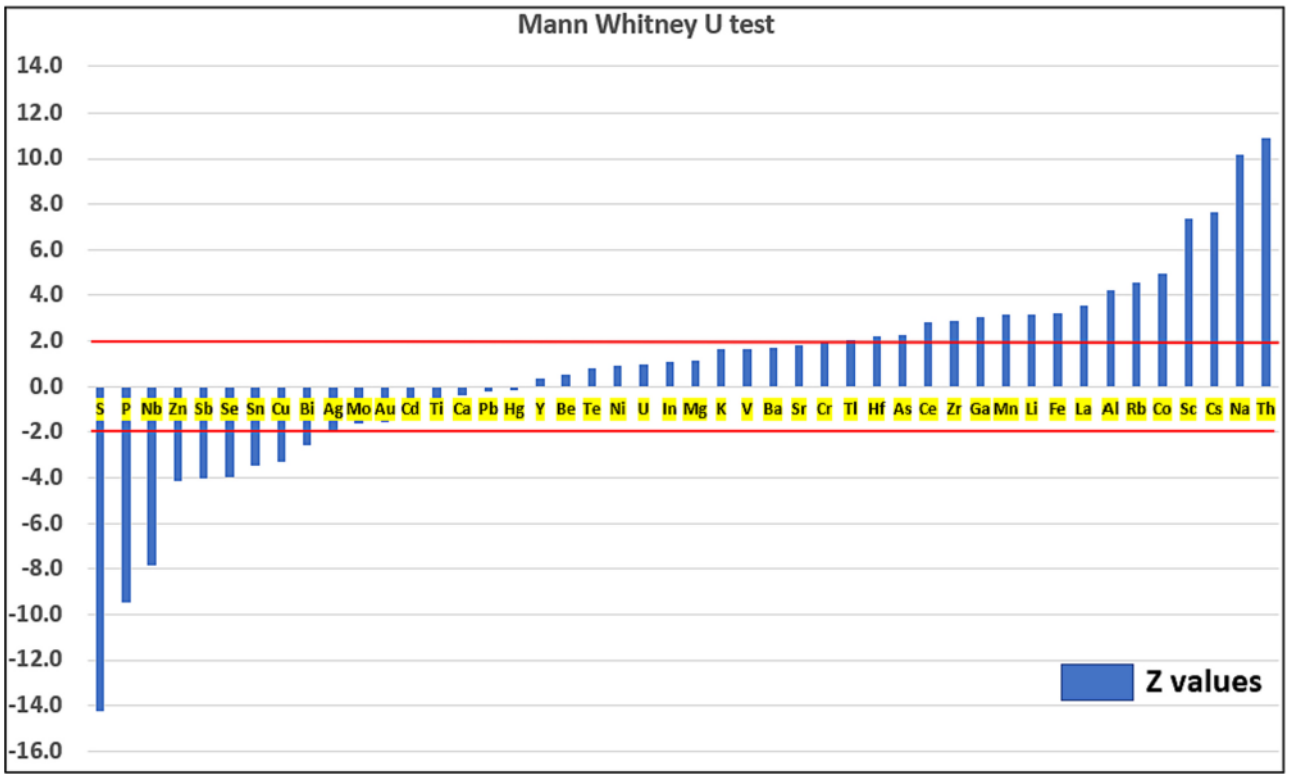

Fig. 5. Mann Whitney U test to assess the variations of elemental levels between the topsoil and subsoil samples. Elements with negative Z values have higher elemental levels in topsoils whereas elements with positive Z values have higher elemental levels in subsoils.

