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Application of Multivariate Statistical Methods for Determining Geochemical Trends of Elements on the Territory of Slovenia

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Abstract: The main objective of this study is to map multi-element geochemical anomalies in soil on a regional scale. We aimed to determine and evaluate the baseline geochemical values and main geochemical trends in soil that may serve as reference values against any future changes. A total of 817 topsoil samples (0–10 cm) were collected in a 5 × 5 km grid and analyzed for 35 elements using ICP-ES after multi-acid digestions ($HClO_4/HNO_3/HCl/HF$) and 53 elements using ICP-MS after modified aqua regia digestion ($HCl/HNO_3/H_2O$). The analytical results for the two different digestion methods (multi-acid digestion vs. aqua regia) were also compared for each chemical element. Multivariate statistical methods were applied to identify the geochemical trends and main sources of trace elements over the territory of Slovenia. Based on these results, seven natural and one mixed natural/anthropogenic geochemical association were established. The contents and trends of the determined factors are presented according to 8 natural units, 4 drainage areas, and geological units characteristic of Slovenia. The identified anthropogenic geochemical association combines toxic elements (Ag, Bi, Cd, Hg, P, Pb, S, Sn, and Zn). Increased values of these elements can be found in mining areas and metallurgic centers, in Quaternary sediments of the Sava River, and Adriatic Basin as the consequence of past mining activities and in the Julian Alps, where their origin could be connected to the atmospheric deposition.

Keywords: soil; geochemical mapping; distribution of geochemical elements; factor analysis; cluster analysis

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1. Introduction

In addition to air and water, soil is one of the major natural resources of any country. Due to geological and climatic variations over time and distances, soil can differ widely in its attributes. A major influence on the environment and, consequently, on the soil is also human impact. The accelerated rate of industrial processes, fossil fuels, and mineral extraction has increased the abundance of toxic metals in the soil. One of the soil's roles is filtering to prevent the entry of harmful substances into the hydrosphere, atmosphere, and living organisms and to protect the system of underground drinking water. To summarize, soil contains trace elements from different sources: (1) geogenic elements derived from the bedrock; (2) pedogenic elements from lithogenic sources but which are subsequently changed, and (3) anthropogenic elements which are the consequence of human activities [1–4].

It is necessary to determine the natural distribution to identify anthropogenic anomalies in the natural environment. It should be mentioned that the natural background itself is variable, so higher concentrations of some elements may be normal in one area but in another represent anomalies [5–11]. Anthropogenic activities can contribute significantly to the levels of trace elements in soil and water and, as a consequence, affect human health. The human impact on the environment is very important, and it has led to irreversible changes. The problems of ecosystem degradation due to pollution became increasingly serious during the latter decades of the 20th century. Therefore, the documentation and analysis of geochemical soil structure [12–17] is very important, as the contamination of soil is very often constant and lasts longer than other parts of the environment, especially its contamination with trace elements, which is almost permanent [6,18–20].

There are a large number of studies dealing with geochemical distribution in soil in Europe and the world. Particular attention has been paid to the systematic studies of potentially toxic elements (PTE) in soil [6,18,19,21–41], where the geochemical features and spatial distribution of elements have been presented at the national [8,20,33,36,38,39,42–50] or European level [51–55].

Despite the important results of extensive geochemical investigations into Slovenian soils [56–65], there is a demand for re-analysis and re-investigation from the need for a broader set of chemical elements that can serve as a basis for determining geochemical baselines and as a reference against any future changes. Studies focused on a broader set of determined elements enabled the application of multivariate statistical methods [66–84] for identifying geochemical trends in the territory of Slovenia. In this paper, results from the re-investigation and re-analysis of soil samples are reported and compared to the results from the previous analysis [56]. Data for statistical processing were supplemented by the higher number of analyzed chemical elements based on the multi-acid digestion method used in 1994 and the results of chemical analysis after utilizing an additional aqua regia digestion method according to the demand of the Slovenian [85] and European legislation [86]. This study presents the regional soil survey to which different multivariate statistical methods have been applied to determine geochemical trends in the territory of Slovenia.

The main purpose of this study is to provide consistent systematic data on the elemental composition of soil across the county based on the analysis of 817 soil samples using two digestion methods (multi-digestion vs. aqua regia). Median values and geochemical trends via multi-acid (MA) and aqua regia (AR) are compared with data from Europe [51,52,87] and separately for Southern Europe [53–55]. However, significant differences in the spatial distribution of many elements are observed between Northern and Southern Europe.

The principal goal of this study is to determine important geochemical trends using two digestion methods, the multi-acid method (MA) as total digestion and the partial method (sequential), in which no silicates are dissolved (AR). The spatial distribution of most elements is not influenced by these digestion methods, but some elements are strongly influenced by the digestion method used and represent different (individual) geochemical trends. The best examples are the distribution of Al, Cs, Ga, Sn, Na, and Rb after MA, which show one distribution, but after the samples have been partially digested with aqua regia, they show a completely different distribution.

2. Study Area

The summarized geographical description is taken from “The geography of Slovenia, 2020” [88–94]. Slovenia is situated in Central Europe and covers an area of 20.273 km^2 (Figure 1). In Slovenia, four geographical units meet the Alps, including the Pannonian Basin, the Dinarides, and the Mediterranean, reflecting the great diversity of its geology, climate, relief, vegetation, and pedological characteristics. The interaction of three major climate systems (Continental, Alpine, and sub-Mediterranean) in the territory of Slovenia strongly influences the country’s precipitation regime. The average density of the watercourses in Slovenia is 1.33 km per square km, which is among the highest densities found in Europe. The average annual precipitation is 1570 mm. The spatial variability of the precipitation is high—the annual precipitation sum varies from 800 mm in the northeastern part of the country to more than 3500 mm in the northwest [95]. Because of its diversity and distinct variation over short distances, bedrock is the most important pedogenetic factor in Slovenia [96].

