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Geochemical Characteristics and Preliminary Assessment of Geochemical Threshold Values of Technology-Critical Elements in Soils Developed on Different Geological Substrata Along the Sava River Headwaters (Slovenia, Croatia)

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Abstract

The increased demand for technology-critical elements (TCEs) in emerging technologies brings about the need to determine their spatial distribution in the environment and establish regulatory guidelines. In this paper, concentrations of Li, Sc, Nb, W, Ga, Ge, and REY (rare earth elements, including yttrium) in soils collected from different parent materials in the upper catchment of the Sava River (Slovenia, Croatia) were analysed. Results of multivariate (principal component analysis) and univariate (threshold methods) statistical techniques were used to determine geochemical characteristics of studied soils to identify the background variations and to establish geochemical threshold values. The investigated area is characterized by great lithological diversity and substantial variation of TCE concentrations. Among methods for assessment of geochemical threshold, the TIF (Tukey inner fence) and 97.5th percentile delivered the most reasonable results. Some exceedances above the 97.5th percentile were natural in origin, caused by local geology. These findings can provide baseline data because little is known about TCE variation on different geological substrata.

Technology-critical elements (TCEs) are a heterogeneous group of elements (rare earth elements, platinum group elements, germanium, gallium, niobium, lithium, tungsten, antimony, etc.) with growing application in the emerging technologies (Cobelo-García et al. 2015; Romero-Freire et al. 2019). As their usage increased, it has become important to provide basic knowledge about their natural spatial distribution in different environmental compartments, soils

particularly (Alfaro et al. 2018; Filella and Rodríguez-Murillo 2017; Négrel et al. 2019).

Soils along the upper catchment of the Sava River, an area spread in Slovenia and northwestern part of Croatia, have developed on diverse lithological units, which makes them very suitable for studying the variation of TCE concentrations. Heretofore, there is a lack of data on TCE geochemistry in soils developed on different geological substrata at the European scale. The most important studies include the European geochemical mappings (Reimann et al. 2018 and references therein; Salminen et al., 2005) and geochemical investigation of TCEs in soils of southwestern Spain (Fernández-Caliani et al. 2020). In the Sava River Basin, the majority of geochemical investigations have been related to evaluating mining (Šajin and Gosar 2014) and different industrial activities (Šajin 2003, 2005). A stepping stone was made by extensive geochemical surveys (Gosar et al. 2019; Halamić and Miko 2009) that encompassed different soil parent materials. However, many TCEs (Ge, W, and some REE) were omitted from these studies or their concentrations were below the detection limit. Consequently, their geochemical background and threshold values are not determined.

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The geochemical background can be considered as a concentration range of a chemical element in a sampled environment concerning its spatial and temporal variability (Gałuszka 2007; Reimann and Garret 2005). The outermost limit of geochemical background separating the normal and anomalous element concentration (Gałuszka and Migaszewski 2011; Matschullat et al. 2000) is usually termed the geochemical threshold. Providing these values are very important because their determination may be the first step towards establishing regulatory guidelines (Alfaro et al. 2018; Fedele et al. 2008).

The main objectives of this study included: (a) investigation of the mutual relationship between technology critical and major elements using multivariate principal component analysis—a proxy for determining the host phases of TCEs (mineralogy); (b) evaluation of background variation of TCEs and their comparison with concentrations in the literature data; and (c) preliminary assessment of geochemical threshold values for TCEs.

Material and Methods

Study Area

The investigated area encompasses territory along the upper catchment of the Sava River in Slovenia and the northwestern part of Croatia (Central Europe). The Sava River is a major Danube tributary that flows through Slovenia and Croatia, along the northern border of Bosnia and Herzegovina, and finally through Serbia. It is 990 km long, with drainage basin covering 97,713 km². The upper studied course comprises 12,680 km² of surface area. The headwaters are dominated by mountain terrains, whereas the middle and lower part of the basin are characterized by a very low slope (Babić-Mladenović et al. 2013). The Sava River Basin intersects three climate types: alpine, submediterranean, and continental (Tošić et al. 2016). On average, the amount of annual rainfall for the Sava River headwaters in the period 1961–1990 was 1,600 mm and more than 3,000 mm in the Alpine region (Ogrinc et al. 2008; Zanon et al. 2010). The average annual temperature for the entire Sava basin was 9.5 °C.

The geological setting of the investigated area is highly complex because it is positioned between the five main geotectonic units: (1) the Adriatic–Apulian foreland; (2) the Dinarides; (3) the Southern Alps; (4) the Eastern Alps; and (5) the Pannonian Basin (Placer 2008). In general, the uppermost part of the Sava River (along the Sava Dolinka and Bohinjka rivers) is dominated by the Triassic and Jurassic dolostone and limestone (Fig. 1).

Downstream of their confluence, a thick accumulation of fluvioglacial sediments prevails, deposited mainly during

the Quaternary (Vidic et al. 1991). The mineralogical composition of Quaternary sediments reflects the geology of the source area showing predominance of carbonates (> 86%) with a minor contribution of siliciclastic detritus. Besides these younger sediments, the Ljubljana Basin also is characterized by Paleozoic rocks, consisting of shales, quartz sandstones, and conglomerates. From the Zasavje area, the geological background is made of Triassic carbonates, together with Paleogene–Neogene volcanic and clastic rocks of the Pannonian Basin (Placer 2008). Surrounding the Sava River in the northwestern part of Croatia, the Triassic dolostone and Cretaceous limestone prevail in alternation with Quaternary deposits consisting of sands, marls, and clays rich in carbonate component (Šikić et al. 1979).

Due to lithological diversity of investigated area, the pedology is quite heterogeneous (Vrščaj et al. 2017). The dominant soil type is the Fluvisol, apart from the upper section in which Rendzina on carbonate rocks prevails. In the Ljubljana Basin, the Fluvisol alternates with Dystric and Eutric Cambisol and leached soils on different parent materials (Luvisols). The downstream section of the Sava River in Slovenia and northwestern part of Croatia is characterized by Fluvisol, Stagnosol, and Eutric Cambisol (Bogunović et al. 1997).