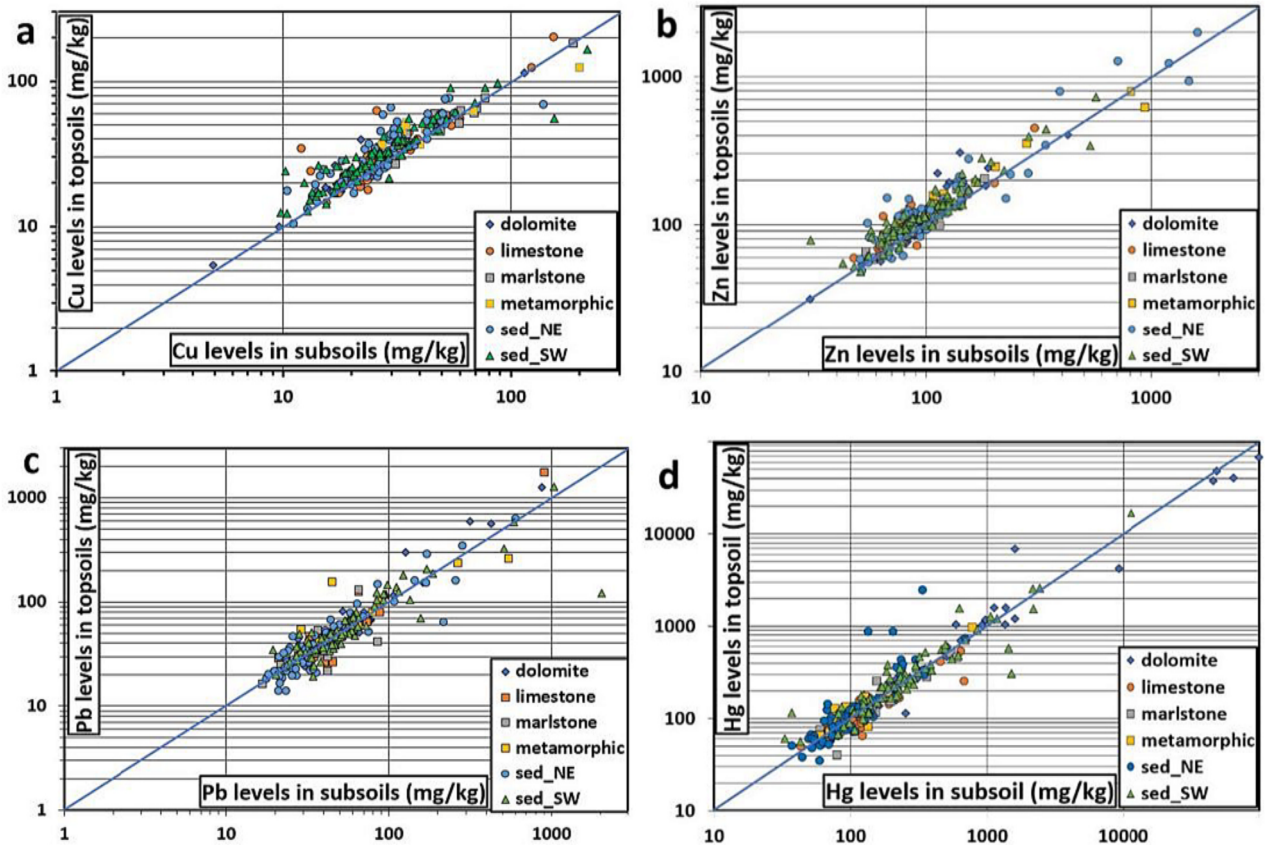

Fig. 6. Comparison of Cu(a), Zn(b), Pb(c), and Hg(d) levels (lognormal values) between topsoil and subsoil samples.