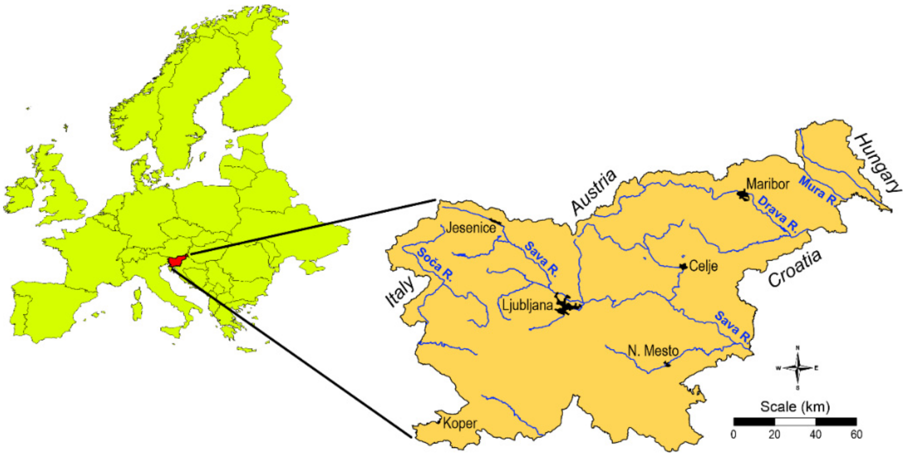

Figure 1. Study area.

The interpretation of results and spatial distribution of determined factors was performed according to natural geographic units, the main drainage areas, and the geological units of Slovenian territory. Slovenia was divided into natural units based on the units defined by [97] and based on the geographical and geological characteristics of the Slovenian territory. We distinguished eight natural units that were used in this study for the interpretation of the spatial distribution of factors: Western Alps (12% of Slovenian territory), Eastern Alps (10%), Western Prealps (11%), Eastern Prealps (14%), Western Dinarides (8%), Eastern Dinarides (21%), Interior Basin (5%) and Pannonian Basin (19%) (Figure 2).

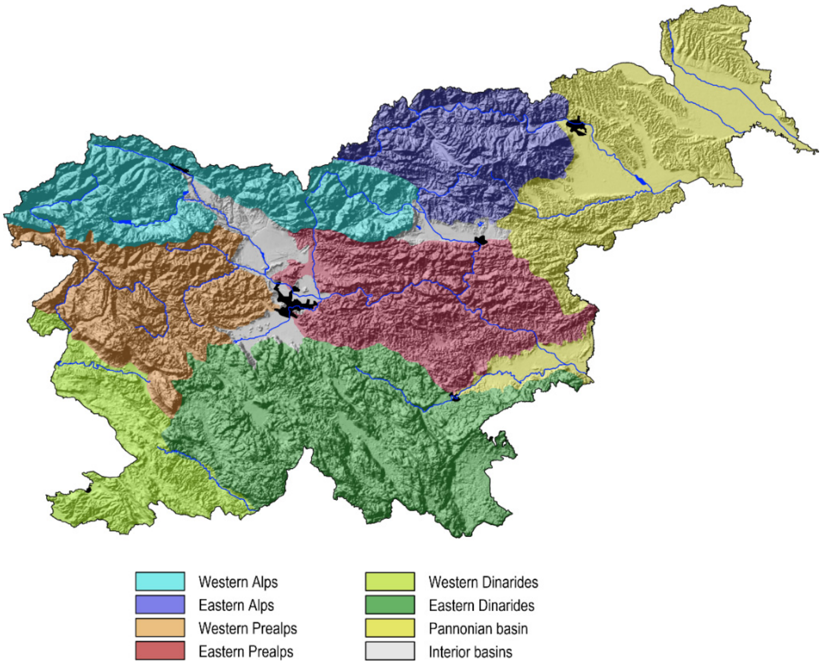

Figure 2. The main natural units in Slovenia [61].

The main drainage areas in Slovenia are the Adriatic Basin (19%), Sava watershed (32 %), Sava watershed (Karstic area) (26%) and Drava watershed (23%) (Figure 3).

Simplified geological units were used for the interpretation of the results according to the geological and geographical characteristics and drainage areas of the Slovenian territory (Figure 4). These units include Quaternary (Q) alluvial sediments (21%), Neogene (Ng) clastitic sediments (15%), Paleogene (Pg) clastitic sediments (5%), Cretaceous (K) clastitic sediments (2.8%), Triassic (T) clastic sediments (6%), Paleozoic (Pz) clastitic sediments (5%), Paleogene (Pg) carbonate rocks (2%), Cretaceous (K) carbonate rocks (11 %), Jurassic

(J) carbonate rocks (8%), Triassic (T) carbonate rocks (17%), Magmatic rocks (3%) and Metamorphic rocks (4%) [1–4].