Samples Collection

Soil sampling was conducted during May 2017. Sampling locations (Fig. 2) were chosen based on the Basic geological map of Slovenia 1:100 000, available online at <https://biotit.geo-zs.si/ogk100/>. The main intention was to sample soil developed on different parent material presented along the watercourse of the Sava River and tributaries. A total of 31 composite topsoil samples was collected. At each sampling site, three subsamples were collected from a depth of approximately 5–20 cm and blended into a composite sample (1–2 kg). The samples were air-dried and sieved through a 2 mm sieve to eliminate gravel and coarse organic debris.

Analytical Methods

Particle size analysis of soils was carried out using a laser-based particle size analyser (LS 13,320, Beckman Coulter Inc.) The particle size distribution (PSD) was calculated on the basis of the Mie theory of light scattering (optical parameters: refractive index = 1.53; absorption index = 0.1). PSD was determined for native and chemically dispersed soil samples. The samples were treated with 30% H₂O₂ solution; 0.5 M (NaPO₃)₆ was added afterwards to avoid flocculation of particles before analysis.

Organic matter (OM) content was estimated using the loss on ignition (LOI) method (Salehi et al. 2011). LOI was

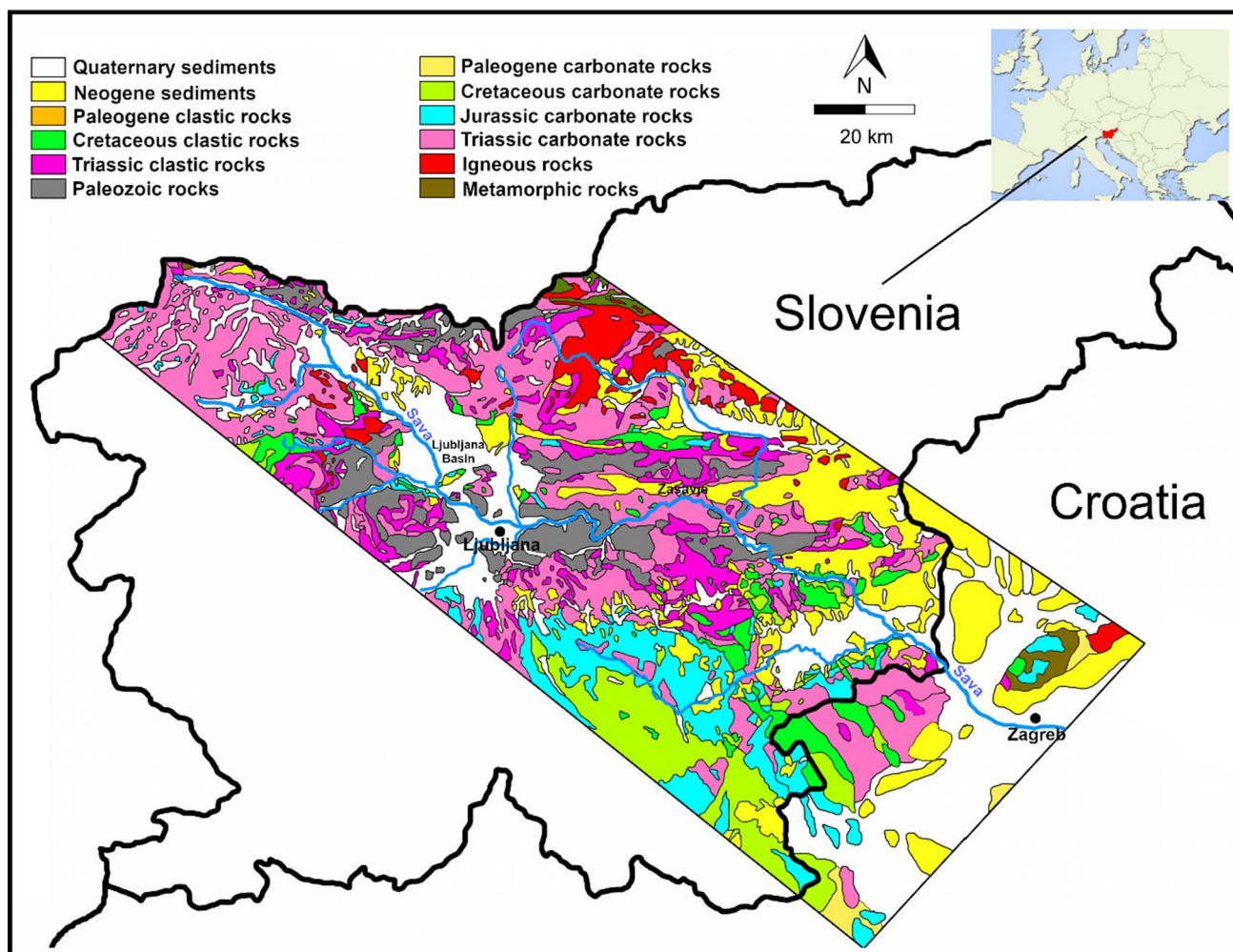


Fig. 1 Basic lithological units along the upper catchment of the Sava River [modified after Gosar et al. and references therein (2019) and Velić (2007)]

determined gravimetrically after dry ashing at 360 °C over 2 h.

Before geochemical analyses, a portion of each soil was ground to a fine powder using a ball-mill (Pulverisette 7; Fritsch). Samples were subjected to total digestion using microwave oven (Multiwave 3000, Anton Paar, Graz, Austria) in a two-step procedure; I-5 ml HNO₃ (65%, pro analysis, Kemika) + 1 ml HCl (37%, VLSI Grade, Rotipuran) + 1 ml HF (47–51%, for trace analysis, Fluka); II-6 ml H₃BO₃ (40 g l⁻¹, Fluka). After digestion, soil samples were diluted tenfold, acidified with 2% (v/v) HNO₃ (65%, s.p., Fluka), and indium (In, 1 µg L⁻¹) was added as internal standard. The multielement analysis was performed using a High-Resolution Inductively Coupled Plasma Mass Spectrometer (HR ICPMS) Element 2 (Thermo, Bremen, Germany). Several isotopes on different instrumental resolutions were examined to define isotopes free of interferences and obtain the best detection limits (Fiket et al. 2017b;