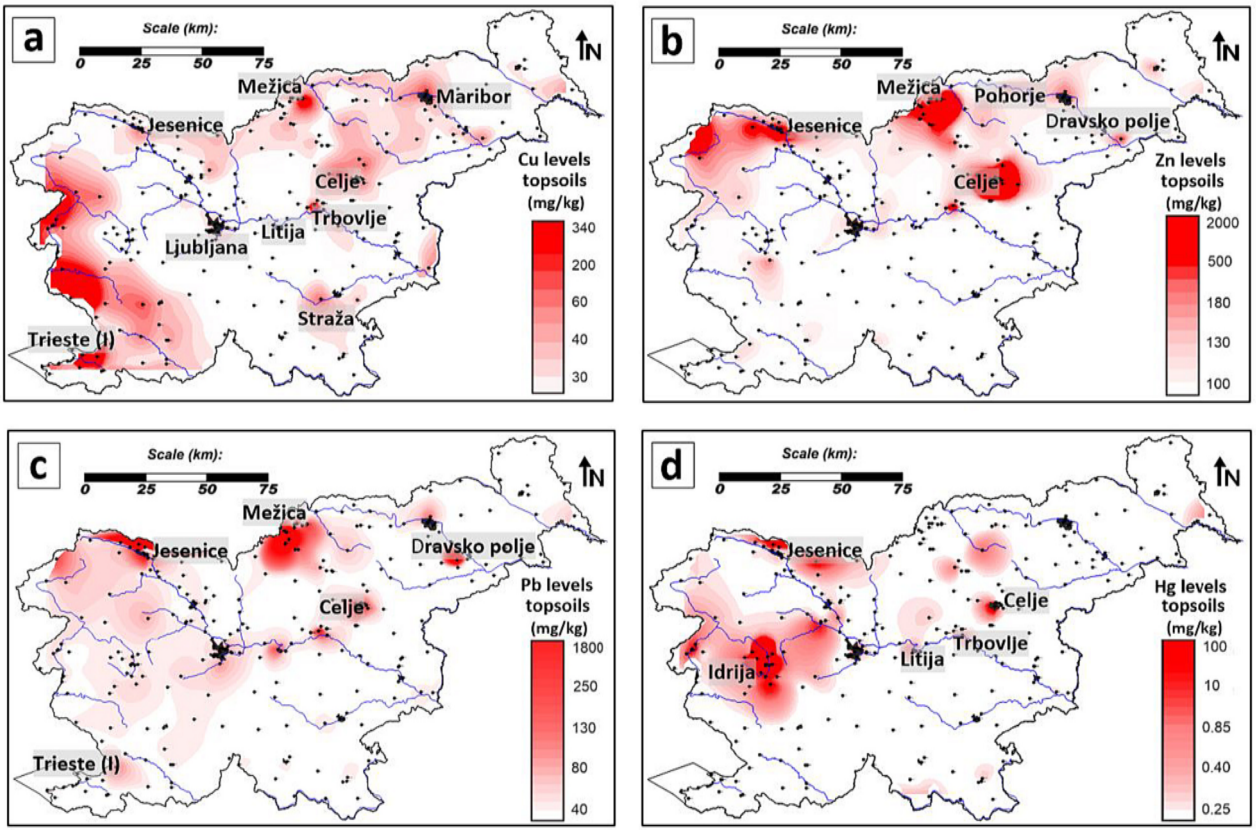

Fig. 7. Spatial distribution of Cu(a), Zn(b), Pb(c), and Hg(d) in topsoil.

mill and former Zn smelter in Celje, the steel mill in Jesenice, around old zinc mine workings Mežica, around old mine workings Litija and on the Pohorje massif (Fig. 8b), as well as generally throughout the whole study area.

However, similar regional trends were not observed in the case of Pb and Hg, and local trends prevail. Fig. 8c shows that the location of biggest discrepancies in the levels of Pb between topsoils and subsoils occur in a historic lead mining area of Mežica where the levels of Pb in topsoils reach up to 1750 mg/kg and in subsoils up to 906 mg/kg. Areas where higher differences of Hg levels between the two layers are around the historic mercury mining town of Idrija and its surroundings, around Litija and Trbovlje mining towns, around Celje's abundant Zn smelter around the industrial town of Jesenice and in the NW part of Slovenia (Fig. 8d). Noticeable increase of Hg levels differences is also observed in NW Slovenia in the mountainous area of Julian Alps.

5. Discussion

The results of the geochemical investigation of samples from soils superimposed on different lithological units show that among the analysed elements the biggest differences in the median values of elemental levels between different lithologies have been observed for elements Ti, Zr, Ca, and Ni (Fig. 2). Relatively higher amounts of Ti were noticed in topsoils and subsoils overlaying metamorphic and igneous rocks of the Pohorje massif, which is most probably the result of chemical weathering of Ti silicates and oxides originating from metamorphic and igneous rocks from the area (Miler et al., 2019) and its mobilisation into soils. Higher amounts of Ti have also been noticed in soils on top of alluvial sediments from the NE part of Slovenia, which have mainly derived from the metamorphic and igneous rocks of the Pohorje and similar mountain ridges, composed of igneous and metamorphic rocks. The median values of Ti from soils from both lithological units are a few times higher than those from other lithological units (Fig. 2). Higher Ti values in soils from igneous and metamorphic rocks were also observed by Abbaslou et al. (2013), who studied the elemental composition of soils developed on igneous parent rocks in southern Iran. Based on findings from Abbaslou et al. (2013) it was anticipated that median values of Zr would also be higher in soils from igneous and metamorphic lithological units, but an opposite trend was observed in our study in which higher levels of Zr were observed in carbonates. It is presumed that the elemental composition of igneous and metamorphic rocks of the Pohorje massif is such that the element Zr is not present in sufficient amounts to enrich the soils during the soil forming processes. However, more in-depth studies would need to be conducted to support such an assumption.

An opposite trend to Ti was observed for the element Ca, i.e. metamorphic and igneous rocks, and alluvial sediments from the NE part of Slovenija show significantly lower median levels to lithological units consisting mostly of carbonate rocks. Since Ca is one of the main components of carbonates higher median levels are most likely due to the mobilisation of Ca into soils during the soil forming processes, or due to the presence of skeletal particles of carbonate rocks in sampled soils. Fig. 3c shows higher median levels of Ca in subsoils than in topsoils which is most likely due to Ca being diluted from topsoils and accumulating in lower soil layers. This is also in agreement with Lichter (1998) who observed the depletion of Ca in surface soil horizons. In analysed soil samples amounts of Ni were also higher in marlstones in comparison to other lithologies (Fig. 4a and b). The reason for this could be higher amounts of Ni in the flysch sedimentary sequence which is included in the marlstone lithological unit and forms the bedrock lithology. Elevated levels of Ni and Cr in the flysch sequence from the coastal area of Slovenia have also been reported by Lenaz et al. (2003), Mikes et al. (2006), Šajn et al. (2012), and others. Other geogenic variations in the elemental composition of soils which were detected in this study and would be worth future investigations are Mo, Ce, and La enrichments on soils developed on limestones, Sr enrichment on clastic