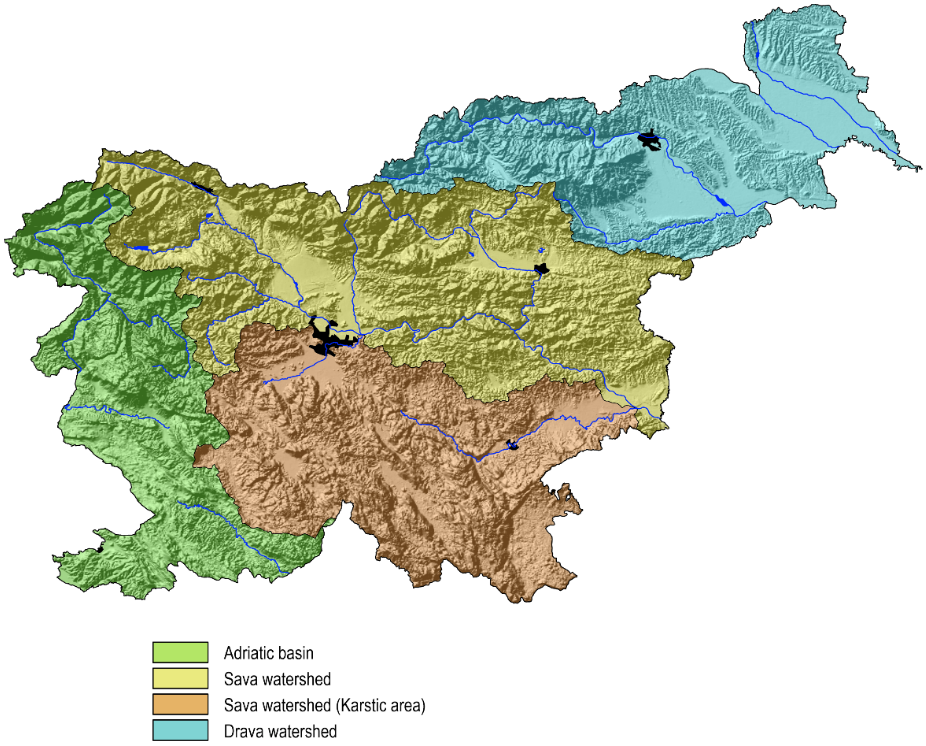

Figure 3. The main drainages regions in Slovenia.

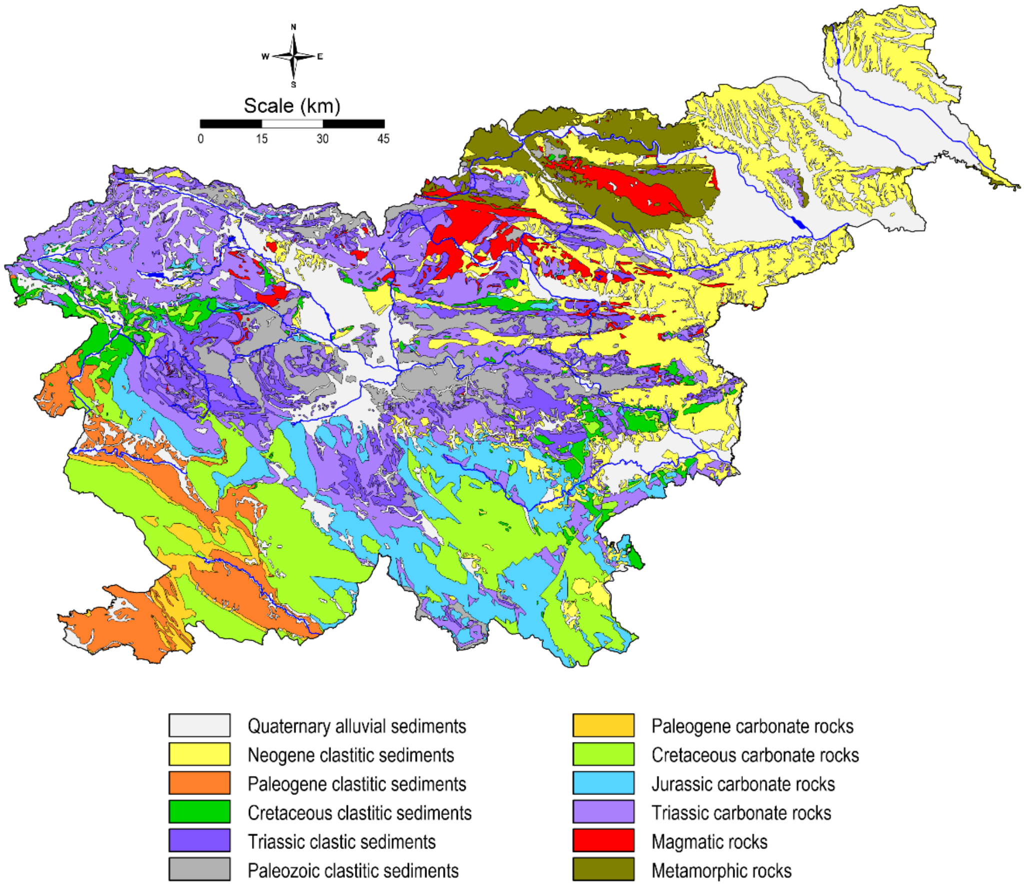

Figure 4. Simplified geological map of Slovenia [98,99].

In the highest parts of Slovenia (Alpine and Subalpine Slovenia), there is poorly developed regolith, shallow lithic leptosol, and eutric and calcaric regosol ((A)-C soil profile). These groups of soil cover only 2% of the entire territory of Slovenia. On the steep slopes and the lower terrain or karst areas of the Alps, Prealps and Dinarides, humus accumulative soils are formed with a soil profile (sp) of A-C or A-R, eutric and dystric leptosol are developed on non-carbonates (about 4% of the territory) and rendzic and mollic leptosol form on limestone and dolomites, the most widespread soil type, covering about 27% of the territory. The cambisols (sp: A-(B)-C) are present throughout Slovenia and cover almost half of the country. Eutric cambisols and district cambisols are found on non-carbonate soils, which together cover 34% of the territory. Calcareous cambisols and chromic cambisols (terra rossa) are mainly developed on carbonated rocks. In total, they cover about 15% of the territory. Cambisols are found in the valleys and basins of central Slovenia (Ljubljana Basin, Celje Basin) and represent the most fertile agricultural land in Slovenia. In north-eastern Slovenia, planosols (sp: A-Eg-Bg-C), gleysols (sp: A-G), and fluvisols (sp: (A)-C) predominate due to the many surface waters and the relatively flat surface. They cover about 13% of the territory, and due to the flat surface, this is the most important agricultural area in Slovenia. Anthrosol (sp: I-II-II) covers approximately 3% of the territory. Other soil types (luvisol, podzol, and histosol) are present only locally [93,100–103].