Filella and Rodushkin 2018). The selected isotopes of TCEs were measured at three resolutions: low resolution; (⁷Li), medium resolution (⁴⁵Sc, ⁶⁹Ga, ⁷⁴Ge, ⁹³Nb, ¹²¹Sb, ¹⁸⁶W, and REY subgroup—⁸⁹Y, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁵Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁷Er, ¹⁶⁹Tm, ¹⁷¹Yb, ¹⁷⁵Lu), and high resolution (¹⁵⁷Gd). External calibration method was used for quantification, with diluted multielement standard solutions (in the range of 0.1–10 µL⁻¹) prepared from the multielement or combining single reference standard solutions (Analytika, Prague, Czech Republic). Analytical quality control was performed by simultaneous analysis of procedural blanks and certified reference material of soil NCS DC 773,902 (GBW 7410). Recoveries for elements Li, Sc, Sb and REE varied between 86 and 105% (Fiket et al. 2017b) and for elements Ga, Ge, Nb, and W between 91 and 110% (Mikac et al. 2019). The limit of detection (LOD) of the method, calculated as three times the standard deviation of ten consecutive measurements of the procedural blank,

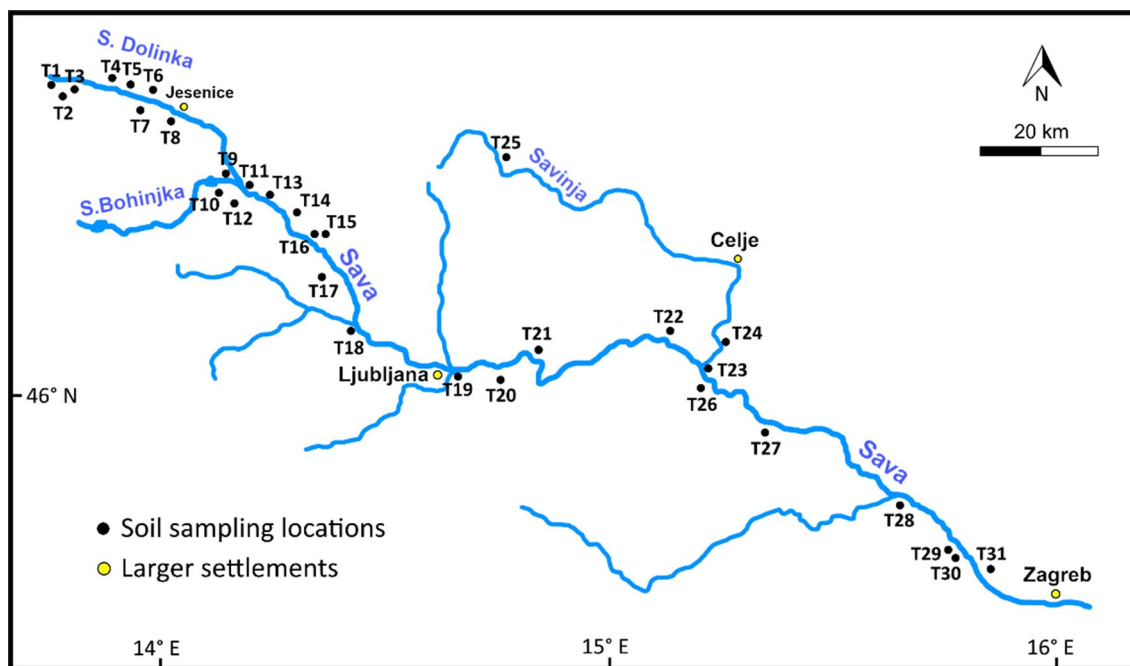


Fig. 2 Soil sampling locations along the upper catchment of the Sava River

varied for REE, Ge, and Sb between 0.01 and 0.03 mg kg⁻¹, and for elements Li, Ga, Nb, Sc, and W between 0.1 and 0.2 mg kg⁻¹. The limit of quantification (LOQ) was calculated as ten times the standard deviation and was about three times higher than LOD values.

Statistical Analysis

The compositional data are defined as vector of positive components with a constant sum constraint (c), such as 1 (proportions), 100 (percentages), or 10⁶ (mg kg⁻¹). It is obvious thereof that geochemical data are subjected to closure and statistical analysis directly applied to them can give us a misleading conclusion (Pearson 1897, Aitchison 1986). In order to reduce data closure effect and make the compositional data free from the unit sum constraint (Aitchison 1986), we applied centered log-ratio (clr) transformation before principal component analysis (PCA). The clr transformation can be derived by dividing each compositional variable (element) by the geometric mean of the composition and then taking the logarithm of each quotient (Drew et al. 2010).

The exception concerning the closure effect makes univariate statistics in which compared values do not come from a single, closed composition, as geochemical threshold values (Reimann et al. 2018). Thus, before their identification, preferably a simple log-transformation (base 10) was performed. The geochemical threshold values refer to simplistic statistical methods for recognizing the unusually high

(low) element concentrations and here we used the most effective methods proposed by Reimann et al. (2018). First relates to the calculation of Median + 2MAD (MD2MAD) approach on the log-transformed data (e.g., using log base 10), because they are usually right-skewed, which are then back-transformed to be shown as threshold according to the formula:

$$\text{Threshold} = 10^b \quad (1)$$

$$\text{where } b = (\text{median}_i(\log_{10}(x_i)) + 2 \times \text{MAD}_i(\log_{10}(x_i))) \quad (2)$$

$$\text{MAD}_i(x_i) = \text{median}_i|x_i - \text{median}_j(x_j)| \quad (3)$$

The second method (also computed using log base 10) is based on the Tukey inner (upper) fence (TIF) or upper whisker in a boxplot and is calculated by the formula:

$$\text{TIF} = Q3 + 1.5 \times \text{IQR} \quad (4)$$

where Q3 refers to 75th percentile, and IQR is the interquartile range (75th–25th percentile). The multiplying factor of 1.5 in the formula is based on the assumption of a symmetrical data distribution (Reimann and Caritat 2017).

Finally, the most simplistic approach relies on calculation of percentile of a given data set. We focused on the 90th, 95th, and 97.5th percentile (P90, P95, and P97.5) methods, which indicate 10%, 5%, and 2.5% of all samples as upper outliers.