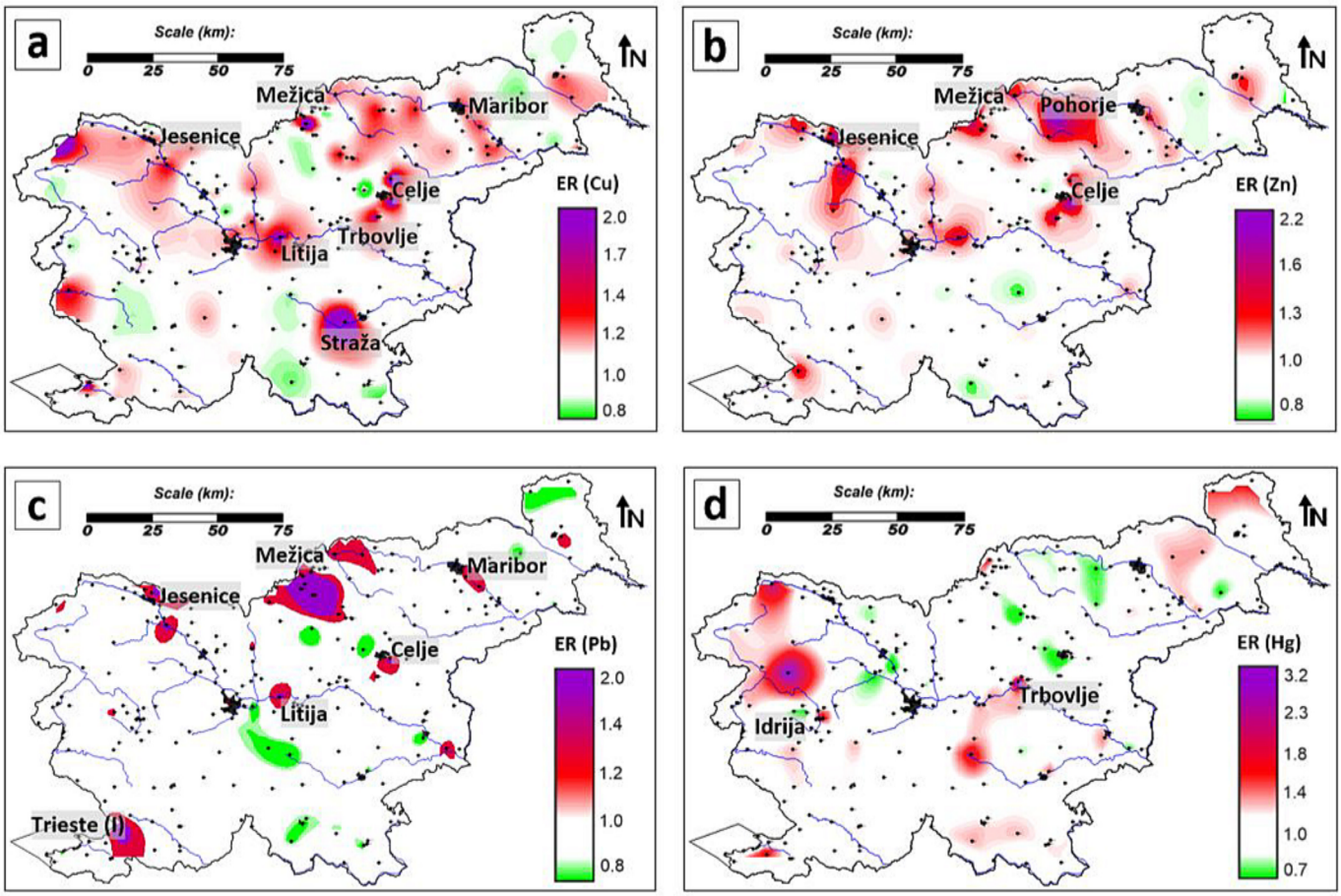

Fig. 8. Enrichment ratio for Cu (a), Zn (b), Pb (c), and Hg (d). Red and purple colours represent areas with higher concentrations of certain elements in topsoils and green areas show higher concentrations in subsoils. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

sedimentary rocks, Sb enrichment on igneous and metamorphic rocks and Nb enrichment on metamorphic and igneous rocks and limestones, and its depletion on clastic sedimentary rocks.

The next part of the discussion will be dedicated to the distributions of anthropogenically influenced elements in soils. Distribution of ER for Cu between top and sub-soil layers (Fig. 8a) shows the most uneven spatial patterns pointing out that many different natural and anthropogenic factors play a role in the Cu distribution. Levels of Cu are generally higher in topsoils compared to subsoils in north-eastern and south-western parts of Slovenia, and around industrial and mining areas (Fig. 8a). Higher Cu values in topsoils in agricultural lands in north-eastern and south-western parts of Slovenia might indicate a possible link between Cu accumulation in topsoils and agricultural and wine-growing practices, which has also been highlighted by many other authors (Adrees et al., 2015; Micó et al., 2006; Rusjan et al., 2007; Yruela, 2005). The main reason could be the application of Cu containing compounds (e.g., Bordeaux mixture as fungicide) which are broadly used to fight and control fungal diseases (Gianessi and Williams, 2011). Hence areas of intensive agriculture and wine growing regions (Pomurska ravnina, Dravsko polje, Sub-Mediterranean vineyard region) show elevated levels of Cu in topsoils also in this study. For instance, median Cu levels in topsoils on Dravsko polje and Goriška Brda are 48 mg/kg and 90 mg/kg respectively, while the median concentration in subsoils are 30 mg/kg and 55 mg/kg respectively (Fig. 6a).