3. Materials and Methods

3.1. Sampling and Sample Preparation

During the regional geochemical survey in 1990–1993, soil sampling was performed in a 5 × 5 km grid (Figure 5) with a randomly selected starting point to ensure systematic sampling. A total of 817 topsoil (0–10 cm) samples were collected [56]. Air-dried samples were gently disaggregated in a ceramic mortar, sieved through a 2 mm sieve, and stored. The samples were deposited airtight in the cool storeroom. In 1993, the soil samples were analyzed after pulverization in a vibration mill, which most probably caused elevated concentrations of Co and W. To avoid contamination from the preparation method, the stored soil samples (<2 mm) were taken out of the depot at the Geological Survey of Slovenia and pulverized in an agate mill to a fine grain size (<0.075 mm). The soil samples were then sent for chemical analysis.

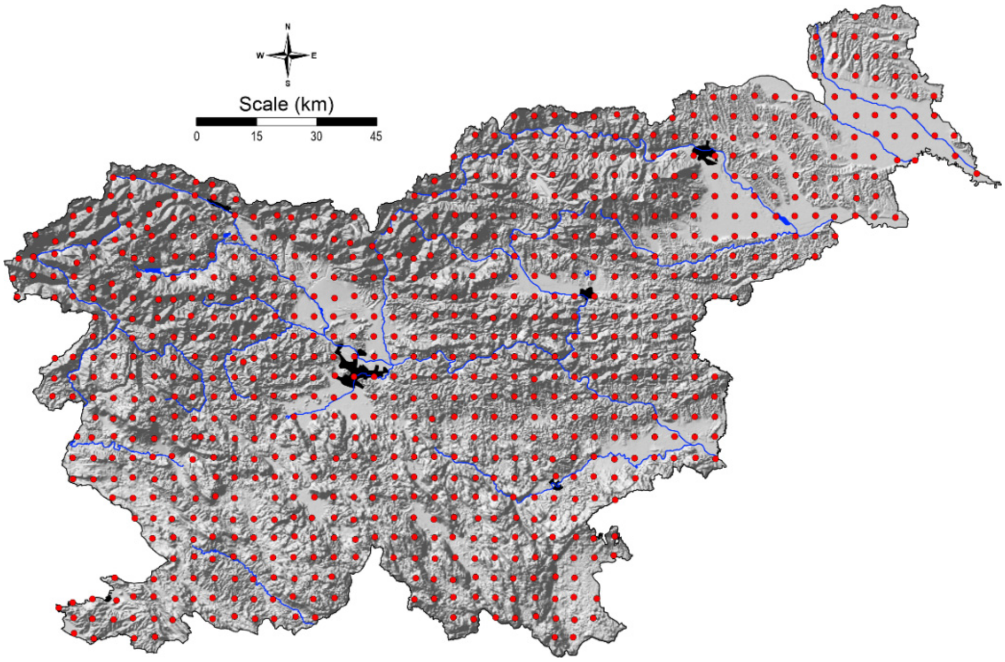

Figure 5. Sampling locations.

3.2. Chemical Analyses

Element concentrations were analyzed at Acme Labs, Vancouver, Canada (accredited under ISO 9001:2008). In 1993, 35 elements (Ag, Al, As, Au, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Sb, Sc, Sn, Sr, Th, Ti, U, V, W, Y, Zn, Zr) were analyzed via inductively coupled plasma emission spectroscopy (ICP-ES) after multi-acid digestion (0.25 g of the soil sample was digested in a 10 mL mixture of $HClO_4$, HNO_3, HCl and HF) [56].

In 2011, the concentrations of 53 (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr) chemical elements were determined with inductively coupled plasma mass spectrometry (ICP-MS) after the digestion of an aliquot of a 15 g sample material with aqua regia (1:1:1 $HCl:HNO_3:H_2O$) for 3 h at 95 °C. This higher sample weight ensured the higher representativeness of the analytical results [104].

In addition, multi-acid digestion ultra-trace ICP-MS analysis was also applied to soil samples to compare the analytical results to the results from the previous analysis [57]. In total, 0.25 g of the sample material was digested with a mixture of hydrofluoric acid (HF), nitric acid (HNO_3), and perchloric acid ($HClO_4$). The residue was dissolved in HCl. The total concentrations of 55 (Ag, Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hf, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pr, Rb, S, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tm, U, V, W, Y, Yb, Zn, Zr) elements were measured using inductively coupled plasma mass spectrometry (ICP-MS) [104].

3.3. Sensitivity, Accuracy, and Precision of Analysis

The analytical set included routine soil samples, analytical soil replicates and the certified reference material (CRM) for quality control purposes: OREAS43P, OREAS44P, and OREAS45P. In addition to shipped CRMs, three more CRMs (DS8, OREAS 24P, and OREAS45CA) were provided by the ACME lab [104]. The shipment of samples, duplicates and geological standards to the laboratory was carried out in a random order to distribute evenly any errors due to laboratory performance. This procedure ensured an unbiased treatment of samples and a random distribution of the possible drift of analytical conditions for all samples. Objectivity was assured using neutral laboratory numbers. To test the quality of analysis (QA), accuracy and precision were calculated. The quality control of data showing detection limits, precision and accuracy are shown in Table 1.

Table 1. Estimation of accuracy and precision.