Results

Detailed data of soil properties can be found in the Online Appendix. The soil organic matter (SOM) content varied significantly, with an average of 4.7%, which is comparable with the average of 4.3% found by Vrščaj et al. (2017). The lowest value (0.3%) was obtained in poorly developed soils T7 and T10 on steep slopes underlined by carbonate lithology, whereas the highest value was determined for the wetland soil (T1) at the spring of the Sava River (12.1%).

The predominant soil fraction was silt, accounting for 60.8%. The exceptions were samples T23, T25, and T28 in which the main fraction was sand. On average, the proportion of sand and clay particles was 29.4% and 9.8%, respectively. After organic matter removal, an increase of clay content and, consequently, lower mean grain size (M_z) in all samples were observed. The soils with the least visible change of PSD were those located closest to the river (T4, T13, T23, and T29) and carbonate-rich, in which more sand grains were observed. According to USDA (1987) textural soil classification, soils were mostly defined as silt loam, followed by silty clay loam and one sample of loam.

Concentrations of TCEs

The basic descriptive statistics for TCEs is shown in Table 1, whereas the whole data set can be found in Online Appendix. Concentrations of the TCEs in soil samples varied in a wide range depending on the soil parent material. The lowest concentrations of Li (11.5 mg kg^{-1}), Sc (2.5 mg kg^{-1}), Nb (2.2 mg kg^{-1}), W (0.29 mg kg^{-1}), Ga (3.0 mg kg^{-1}), Ge (0.22 mg kg^{-1}), and Sb (0.31 mg kg^{-1}) were observed in carbonate-rich soils (T4, T6, T7, T14, and T22) affected by frequent erosion, which disabled their deeper development. The highest concentrations for the same elements—Li (123 mg kg^{-1}), Sc (18.9 mg kg^{-1}), Nb (20.1 mg kg^{-1}), W (3.3 mg kg^{-1}), Ga (24.6 mg kg^{-1}), Ge (2.3 mg kg^{-1}), and Sb (2.8 mg kg^{-1})—were measured in soils developed on shale (T3, T21, and T26) and moraine debris (T8).

Concentrations of REYs

Rare earth elements in the data set were divided into several groups: the light rare earths (LREE, including elements from La to Gd); the heavy rare earths (HREE, including elements from Tb to Lu); and the middle rare earths (MREE, overlapping the first two groups and including the elements from Sm to Ho). Their concentrations in all analysed

Table 1 Descriptive statistics (mg kg^{-1}) for investigated soils ($n=31$). TCEs are arranged following the periodic table groups. REYs are listed at the end

	Min	Max	Mean	Median	Standard deviation	Skewness
Li	10.9	123	41.0	35.3	27.7	1.3
Sc	2.5	18.9	9.0	7.8	4.6	0.65
Nb	2.2	20.1	9.8	9.8	5.0	0.31
W	0.29	3.4	1.7	1.6	0.91	0.24
Ga	3.0	24.6	11.7	10.7	6.5	0.58
Ge	0.22	2.3	1.1	1.1	0.58	0.34
Sb	0.31	2.8	1.3	1.2	0.62	0.32
Y	4.8	46.2	17.5	15.0	9.8	1.2
La	6.3	51.3	24.5	21.7	12.5	0.52
Ce	12.3	106	50.4	44.6	26.5	0.52
Pr	1.2	13.5	6.0	5.1	3.3	0.62
Nd	5.0	53.6	23.0	19.7	12.9	0.71
Sm	1.2	12.0	4.8	4.2	2.7	0.82
Eu	0.16	2.5	0.94	0.83	0.53	1.0
Gd	0.85	11.0	4.0	3.5	2.2	1.2
Tb	0.13	1.7	0.58	0.49	0.34	1.3
Dy	0.84	9.1	3.4	2.9	1.9	1.2
Ho	0.16	1.8	0.7	0.59	0.37	1.1
Er	0.46	4.9	1.9	1.7	1.1	1.0
Tm	0.07	0.70	0.27	0.24	0.15	0.89
Yb	0.42	4.5	1.8	1.6	1.0	0.90
Lu	0.06	0.62	0.3	0.23	0.14	0.66
ΣREE	30.3	273	121	107	63.7	0.58

samples ranged over four orders of magnitude, from 0.06 (Lu) to 106 mg kg⁻¹ (Ce), with \sum REEs ranging from 30.3 to 273 mg kg⁻¹. Yttrium concentrations varied from 4.8 to 46.2 mg kg⁻¹. Similar to other TCEs, the lowest average \sum REE concentration was determined in soils on carbonates (T4, T6, and T7), whereas the highest was obtained in soils on shales (T3, T21, and T26), fluvioglacial terraces (T16), and particularly moraine debris (T8). LREEs were found to be more abundant, with LREEs/HREEs ranging from 9.5 to 21.5. The lowest value of LREEs/HREEs was obtained for sample T25 on andesite parent material and the highest one for sample T21 on shale.

European Shale-Normalised Patterns and Observed Anomalies

Concentrations of REY (La to Lu, including Y) in the analysed samples were normalised with respect to the estimated and updated average composition of the European Shale (EUS) (Bau et al. 2018) and depicted in Figs. 3a and b. The normalised ratios (LREE/HREE, LREE_N/HREE_N, La_N/Lu_N, La_N/Sm_N, Sm_N/Lu_N, Gd_N/Lu_N; subscript N indicates that the corresponding REY is normalised to EUS) and calculated anomalies [(Eu/Eu* = Eu_N/(Sm_N × Gd_N)^{0.5}, Ce/Ce* = Ce_N/(La_N × Pr_N)^{0.5}] are shown in Table 2. Soils revealed a slight variation for Eu/Eu* (0.88–1.03) and Ce/Ce* (0.99–1.13) and showed a rather narrow range. The normalised patterns of soils developed on carbonate-rich terrains were characterized with a flat shape of the normalised curve and minor variation of calculated ratios (La_N/Lu_N,

Fig. 3 European shale (EUS)-normalised REE patterns of soil samples developed on different parent materials; **a** carbonate lithology; **b** siliciclastic and igneous rock lithologies