In the area of Dravsko polje we also detected a potential influence of intense traffic from the city of Maribor, which is with approximately 110.000 inhabitants the second largest city in Slovenija. Elevated levels of Cu in the area around Maribor were previously also detected by Gaberšek and Gosar (2018). Higher Cu values have also been recorded in the capital city of Slovenia Ljubljana, where intense traffic is also believed to be the reason for this (Teran et al., 2020). Cu anomalies have also been noticed in industrial areas, like Celje and Straža na Dolenjskem (Fig. 8a). Higher amounts of Cu in topsoils around Celje and Štore can be assigned to the influence of heavy industrial and steel manufacturing facilities located in the vicinity of the town. Cu enrichment around steel production areas has already been recognised by researcher Harber and Forth (2001). Regarding higher Cu amounts in topsoils in Straža na Dolenjskem the source could be the nearby wood industry, which can potentially use wood preservatives that contain Cu (Temiz et al., 2006). Elevated levels of Cu in soils have also been detected in historical and current mining areas like Litija, Velenje, and Mežica (Fig. 7a). An interesting pattern was observed in NW Slovenia in the mountainous areas of the Julian Alps, where Cu is enriched in the topsoil layer. This enrichment could be attributed to the impacts of the old mining area Rabelj or to the regional transport of the contamination by SW winds from the industrialised area of Po Valley in Italy or perhaps even to the natural emissions from the volcano Etna in Sicily (Calabrese et al., 2011). Another possible source for Cu enrichment could also be iron ore processing activity in Spodnja Radovna which finished at the end of the 19th century and left an environmental footprint in its vicinity (Ferjan Stanič et al., 2013).

A comparison between Zn and Pb levels in topsoils and subsoils reveals that in the area of Mežica and its surroundings, higher amounts of both of these potentially toxic elements (PTEs) have been detected in topsoils (Fig. 7b and c). At this location levels of Pb and Zn in surface soils reach 1750 mg/kg and 450 mg/kg respectively and in subsoils it

reaches 906 mg/kg and 425 mg/kg respectively (Fig. 7b and c). The reason for elevated levels in top and sub soils is due to historical mining and smelting of base metal ore in the Mežica Valley. As described by many authors (Bole et al., 2002; Fux and Gosar, 2007; Gosar and Miler, 2009; Miler and Gosar, 2010; Svete et al., 2001) enrichment of Pb, Zn, and other PTEs in soils, sediments, water, and dust is a result of 300 years of lead and zinc mining and smelting in this area. Although mining and smelting activities ceased in 1993, the negative footprint they left on the different ecosystems is still present and is burdening the environment. Increased levels of Pb and Zn in topsoils, compared to subsoils indicate, that the anomaly is anthropogenically produced, where the source of elements was the dust emissions from the historic smelter and these particles were transported by air and deposited on the uppermost soil layer. Another source of Pb and Zn could also be the washing of enriched material from mine waste deposits which were piled in the nearby hills (Miler et al., 2022). If natural (geogenic) enrichment is the reason for this anomaly, higher Pb and Zn levels would probably be recorded in the bottom layer, which was not the case in this study. The next noteworthy topsoil Pb and Zn anomaly is located near the industrial town of Jesenice. Levels of Pb reach 1300 mg/kg in topsoils and 1030 mg/kg in subsoils and levels of Zn reach 730 mg/kg in topsoils and 566 mg/kg in subsoils (Fig. 7b and c). The source of elevated Pb and Zn levels is believed to be related to the ironwork industry, which is also in agreement with Teran et al. (2020). Another Pb anomaly in topsoils is located on the coast, near the border between Slovenia and Italy (Fig. 8c). Topsoil Pb values reach 126 mg/kg and subsoil values 65 mg/kg. Elevated values in topsoils in this location are believed to be related to the emissions from the ironwork industry in Trieste, which was also recognised by Teran et al. (2020).