		Multi-Acid Digestion (MA)					**Aqua Regia Digestion (AR) [5]**				
	Unit	**DL**	**UL**	**$N_{(DL)}$**	**A (%)**	**P (%)**	**DL**	**UL**	**$N_{(DL)}$**	**A (%)**	**P (%)**
Ag	µg/kg	20	200,000	777	4.7	24.0	2	100,000	817	1.6	17.2
Al	%	0.02	20	816	1.8	5.3	0.01	10	817	3.0	10.7
As	mg/kg	0.2	10,000	816	−1.7	12.3	0.1	10,000	817	0.2	8.7
Au	mg/kg	0.1	200	0	-	-	0.2	100,000	797	−1.5	43.1
B	mg/kg	-	-	-	-	-	1	2000	631	5.0	21.5
Ba	mg/kg	1	10,000	816	2.9	5.9	0.5	10,000	817	−6.2	6.4
Be	mg/kg	1	1000	754	-	26.6	0.1	1000	814	0.7	20.8
Bi	mg/kg	0.04	4000	816	28.6	13.7	0.02	2000	817	1.3	14.4
Ca	%	0.02	40	816	2.1	7.0	0.01	40	813	1.9	10.5
Cd	mg/kg	0.02	4000	816	2.1	11.9	0.01	2000	813	−1.8	13.6
Ce	mg/kg	0.02	2000	816	1.7	9.7	0.1	2000	817	−4.1	10.3
Co	mg/kg	0.2	4000	816	3.6	7.9	0.1	2000	817	0.9	6.7
Cr	mg/kg	1	10,000	816	1.8	7.1	0.5	10,000	817	1.9	7.8
Cs	mg/kg	0.1	2000	816	−1.8	6.4	0.02	2000	817	2.5	14.3
Cu	mg/kg	0.02	10,000	816	−1.3	9.1	0.01	10,000	817	−0.1	7.9
Dy	mg/kg	0.1	2000	816	−7.0	10.4	-	-	-	-	-
Er	mg/kg	0.1	2000	816	−12.1	8.9	-	-	-	-	-
Eu	mg/kg	0.1	2000	815	6.5	11.6	-	-	-	-	-

Table 1. *Cont.*

		Multi-Acid Digestion (MA)					Aqua Regia Digestion (AR) [5]				
	Unit	**DL**	**UL**	**$N_{(DL)}$**	**A (%)**	**P (%)**	**DL**	**UL**	**$N_{(DL)}$**	**A (%)**	**P (%)**
Fe	%	0.02	60	816	−15.7	2.6	0.01	40	817	2.2	4.3
Ga	mg/kg	0.02	100	816	3.1	5.0	0.1	1000	817	3.2	8.1
Gd	mg/kg	0.1	2000	816	−5.1	12.3	-	-		-	-
Ge	mg/kg	-	-	-	-	-	0.1	100	31	−13.9	1.0
Hf	mg/kg	0.02	1000	816	−4.1	8.4	0.02	1000	658	0.6	22.8
Hg	µg/kg	-	-	-	-	-	5	50,000	817	0.8	16.4
Ho	mg/kg	0.1	2000	813	−4.5	11.5	-	-	-	-	-
In	mg/kg	-	-	-	-	-	0.02	1000	709	0.7	24.4
K	%	0.02	10	816	−0.9	3.8	0.01	10	816	2.6	13.3
La	mg/kg	0.1	2000	816	7.0	11.4	0.5	10,000	817	2.2	10.3
Li	mg/kg	0.1	2000	816	−5.9	6.3	0.1	2000	817	10.0	10.4
Lu	mg/kg	0.1	2000	781	−7.0	12.8	-	-	-	-	-
Mg	%	0.02	30	816	−2.7	4.6	0.01	30	817	1.0	7.3
Mn	mg/kg	2	10,000	816	−7.4	4.8	1	10,000	817	−4.7	6.8
Mo	mg/kg	0.05	4000	816	−3.6	13.0	0.01	2000	817	−6.0	10.3
Na	%	0.002	10	816	−9.1	5.6	0.001	5	806	7.0	13.7
Nb	mg/kg	0.04	2000	816	−11.9	7.5	0.02	2000	816	−26.0	14.9
Nd	mg/kg	0.1	2000	816	−3.1	8.6	-	-	-	-	-
Ni	mg/kg	0.1	10,000	815	5.9	8.1	0.1	10,000	817	4.3	10.3
P	%	0.001	5	816	−6.7	5.9	0.001	5	817	1.5	6.0
Pb	mg/kg	0.02	10,000	816	3.3	5.4	0.01	10,000	817	−5.2	6.3
Pd	µg/kg	-	-	-	-	-	10	100,000	10	14.6	-
Pr	mg/kg	0.1	2000	816	5.8	10.1	-	-	-	-	-
Pt	µg/kg	-	-	816	-	-	2	100,000	47	3.2	6.0
Rb	mg/kg	0.1	2000	816	−1.6	9.7	0.1	2000	817	1.2	12.9
Re	µg/kg	-	-	-	-	-	1	100	255	1.6	18.9
S	%	0.04	10	306	-	8.3	0.02	5	668	9.3	13.5
Sb	mg/kg	0.02	4000	816	−1.3	6.6	0.02	2000	817	−8.5	11.4
Sc	mg/kg	0.1	200	816	−0.5	5.3	0.1	100	817	13.8	10.5
Se	mg/kg	-	-	-	-	-	0.1	100	778	−8.7	36.1
Sm	mg/kg	0.1	2000	816	2.9	11.1	-	-	-	-	-
Sn	mg/kg	0.1	2000	816	−10.0	10.1	0.1	100	817	0.1	14.4
Sr	mg/kg	1	10,000	816	7.6	5.4	0.5	10,000	817	−5.1	9.9
Ta	mg/kg	0.1	2000	813	8.9	13.4	0.05	2000	0	-	-
Tb	mg/kg	0.1	2000	811	−2.7	12.5	-	-	-	-	-
Te	mg/kg	-	-	-	-	-	0.02	1000	607	−5.5	41.8
Th	mg/kg	0.1	2000	816	3.7	10.2	0.1	2000	816	−0.2	12.3
Ti	%	0.001	10	816	−28.2	7.8	0.001	5	782	−1.4	15.0
Tl	mg/kg	-	-	-	-	-	0.02	1000	817	1.4	7.6
Tm	mg/kg	0.1	2000	790	−8.6	13.3	-	-	-	-	-
U	mg/kg	0.1	4000	816	−8.7	7.6	0.05	2000	817	−1.2	8.8
V	mg/kg	1	10,000	816	2.3	4.2	2	10,000	817	−1.3	7.4
W	mg/kg	0.1	200	816	−21.5	12.5	0.05	100	335	−38.6	10.5
Y	mg/kg	0.1	2000	816	−10	8.2	0.01	2000	817	−3.3	7.7
Yb	mg/kg	0.1	2000	815	−13.7	11.8	-	-	-	-	-
Zn	mg/kg	0.2	10,000	816	2.0	5.7	0.1	10,000	817	−2.5	7.7
Zr	mg/kg	0.2	2000	816	−22.7	6.2	0.1	2000	800	−12.0	14.0