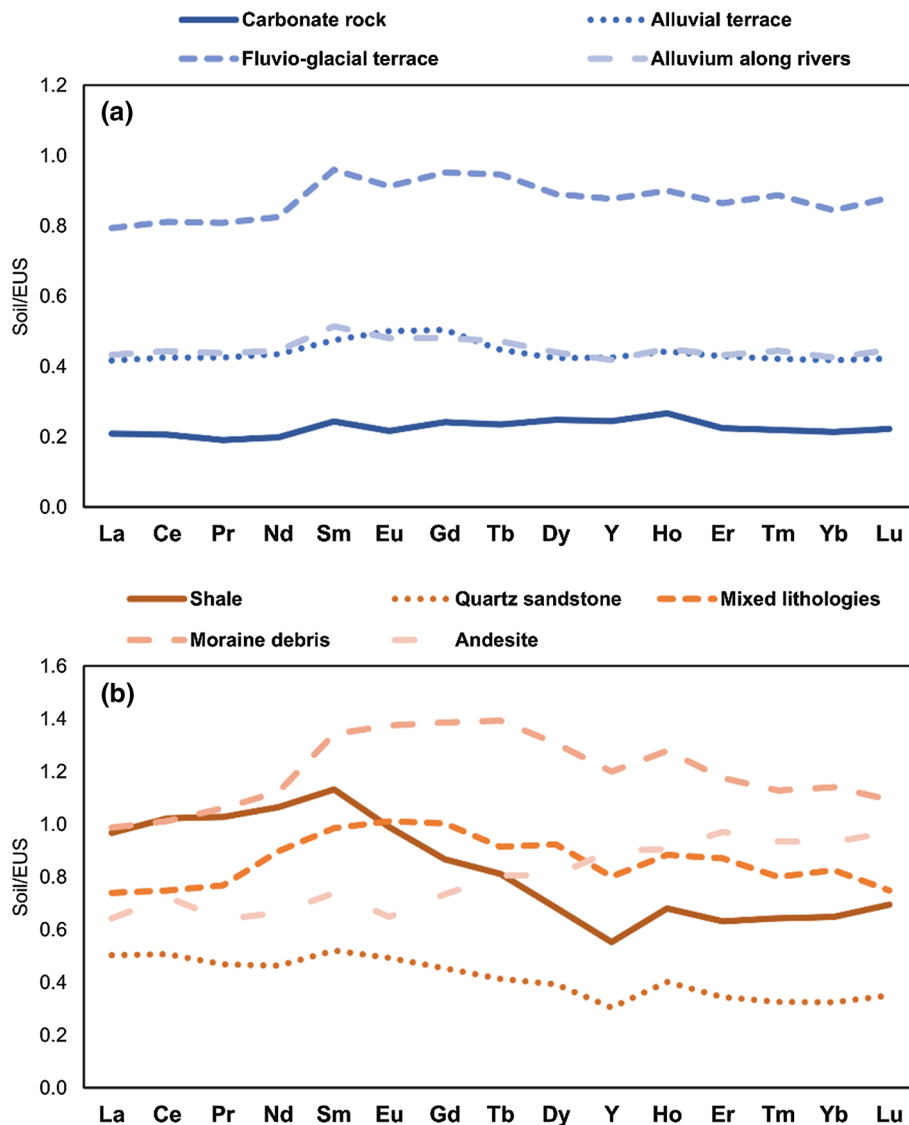


Table 2 Calculated ratios and anomalies for the studied soils arranged according to dominant geological substrata. The subscript N indicates that the corresponding REY is normalised to the European shale (EUS)

	Carbonate terrain				Silicate-igneous terrain				
	Carbonate	Fluvioglacial terrace	Alluvium	Alluvial terrace	Shale	Quartz sandstone	Mixed lithology	Moraine debris	Andesite
LREE/HREE	11.6	11.8	12.8	12.8	19.3	17.1	11.4	10.9	9.9
LREE _N /HREE _N	0.96	0.97	1.03	1.06	1.49	1.33	1.02	0.97	0.76
La _N /Lu _N	0.94	0.9	0.97	0.99	1.39	1.43	0.99	0.9	0.66
La _N /Sm _N	0.89	0.84	0.85	0.88	0.85	0.97	0.76	0.75	0.87
Sm _N /Lu _N	1.09	1.09	1.15	1.12	1.63	1.49	1.31	1.23	0.76
Gd _N /Lu _N	1.08	1.08	1.08	1.19	1.25	1.29	1.34	1.27	0.76
Eu/Eu*	0.91	0.97	0.97	1.03	0.99	1.01	1.02	1.01	0.88
Ce/Ce*	1.04	1.02	1.02	1.01	1.02	1.04	0.99	0.99	1.13

Eu/Eu* (europium anomaly) = $(Eu_N / (Sm_N \times Gd_N)^{0.5})$,

Ce/Ce* (cerium anomaly) = $(Ce_N / (La_N \times Pr_N)^{0.5})$

La_N/Sm_N, Sm_N/Lu_N, Gd_N/Lu_N). Moreover, the normalised curve of soils on Holocene alluvial terraces resembled that of alluvial soils along the investigated rivers. Somewhat different patterns exhibited soils with more siliclastic and igneous rock influence. Greater convexity of the normalised LREE curve was observed on shale and quartz sandstone, with LREE_N/HREE_N values of 1.49 and 1.33, respectively. Except for these two groups, all other soils displayed lower values of La_N/Lu_N ratio (< 1). A similar pattern was determined for soils developed on mixed lithologies and moraine material. Samples were characterized by dominance of elements from Sm to Dy resulting in a convex shape of the normalised curve and higher values of Sm_N/Lu_N (1.23–1.31) and Gd_N/Lu_N (1.27–1.34), and decreased ratio of La_N/Sm_N (0.75–0.76). Compared with other samples, the soil developed on andesite displayed prominent lower LREE_N/HREE_N value (0.76).