Levels of Zn are generally higher in topsoils than in subsoils in the whole study area. The area where the largest discrepancy has been noticed is on the Pohorje massif (Fig. 8b), where levels of Zn in the topsoil layer are up to three times higher than in the subsoils. While Zn levels in topsoil in this area are within the normal regional value (Fig. 7b), and no extensive usage of phytopharmaceutical substances that could contain Zn has been recorded in the vicinity, a potential reason for this observation could be the depletion of Zn from the granodiorite massif of Pohorje, combined with regional transport of Zn-enriched dust from the historic mining area of Mežica and other industrialised areas in the vicinity by SW winds and its deposition on this elevated terrain (between 1000 and 15,000 m a.s.l.) by orogenic precipitation. However, future studies would be needed to identify the underlying process to explain this observation. Higher levels of Zn and Pb in topsoils have also been detected in the areas next to the Drava River on the area of Dravsko polje (Fig. 7b) where contamination from the Drava River alluvial sediments from historic Pb-Zn mines upstream (Šajn et al., 2012) is suspected to be the reason for the anomaly. Maximum levels of Zn in topsoils and subsoils have been measured around the industrial town of Celje, where amounts of Zn reach 1990 mg/kg in topsoils and 1500 mg/kg in subsoils, in comparison to the median value of 90.9 mg/kg for topsoil in this study. The reason for this is the atmospheric dust deposition emitted from historical Zn smelter, which was operational between 1873 and 1970. Although it ceased production in 1970 the effect of this smelter in soils can still be detected up to 14 km away (Žibret and Šajn, 2008).

Extremely high levels of Hg were detected in soil samples in the old Hg mining town of Idrija and its surroundings (Fig. 7d). This is due to 500 years of mining and ore roasting at the world's second-largest historical Hg mine. Since environmental regulations and safety standards were very poor throughout the time that the mine and processing plants were in production, Hg emissions heavily contaminated the environment and very high levels of Hg have been reported in this area in soils, sediments, water, and dust by numerous researchers (Bavec, 2014; Biester et al., 2000; Gosar and Šajn, 2001; Hess, 1993; Kocman et al., 2004; Teršič, 2011; Žibret and Gosar, 2006). The sampling campaign, which was carried out as part of this study recorded Hg levels in topsoils up to 68 mg/kg and in subsoils up to 99 mg/kg. In a few locations in the Idrija historical mining area levels of Hg in subsoil samples are higher than in topsoil samples (Fig. 8d). This could be due to the mobilisation of Hg from lower horizons, especially from potential historical mine waste dumps or ore roasting sites around the mine. We can also seek geogenic origin for this observation - these anomalies might be identifying previously unrecognised mineralised zones, especially in the vicinity of known mineralisation. The third explanation for Hg enrichment in the bottom soil from the area is that native Hg evaporated from the upper soil layer because of the effect of solar radiation, which is also in agreement with Gustin et al. (2002) However this cannot be the case if Hg is present in form of cinnabar. Apart from Idrija, slightly elevated levels of Hg were also detected around Litija and Trbovlje mining towns (Fig. 7d), where Hg levels reach 1.5 mg/kg in topsoils and 0.9 mg/kg in subsoils. The reason for elevated levels of Hg around Litija is assumed to be the previous extraction of Hg from poly-metallic orebodies and the presence of Hg in numerous waste deposits, which continue to leach PTEs into the environment (Gosar et al., 2016; Miler et al., 2022). Since the cement industry has been recognised as an anthropogenic source of mercury (Kogut et al., 2021) emissions from burning waste in the cement kilns in the Lafarge cement plant in Trbovlje could be the source of elevated levels of Hg in Trbovlje and its surroundings. Another reason could be elevated levels of Hg in mine waste material from the Trbovlje coal mine, which was often used in this area as aggregate material.

Further areas of high Hg levels in topsoils are found around the industrial towns of Jesenice and Celje. As with some previously mentioned PTEs (Cu, Pb, Zn), in Jesenice elevated Hg can be associated with iron works (Šajn et al., 1998; Teran et al., 2020) and around Celje with old Zn smelter (Žibret and Čeplak, 2021). As indicated in Fig. 7d, elevated levels of Hg have also been detected in the belt stretching N-S in the NW part of Slovenia. This can be explained by the intense usage of Hg-containing explosives during the Soča (Isonzo) front in the First World War, as some of the heaviest battles of the conflict happened in this area. This observation is also in agreement with previous study of Pirc and Budkovič (1996) who recognised the use of explosives containing Hg fulminate during the First World War as a Hg source in the area of the Soča front.

Comparison between the results of elemental analyses of topsoils and subsoils which developed on alluvial sediments shows that generally levels of Cu, Pb, Zn, and Hg are higher in topsoils than in subsoils (Fig. 8). This can be explained by the fact, that major urbanised areas in Slovenia, together with accompanying amenities (industrial facilities, foundries, human dwellings, waste deposits, heavy traffic infrastructure, etc.), have been developed mainly on low-lying alluvial plains. As has been indicated by many researchers (Gaberšek et al., 2022; Miler and Gosar, 2010; Teran et al., 2020; Žibret et al., 2018) these anthropogenic activities have a high potential to enrich soils with different PTEs. Median levels of the above-mentioned elements are also higher in topsoils overlaying metamorphic rocks. It can be seen on maps in Fig. 8 (a-c) that the distribution of geochemical anomalies is not evenly distributed across the entire area of metamorphic rocks but is instead concentrated in the vicinity of base metal mining area Mežica with its former metallurgical processing plants. This indicates that elevated levels of trace elements Zn, Cu, and Pb are not a result of weathering of metamorphic rocks, which would increase levels of these elements in topsoils but are most likely the result of various anthropogenic activities.