DL—detection limits; UL—upper limit; $N_{(DL)}$—amount of analysis above detection limits; A (%)—accuracy; P (%)—precision; Data rounded at two digits.

The sensitivity of the analysis, in the sense of the lower limit of detection, was adequate for 53 out of 55 of the determined elements (MA digestion), i.e., Au and S were below the lower detection limit. In the case of AR digestion, six elements, Ge, Pd, Pt, Re, Ta, and W, were removed from the final database used in the statistical analysis since their contents in most analyzed samples were below the lower detection limit of the analytical method or the detection limit of the analytical method (Table 1). Biver and Filella, 2018 [105] explained the

Ge losses due to an inadequate open system digestion procedure like aqua regia. Sample digestion, which involves steps from simple dilution to partial or total digestion, is a crucial step for achieving reproducible and accurate analytical results [106].

The accuracy of the analytical method for elements was estimated via the calculation of the relative systematic error between determined (X_A) and recommended values (X_P) of geological standards using the following Equation:

$$A = \frac{|X_A| - |X_P|}{X_P} * 100\ [\%] \tag{1}$$

Most of the elements showed very low deviations from the recommended range of values, i.e., the mean of all determined elements in the standards generally differed by less than 15% of the recommended values (Table 1). Large absolute deviations were observed only for Bi, Ti, W, and Zr (MA digestion) and Nb and W (AR digestion).

Precision is a measure of the repeatability of determining a parameter in the same sample regardless of deviation from the true value [107]. Precision (P) was tested by the relative differences between pairs of analytical determinations (X_1, X_2) of the same sample using the following Equation:

$$P = \frac{2|X_1 - X_2|}{(X_1 + X_2)} * 100\ [\%] \tag{2}$$

Fifteen randomly selected samples were replicated for the estimation of precision. Precision was considered good. Only Ag and Be (MA digestion) and Ag, Au, B, Be, Hf, Hg, In, Se, Re, and Te (AR digestion) showed large deviations greater than 15% but lower than 50% (Table 1).

The reliability of the analytical procedures was considered adequate for the majority of analyzed elements for both digestion methods using the determined elemental contents in further statistical analyses. Of the 55 elements that were determined after MA digestion analyses, Au and S were removed from any further analysis because of the insufficient reliability of the analytical method. Of the 53 elements that were determined after AR digestion, the following elements were eliminated: Ge, Pd, Pt, Re, Ta, and W. The concentration of these elements was below the detection limit in more than 50% of the analyzed samples.

3.4. Data Processing

3.4.1. Basic Statistical Analysis and Transformation

All data processing and calculations, including geostatistical data interpretation and visualization (mapping), were performed using the following software: Statistica [108], QGIS [109], and Surfer [110].

The data were evaluated using a series of data analysis and statistical procedures. Individual elements were evaluated using univariate, bivariate, and multivariate data analysis techniques and the spatial mapping of each element's contents. The basic statistics for both digestion methods are shown in Appendices A and B (Tables A1 and A2, Figures A1–A4). For data normalization, the Box–Cox transformation method [82] was applied to this study. Transformed data fit the hypothetical normal distribution much better than untransformed data. Since many statistical techniques are sensitive to non-normally distributed data, the Box–Cox transformed values were used in further geostatistical analysis and map constructions. The Box–Cox transformation improved this feature, especially for the skewness and level of normality of the data sets.

The Box–Cox transformation is given by the following Equation:

$$y = \frac{x^{\lambda} - 1}{\lambda}; \lambda = 0 \tag{3}$$

$$y = \mathrm{In}(\lambda); \lambda = 0 \tag{4}$$

where y represents the transformed value and x presents the value to be transformed. Parameter λ is estimated based on the assumption that the transformed values are normally distributed, and when $\lambda = 0$, the transformation becomes the logarithmic transformation.

3.4.2. Bivariate and Multivariate Analysis

Concentration ratios (CRs) were calculated to compare the following: (1) the analytical results between European and Slovenian medians for both digestion methods (Table 2); (2) different digestion methods (MA vs. AR digestion) for each chemical element, as well as comparing the analytical results from 1994 with the analytical results from 2011 to estimate the contamination of the sample by milling.

Table 2. Estimated European and Slovenian medians and concentration ratios (Slovenia vs. EU).