Discussion

Relationship Between Technology Critical and Major Elements

To explore geochemical characteristics and the relationship between technology critical and major elements (Al, Ca, Fe, K, Mg, Na, and Ti), we performed principal component analysis (PCA), which also can serve as a proxy for mineralogy (Grunsky et al. 2008). The results of PCA are shown in the form of a biplot (Fig. 4). The first three principal components account for 93% of the total variability in studied soils. The biplot of PC1 versus PC2 reveals four assemblages of variables positioned at an angle of approximately 90°. Such positioning of variables may suggest the existence of four different geochemical processes that govern elements'

distribution. PC1 accounts for ~77% of the total variability and is characterized by strong negative loadings of Mg and Ca and positive loadings of Nb, Ti, Ge, W, Fe, Ga, Li, Sc, Al, LREE, MREE, K, and HREE. This shows a clear separation of soils developed on carbonate-rich parent materials from those more affected by siliclastic lithologies. An exception makes soil developed on fluvioglacial terraces from which carbonate component was leached, and thus, they are positioned along positive PC1 axis, characteristic for soils dominated by aluminosilicate fraction (Vidic et al. 1991). From the biplot, it is evident that most of TCEs are grouped around major geogenic elements. The Nb, W, and Ge are closely related to Ti, which usually occurs in aluminosilicate minerals as isomorphously substituted Ti or free TiO₂ form as minerals rutile, anatase, and ilmenite (Dobrzyński et al. 2018; Meinhold 2010; Scott 2005). Moreover, grouping of Ga–Fe and Li–Sc–Al–LREE on the same part of biplot may imply their incorporation and adsorption onto clay minerals and Fe–Al oxides/hydroxides (Benedicto et al. 2014; Négrel et al. 2018; Starkey 1982). The MREEs and HREEs can be related to K as a main constituent of phyllosilicates and feldspars. They represent a group of elements slightly separated from previously mentioned TCEs with a strong affinity for clays (Laveuf and Cornu 2009). Such positioning of MREEs and HREEs point out the intermediate nature and influence of PC2 (12.6% of variance) on their geochemical behavior. PC2 represents the relative enrichment of Na and Y, likely indicative of feldspars and heavy minerals (garnet and zircon) abundant in alluvial soils (Salminen et al. 2005; Vidic et al. 1991 and references therein). The negative PC2 axis yields strong loadings for soil organic matter (SOM) and Sb, suggesting that SOM plays an important role in the adsorption of Sb (Hockmann and Schulin 2013; Wilson et al. 2010). SOM–Sb association is weighted by different types of soils including those developed on alluvium, fluvioglacial

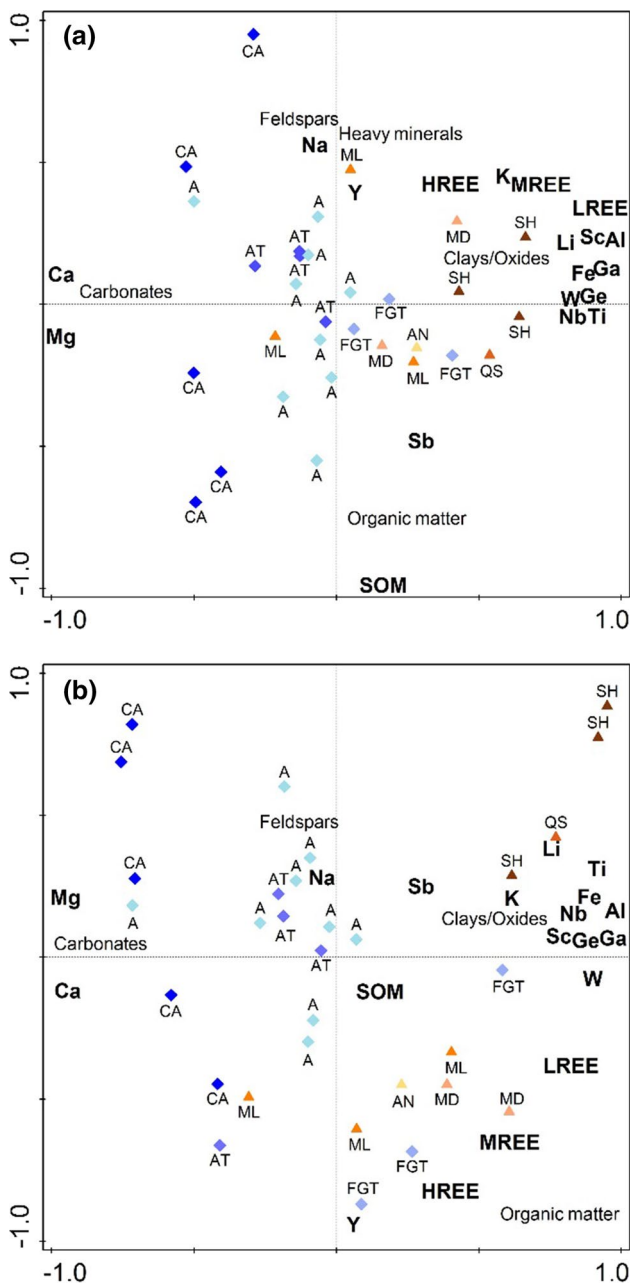


Fig. 4 Biplots for the first three principal components; **a** PC1–PC2, **b** PC1–PC3. Principal component analysis was performed after centered log-ratio (clr) transformation (Aitchison 1986). Diamonds denote soils developed on carbonate lithologies (blue shades), while the upper triangles (brown shades) denote soils more influenced by siliciclastic-igneous lithologies. The abbreviations refer to the names of the soil groups according to their geological substratum: CA—carbonate, FGT—fluvioglacial terrace, A—alluvium, AT—alluvial terrace, SH—shale, QS—quartz sandstone, ML—mixed lithology, MD—moraine debris, AN—andesite

terraces, moraine debris, mixed lithologies, and andesite parent material. Additional insight into the geochemical characterization of soils is given by PC3, which explains ~4% of the variance (Fig. 4b). The negative PC3 axis suggests

that organic matter also could play an important role in REY binding (Fiket et al. 2017a; Pourret et al. 2007). This is especially true for the MREEs, which are positioned on the same direction towards the origin as SOM. A similar conclusion is obtained by calculated ratios with the highest Gd_N/Lu_N and the lowest La_N/Sm_N values reported in soils developed on mixed lithologies and moraine debris. According to Davranche et al. (2011), the MREE enrichment can be caused by their preferential complexation with functional groups of organic matter, which also is assumed here. The positive PC3 axis reflects the assembling of alluvial soils around Na as the main constituent of feldspars—indicative of accumulation of coarser tectosilicate particles caused by sorting effect and their concentrating as the fine particles were removed at high-water stages (Hossain et al. 2017; Nesbitt and Young 1996).