6. Conclusions

The comparison of the elemental composition of topsoil and subsoil samples, which were collected from 249 different locations on a national scale (Slovenia), shows deviations in both soil layers, which can be a consequence of natural processes and anthropogenic activities. Results show increased levels of elements characteristics for rock-forming minerals (Th, Na, Cs, Sc, Co, Rb, Al, La, Fe, Li, Mn, etc.) in the bottom layer of soils, while some common anthropogenic pollutants (Zn, Sb, Se,

Sn) are more abundant in the upper soil layer. A higher abundance of P in topsoil can be explained by the presence of organic matter. The highest deviations of elemental levels in both soil layers related to the bedrock geology have been detected for Ti, Zr, Ca, Ni, Mo, Nb, Hg, and Sr. Ti levels are higher on marlstones, while Ca is, as expected, more abundant on top of carbonates. Although anthropogenic activities (such as mining and ore processing, industrial processes, traffic, agriculture, etc.) usually cause enrichment of various PTEs in topsoil compared to background levels this study also showed that levels of certain metals (e.g., Pb, Cu, Zn) are higher in topsoil compared to the bottom layer of soil, usually for a factor 2 or more, even decades after a certain activity ceased. Such examples were detected in historical mining areas of Mežica, Idrija, and Litija. Elevated levels of PTEs were also measured in topsoils overlaying alluvial sediments. This has been explained by the fact, that urbanised areas, where most point sources of pollution have been identified (such as different industrial facilities, steelworks, heavy traffic, etc.), are positioned on top of alluvial bedrock. In the case of Hg, both soil layers are equally enriched with this element around the historical Hg mine and smelting area in Idrija, compared to the surrounding areas. However, in certain localities close to the Hg ore deposit, this study identified certain areas of higher Hg levels in subsoils compared to topsoil. This could be explained by the exhalation of Hg from the ore deposit. Further studies will focus on elemental distribution in soil profiles on contaminated and control areas to distinguish between natural (geogenic) and anthropogenic enrichments.

CRediT authorship contribution statement

Emil Pučko: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft. **Gorazd Žibret:** Conceptualization, Investigation, Supervision, Validation, Writing – review & editing. **Klemen Teran:** Formal analysis, Investigation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix 1. QAQC data (average RE and RPD) for all analysed elements in topsoil and subsoil samples; and the minimal detection limits (MDL)

Element	Unit	MDL	Topsoil		Subsoil	
			R%	RPD (%)	R%	RPD (%)
Mo	mg/kg	0.01	100[a,b]	3.6	102[g,h,i]	4.3
Cu	mg/kg	0.01	101[a,b,c,d]	1.9	98[e,f,g,h,i]	2.4
Pb	mg/kg	0.01	107[a,b,c,d]	2.4	105[e,f,g,h,i]	2.7
Zn	mg/kg	0.1	99[a,b,c,d]	2.9	100[e,f,g,h,i]	2.4
Ag	µg/kg	2	99[a,b]	5.6	103[g,h,i]	4
Ni	mg/kg	0.1	100[a,b,c,d]	2.2	107[e,f,g,h,i]	3.2
Co	mg/kg	0.1	98[a,b,c,d]	2.3	107[e,f,g,h,i]	3.9
Mn	mg/kg	1	99[a,b,c,d]	1.7	101[e,f,g,h,i]	1.7
Fe	%	0.01	99[a,b,e]	1.3	98[e,f,g,h,i]	1.6
As	mg/kg	0.1	101[a,b,e]	2.3	103[e,f,g,h,i]	2.4
U	mg/kg	0.1	110[a,b,e]	2.0	107[e,f,g,h,i]	5.7
Au	µg/kg	0.2	78[a,b]	34.5	103[e,f,g,h,i]	40.6
Th	mg/kg	0.1	104[a,b,e]	3.5	109[e,f,g,h,i]	3.8
Sr	mg/kg	0.5	112[a,b]	2.4	99[e,f,g,h,i]	4.1
Cd	mg/kg	0.01	106[a,b,c,d]	6.6	110[g,h,i]	8.5
Sb	mg/kg	0.02	94[a,b]	5.8	109[g,h,i]	11.8
Bi	mg/kg	0.02	111[a]	2.7	102[e,g,h,i]	7.3
V	mg/kg	1	103[a,b]	1.2	100[e,f,g,h,i]	1.3
Ca	%	0.01	105[a,b]	1.2	99[e,f,g,h,i]	1.9
P	%	0.001	102[a,b]	3.1	102[e,f,g,h,i]	3.4
La	mg/kg	0.5	103[a,b]	2.4	108[e,g,h,i]	3
Cr	mg/kg	0.5	93[a,b,c,d]	2.2	103[e,f,g,h,i]	3.9
Mg	%	0.01	102[a,b]	1.5	99[e,f,g,h,i]	2.2
Ba	mg/kg	0.5	77[a,b]	2.3	105[e,f,g,h,i]	2.9
Ti	%	0.001	99[a,b]	4.6	101[g,h,i]	4.9
B	mg/kg	20	BDL	BDL	BDL	BDL
Al	%	0.01	106[a,b]	1.5	98[e,f,g,h,i]	1.5
Na	%	0.001	106[a,b]	8.9	82[e,f,g,h,i]	1.8
K	%	0.01	107[a,b]	1.9	101[e,f,g,h,i]	3.3
W	mg/kg	0.1	BDL 97	BDL	BDL	BDL
Sc	mg/kg	0.1	104[a,b]	2.9	105[e,f,g,h,i]	2.4
Tl	mg/kg	0.02	96[a,b]	5.9	99[f,g,h,i]	4.8
S	%	0.02	–	1.2	91[e,f,g,h,i]	0
Hg	µg/kg	5	87[a,b,c,d]	11.0	98[g,h,i]	19.1
Se	mg/kg	0.1	–	21.6	102[g,h,i]	20.2
Te	mg/kg	0.02	113[a,b]	37.2	100[g,h,i]	21.2
Ga	mg/kg	0.1	105[a,b]	3.3	102[e,f,g,h,i]	3.3