	$\mathbf{EU_{(MA)}}$	$\mathbf{EU_{(AR)}}$	$\mathbf{Slo_{(MA)}}$	$\mathbf{Slo_{(AR)}}$	$\mathbf{CR_{(MA)}}$	$\mathbf{CR_{(AR)}}$	$\mathbf{CR_{(MA/AR)}}$	$\mathbf{R_{(MA/AR)}}$
Ag	270	40	82	62	0.3	1.6	1.3	0.72
Al	5.8	1.1	6.4	1.8	1.1	1.7	3.5	0.64
As	7.0	5.6	14	11	2.0	2.0	1.2	0.95
Au	-	1.0	-	1.7	-	1.7	-	-
B	-	2.6	-	2.0	-	0.8	-	-
Ba	380	63	330	75	0.9	1.2	4.4	0.55
Be	<2.0	0.51	2.0	0.90	-	1.8	2.2	0.60
Bi	<0.50	0.18	0.40	0.33	-	1.8	1.2	0.89
Ca	0.66	0.31	0.67	0.44	1.0	1.4	1.5	0.95
Cd	0.15	0.20	0.56	0.48	3.7	2.4	1.2	0.95
Ce	48	27	70	38	1.5	1.4	1.8	0.80
Co	7.8	7.2	16	14	2.1	2.0	1.1	0.98
Cr	60	20	84	34	1.4	1.7	2.5	0.89
Cs	3.7	1.1	6.0	1.4	1.6	1.3	4.3	0.47
Cu	13	15	25	20	1.9	1.4	1.2	0.94
Dy	3.4	-	3.5	-	1.0	-	-	-
Er	2.0	-	1.7	-	0.9	-	-	-
Eu	0.77	-	1.1	-	1.4	-	-	-
Fe	3.2	1.7	3.6	2.9	1.1	1.7	1.3	0.96
Ga	14	3.4	17	5.2	1.2	1.5	3.3	0.66
Gd	3.9	-	4.4	-	1.1	-	-	-
Hf	5.6	<0.020	1.5	0.050	0.3	-	30.2	0.64
Hg	-	0.035	-	0.11	-	3.1	-	-
Ho	0.68	-	0.70	-	1.0	-	-	-
In	0.050	<0.020	-	0.040	-	-	-	-
K	1.6	0.11	1.4	0.11	0.9	1.0	12.7	0.45
La	24	14	34	17	1.4	1.2	2.0	0.79
Li	-	11	48	19	-	1.7	2.6	0.71
Lu	0.30	-	0.20	-	0.7	-	-	-
Mg	0.46	0.28	0.81	0.46	1.8	1.6	1.8	0.95
Mn	500	440	920	790	1.8	1.8	1.2	0.98
Mo	0.62	0.42	0.91	0.72	1.5	1.7	1.3	0.96
Na	0.59	0.005	0.48	0.007	0.8	1.4	69.0	0.25
Nb	9.7	0.52	11	0.60	1.1	1.2	18.3	0.54
Nd	21	-	29	-	1.4	-	-	-
Ni	18	14	40	29	2.2	2.0	1.4	0.94
P	0.056	0.065	0.066	0.054	1.2	0.8	1.2	0.96
Pb	23	18	40	34	1.7	1.9	1.2	0.95
Pr	5.6	-	8.2	-	1.5	-	-	-
Rb	80	14	93	18	1.2	1.3	5.3	0.47
S	-	0.030	-	0.030	-	1.0	-	-
Sb	0.60	0.28	1.3	0.53	2.2	2.0	2.4	0.90
Sc	8.2	2.0	12	3.8	1.5	1.9	3.1	0.77
Se	-	0.40	-	0.40	-	1.0	-	-
Sm	4.0	-	5.6	-	1.4	-	-	-

Table 2. *Cont.*

	EU$_{\text{(MA)}}$	**EU$_{\text{(AR)}}$**	**Slo$_{\text{(MA)}}$**	**Slo$_{\text{(AR)}}$**	**CR$_{\text{(MA)}}$**	**CR$_{\text{(AR)}}$**	**CR$_{\text{(MA/AR)}}$**	**R$_{\text{(MA/AR)}}$**
Sn	3.0	0.81	3.2	1.1	1.1	1.4	2.9	0.67
Sr	89	18	88	14	1.0	0.8	6.3	0.53
Ta	0.68	-	0.80	-	1.2	-	-	-
Tb	0.60	-	0.70	-	1.2	-	-	-
Te	0.030	<0.020	-	0.040	-	-	-	-
Th	7.2	2.5	11	4.1	1.5	1.6	2.7	0.74
Ti	0.34	0.007	0.38	0.006	1.1	0.9	62.9	0.38
Tl	0.66	0.12	-	0.23	-	1.9	-	-
Tm	0.30	-	0.30	-	1.0	-		
U	2.0	0.74	2.6	1.0	1.3	1.4	2.6	0.78
V	60	26	100	40	1.7	1.5	2.5	0.86
W	<5.0	-	1.5	-	-	-	-	-
Y	21	6.5	17	11	0.8	1.7	1.6	0.93
Yb	2.0	-	1.6	-	0.8	-	-	-
Zn	52	46	97	72	1.9	1.6	1.4	0.89
Zr	230	1.6	53	1.8	0.2	1.1	29.5	0.75

EU—European medians [52,54]; Slo—Slovenian medians (2011); (MA)—multi-acid digestion; (AR)—aqua regia digestion; CR$_{\text{(MA)}}$ and CR$_{\text{(AR)}}$ [61]—concentration ratios between European and Slovenian averages; CR$_{\text{(MA/AR)}}$—concentration ratio between MA and AR digestion (Slovenia); R$_{\text{(MA/AR)}}$—correlation coefficients between MA and AR digestion (Slovenia); data rounded at two digits; units are the same as in Table 1.

The equation for the concentration ratio (CR) is given below [111]:

$$\mathrm{CR} = \left[\frac{\mathrm{C_{(EL)}}}{\mathrm{C_{(STD)}}}\right] * 100 \tag{5}$$

where CR is the concentration ratio of the elements, C$_{\text{(EL)}}$ is the concentration of the Slovenian medians for both digestion methods, and C$_{\text{(STD)}}$ is the concentration of the internal standard in our case of European medians for both digestion methods.

The statistical relationship between the distributions of each chemical element determined with both digestion methods was assessed with the Pearson correlation coefficient (r), which is mainly sensitive to a linear relationship between two variables. It was qualitatively assumed that the absolute values of r between 0.5 and 0.7 indicate a moderate association and those between 0.7 and 1.0 indicate a strong association between elements.