Variations of Concentrations of Technology Critical Elements

Studied soils are characterized by geochemical heterogeneity and a wide range of element concentrations. As a result of slow soil genesis and frequent erosion, the mineralogical composition of geological substrata comes out as the main factor of element variability (Repe et al. 2017). A wide range between minimum and maximum element concentrations is governed by great lithological diversity, which includes carbonate lithologies, generally poorer in TCEs, and silicate rocks (especially shale) with their much higher concentrations (Table 3). Compared with average concentrations of TCEs in European soils and floodplain sediments (Salminen et al. 2005), comparable results are found. Unfortunately, there are no sufficient data in the literature to compare analysed elements in soils from the investigated area. A recent study by Gosar et al. (2019) reported on a couple of TCEs. However, the concentrations are difficult to compare because a different digestion procedure was employed. Concentrations of some TCEs (W, Ge, and Nb) were below the detection limit or much lower than in the present study. Similar results were obtained in the Australian surface soils; 90% of locations had concentrations of Ge and W below the detection limit, whereas for Nb and some of REEs (Tm, Lu), this percentage was closer to 50% (Reimann and Caritat 2017). According to Négrel et al. (2016, 2019) and Scheib et al. (2012), for European agricultural soils, aqua regia extraction for Ge and W was estimated on 1% and 3%, respectively, and for Nb more than an order of magnitude lower than x-ray fluorescence (XRF). A very low extraction was also detected for Sc, Ga, Sb, and Y as their concentrations were below 32% of XRF results (Mann et al. 2015). Such discrepancies were mainly attributed to their greater resistance to the digestion procedure because aqua regia cannot dissolve their main hosts (silicates/oxides). However, Biver and

Table 3 Comparison of average TCE (including REY) concentrations (mg kg⁻¹) in studied soils with literature data. Average concentrations of two main soil groups according to parent material are also given (carbonate and silicate-igneous material). TCEs are arranged following the periodic table groups. REYs are listed at the end

	Soil ¹	Carbonate ¹	Silicate-igneous ¹	Europe soil ²	Floodplain sediments ³	Slovenia soil* ⁴	Australia Soil* ⁵	Slovenia Soil ⁶	UCC ⁷	Sava sediments ⁸
Li	41.0	24.9	63.3	–	22.5	20.0	5.6	50.0	21.0	47.8
Sc	9.0	6.0	13.1	8.2	–	4.2	3.5	12.0	14.0	11.1
Nb	9.8	6.7	13.8	9.7	10.0	0.75	0.2	8.3	12.0	10.0
W	1.7	1.2	2.4	–	1.1	<0.1	<0.1	1.4	1.9	1.9
Ga	11.7	7.5	17.5	13.5	11.0	5.3	3.5	–	17.5	13.5
Ge	1.1	0.76	1.6	–	–	–	<0.1	–	1.4	1.2
Sb	1.3	1.0	1.7	0.60	0.74	0.64	0.12	1.1	0.42	1.7
Y	17.5	11.9	24.8	21.0	20.1	14.0	7.5	17.0	21.0	15.8
La	24.5	16.3	36.2	23.5	24.9	18.0	13.8	32.0	31.0	26.7
Ce	50.4	33.1	74.9	48.2	50.2	39.0	28.6	–	63.0	54.3
Pr	6.0	3.9	9.0	5.6	5.5	–	3.2	–	7.1	6.5
Nd	23.0	14.8	35.6	20.8	21.3	–	12.3	–	27.0	25.0
Sm	4.8	3.1	7.4	4.0	4.3	–	2.6	–	4.7	5.1
Eu	0.94	0.61	1.4	0.77	0.87	–	0.5	–	1.0	1.0
Gd	4.0	2.7	6.1	3.9	3.9	–	2.2	–	4.0	3.8
Tb	0.58	0.38	0.87	0.60	0.60	–	0.3	–	0.70	0.62
Dy	3.4	2.2	5.1	3.4	3.5	–	1.6	–	3.9	3.2
Ho	0.7	0.47	1.0	0.68	0.68	–	0.3	–	0.83	0.62
Er	1.9	1.3	2.8	2.0	2.0	–	0.7	–	2.3	1.8
Tm	0.27	0.19	0.40	0.30	0.29	–	<0.1	–	0.30	0.31
Yb	1.8	1.2	2.6	2.0	1.8	–	0.6	–	2.0	1.7
Lu	0.30	0.19	0.39	0.30	0.27	–	<0.1	–	0.31	0.31

¹This study, ² and ³Salminen et al. (2005), ⁴Gosar et al. (2019) *aqua regia soluble concentrations, ⁵Reimann and Caritat (2017) refers to median of *aqua regia soluble concentrations, ⁶Šajn (2003) refers to median concentrations, ⁷Rudnick and Gao (2014), ⁸Lučić et al.—in preparation

Filella (2018) have shown that low extractability of some TCEs (especially Ge) can be a consequence of their loss from the sample due to the volatility of chloride complexes formed in aqua regia extraction, especially if a semiclosed digestion system is used. Therefore, it can be assumed that total digestion or using XRF is a better option for comparing TCE concentrations (particularly Nb, Ge, and W) in different sampled media (sediment or soil). This also pertains to obtaining reliable geochemical background values, which should certainly be considered in future geochemical studies.