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(*continued*)

Element	Unit	MDL	Topsoil		Subsoil	
			R%	RPD (%)	R%	RPD (%)
Cs	mg/kg	0.02	100[a,b]	4.7	104[f,g,h,i]	3.9
Ge	mg/kg	0.1	BDL	BDL	BDL	BDL
Hf	mg/kg	0.02	–	14.8	75[g,h,i]	13.1
Nb	mg/kg	0.02	92[a,b]	4.5	104[g,h]	7.8
Rb	mg/kg	0.1	105[a,b]	2.3	103[e,f,g,h,i]	3.4
Sn	mg/kg	0.1	110[a,b,d]	7.6	104[e,f,g,h,i]	12.6
Ta	mg/kg	0.05	BDL	BDL	BDL	BDL
Zr	mg/kg	0.1	106[a,b]	4.2	82[g,h,i]	8.7
Y	mg/kg	0.01	106[a,b]	1.9	98[e,f,g,h,i]	3
Ce	mg/kg	0.1	101[a,b]	2.1	102[e,f,g,h,i]	2.2
In	mg/kg	0.02	–	16.7	110[e,f,g,h,i]	18
Re	µg/kg	1	BDL	BDL	BDL	BDL
Be	mg/kg	0.1	119[a,b]	13.8	104[g,h,i]	14.1
Li	mg/kg	0.1	107[a,b]	2.3	97[e,g,h,i]	4.7
Pd	µg/kg	10	BDL	BDL	BDL	BDL
Pt	µg/kg	2	BDL 101	BDL	BDL	BDL
Pr	mg/kg	0.02	NA	NA	105[g,h,i]	2.6
Nd	mg/kg	0.02	NA	NA	103[g,h,i]	4
Sm	mg/kg	0.02	NA	NA	102[g,h,i]	3.3
Eu	mg/kg	0.02	NA	NA	97[g,h,i]	4.1
Gd	mg/kg	0.02	NA	NA	100[g,h,i]	4.6
Tb	mg/kg	0.02	NA	NA	98[g,h,i]	4.2
Dy	mg/kg	0.02	NA	NA	100[g,h,i]	4.9
Ho	mg/kg	0.02	NA	NA	98[g,h,i]	5.8
Er	mg/kg	0.02	NA	NA	102[g,h,i]	4.6
Tm	mg/kg	0.02	NA	NA	101[g,h,i]	4.9
Yb	mg/kg	0.02	NA	NA	101[f,g,h,i]	5.2
Lu	mg/kg	0.02	NA	NA	102[g,h,i]	8.7

[a] DS10.
[b] OREAS45EA.
[c] CC141.
[d] BCR-320R.
[e] OREAS45D.
[f] OREAS45E.
[g] BVGE001.
[h] DS11.
[i] OREAS262.

Appendix 2. Elements which were excluded from further statistical analyses due to unsatisfactory QAQC

	Elements which had >20 % of measurements under the detection limit	Mean RE above 20 %	Mean RPD above 30 %	Number of excluded elements
Topsoil	B, Ta, W, Re, Ge, Pd, Pt	U, V, Tl, Te	Au	12
Subsoil	B, Ta, W, Re, Ge, Pd, Pt	Hf	Au	9

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