With regard to the previously established average total concentrations in Slovenian soils (Šajn 2003), slightly lower concentrations are determined for Li, Sc, and La, whereas for Nb, W, and Sb, concentrations are found higher. Compared with UCC, most of TCEs have lower concentrations. This is not surprising because the average upper crust values were calculated on a carbonate-free basis (Rudnick and Gao 2014). As aforementioned, we determined the lowest element concentrations in soils with the highest content of carbonate minerals. Thus, these results mostly reflect a dilution effect, as an increase of carbonate minerals displaces other minerals/elements within a given mass or volume—a

frequent problem in mineralogy/geochemistry where the data are subjected to the constant sum constraint (Aitchison 1986; Bern 2009; Filzmoser et al. 2009). A similar conclusion can be reached when comparing fine-grained sediments and studied soils, which are in fact their main source (Milačič et al. 2017). The fine-grained material is less abundant in carbonate coarser particles, and its composition is dominated by phyllosilicates (mostly clay minerals) with a higher content of TCEs (Table 3).

Geochemical Threshold Values

By observing the geochemical threshold values of investigated soils using five chosen methods of estimation [90th, 95th, 97.5th percentile; median + 2MAD (MD2MAD) and Tukey inner (upper) fence (TIF) are calculated based on logarithmic values], it is evident that the MD2MAD approach gives the lowest thresholds and larger proportion of extreme values in relation to other methods (Table 4), mainly because robust estimates of median and MAD are relatively unaffected by the extreme values of the lognormal data distribution (Reimann et al. 2005). This particularly pertains to Li

Table 4 Geochemical threshold values for TCEs (including REY) estimated by different approaches: P90 (90th percentile), P95 (95th percentile), P97.5 (97.5th percentile); MD2MAD (median + 2 median absolute deviation) and TIF (Tukey inner fence—upper whisker of the boxplot) are calculated based on logarithmic values. TCEs are arranged following the periodic table groups. REYs are listed at the end

	Threshold methods					Number of exceedances above				
	P90	P95	P97.5	MD2MAD	TIF	P90	P95	P97.5	MD2MAD	TIF
Li	82.4	93.0	103.6	79.6	207	4	2	1	4	0
Sc	15.5	17.6	18.9	17.6	34.2	4	2	0	2	0
Nb	16.8	18.1	19.6	20.7	34.5	2	2	1	0	0
W	2.9	3.2	3.3	3.5	7.1	3	1	0	0	0
Ga	22.3	23.7	24.0	22.3	46.3	3	2	1	3	0
Ge	2.0	2.2	2.2	2.2	4.1	3	2	2	2	0
Sb	2.1	2.3	2.4	2.3	4.0	3	1	1	1	0
Y	28.7	33.4	38.9	25.1	48.3	3	2	1	5	0
La	42.0	45.0	46.9	38.9	101	3	2	1	6	0
Ce	88.0	95.5	101	91.3	209	3	2	1	3	0
Pr	10.5	11.6	12.3	9.1	23.7	3	2	1	7	0
Nd	42.6	45.6	48.6	34.9	93.9	3	2	1	8	0
Sm	8.6	9.0	10.0	7.4	21.9	3	2	1	8	0
Eu	1.7	1.8	2.0	1.5	3.6	4	1	1	6	0
Gd	7.5	7.6	8.5	6.0	15.0	3	2	1	5	0
Tb	1.0	1.1	1.3	0.94	2.0	3	2	1	5	0
Dy	6.3	6.5	7.1	5.2	10.3	4	1	1	5	0
Ho	1.2	1.3	1.4	1.0	2.1	2	1	1	5	0
Er	3.5	3.7	4.1	2.9	5.5	3	2	1	6	0
Tm	0.46	0.53	0.60	0.43	0.87	3	2	1	6	0
Yb	3.2	3.4	3.7	3.0	5.4	3	2	1	5	0
Lu	0.44	0.50	0.55	0.42	0.94	3	2	1	5	0

and most of the REYs for which more than 10% of outliers are detected. Moreover, an unrealistically high number of outliers can reflect that fully symmetrical distribution for these elements is not attained by simple log-transformation (Reimann and Filzmoser 2000).

Different results are obtained when calculating the 97.5th percentile, and especially TIF threshold value, as no outlier is determined. According to Reimann et al. (2018), TIF has an advantage because it depends on statistical distribution of the robust inner core of the data and allows the definition of a threshold for outliers even if none is present in the data set. In our case, the maximum values of all elements are lower than TIF threshold. The main reason could be a high data variability between the 25th and 75th percentiles, which implies large interquartile range (IQR) and consequently high TIF values (Gosar et al. 2019). High TIF values also can be an indicator of absence of true outliers and may rather imply the presence of extreme values of a normal distribution caused by geogenic sources, i.e., specific parent materials (shale and moraine debris). Hence, establishing geochemical threshold values is not a straightforward task. Estimated values will always change depending on the size and location of the study area (Reimann et al. 2008). Detailed discernment of causes of high element concentrations requires a sound knowledge of different aspects (geology, climate, weathering, pollution, etc.) that can influence

the observed composition. According to the results presented, the TCE concentrations were mostly controlled by the composition of the geological substrata.

Conclusions

This study reports the geochemical composition of soils developed on different geological substrata along the upper catchment of the Sava River. Special focus was placed on TCEs (including REYs) and understanding of their geochemical behavior. To determine geochemical threshold values the simplistic univariate methods were employed. The main conclusions are as follows:

- (1) The investigated area is characterized by substantial variation of TCE concentrations. The lowest concentrations were observed in carbonate-rich and alluvial soils, whereas the highest concentrations were measured in soils developed on shale and moraine debris. Hence, the lithology is the first-order control on the geochemical composition of studied soils.
- (2) The clay minerals and oxides/hydroxides act as major host phases for most of TCEs (Li, Sc, Nb, W, Ga, Ge, and LREE). HREE and Y tend to be concentrated into

accessory minerals, whereas for MREE and Sb adsorption onto organic matter is assumed.

- (3) Among determined thresholds, 97.5th percentile and TIF values provided the most reasonable results. Some exceedances above the 97.5th percentile were natural in origin and governed by local geology.

The results obtained in this work suggest the importance of digestion method for obtaining reliable geochemical background values and comparison of TCE concentrations between different studies. Future research should be based on the total digestion methods, which ensure better dissolution and could avoid extraction problems caused by using aqua regia in a semiclosed system. Moreover, there is a great need for more investigation of TCEs in soils developed on different parent materials because for many of them (especially Ge and W) literature data are scarcely available and soil guideline values are not established.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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