Multivariate cluster analysis (HCA) (Figure 6) and factor analysis (FA) [71,83,84] were used to reveal the associations of chemical elements. The factor analysis method was introduced in 1904 by Sperman [112]. It represents a complicated system of procedures used to identify the interrelationship among a large set of observed variables. Factor analysis is known as a dimension reduction method, which means presenting data in a more concentrated way [77]. The principal aim of factor analysis is to explain the variation in a multivariate data set through a few representative factors that are not directly measurable but represent certain features inherent in the data [71,80]. In statistics, dimension reduction means reducing the number of variables taken for analysis. The dimension reduction can be divided into feature selection and feature extraction.

The factor analysis method is useful when presenting geochemical maps in regional geochemistry studies. An advantage is that instead of presenting maps for 40–50 (or more) elements, only maps of a few representative factors have to be presented [71]. The product–moment correlation coefficient (r) was used as a measure of the similarity between these variables. Principal component analyses were applied with varimax rotation and an eigenvalue greater than 1 (Kaiser criterion).

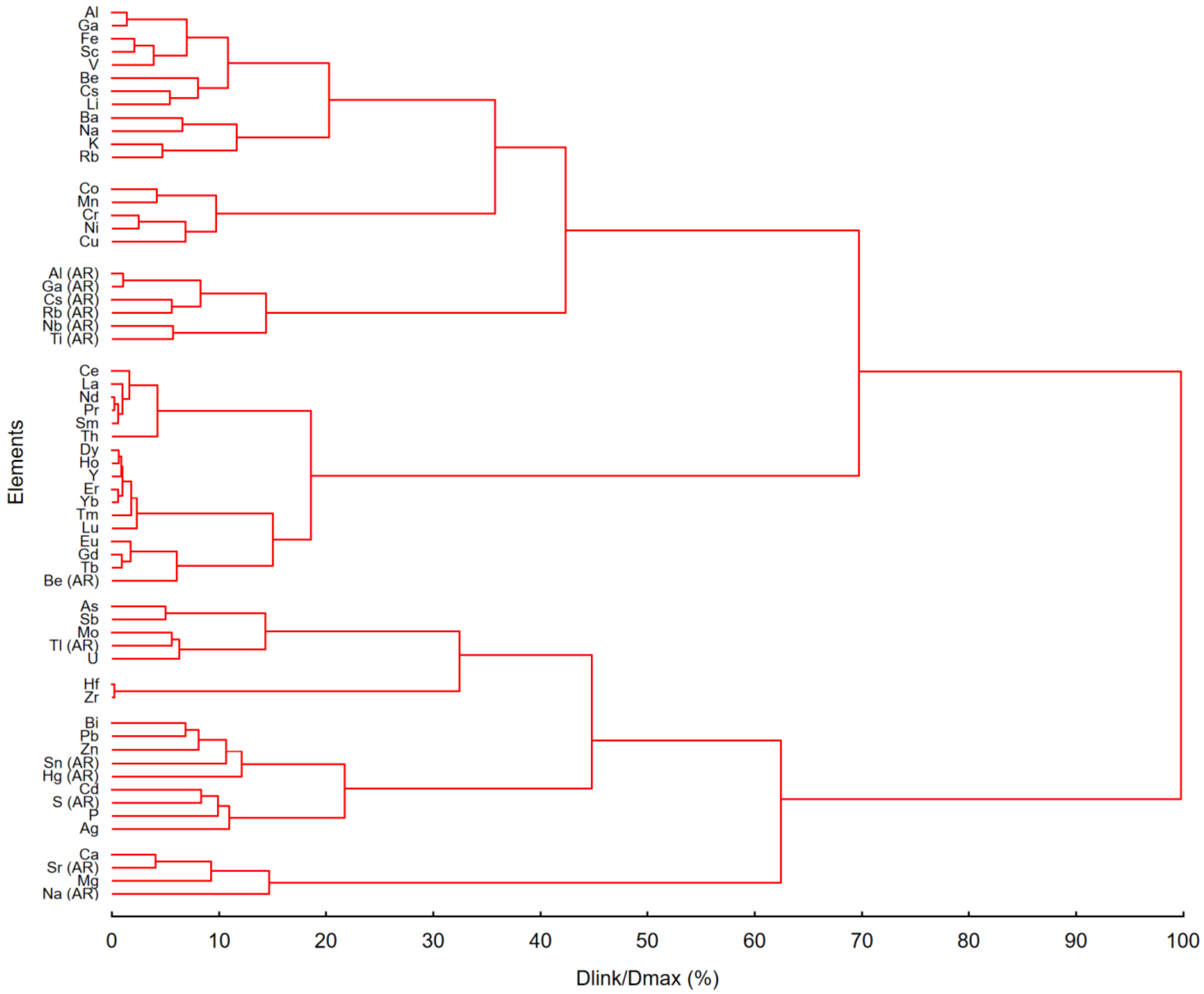

Figure 6. Dendrogram of cluster analyses.

Cluster analysis is another useful multivariate method. It is not one method but a type of proceeding that can be used to find out which objects in a set are similar [69,75]. Cluster analysis is applied to partition multivariate observations into several meaningful multivariate homogeneous groups or centers called centroids. These centroids summarize the group information to better understand the multivariate behavior of a data set [69]. The outcome of cluster analysis is the number of classes as well as the memberships of the observations in the group. Due to the complex nature of regional geochemical data, it is considered that appropriate data transformations must be performed before cluster analysis. Cluster analysis results also depend on the clustering algorithm selected [113]. The Ward method was used as a hierarchical clustering method to form groups, minimizing the variance within the groups. Linear correlation was measured using the Pearson correlation coefficient (r) to determine the strength and direction of the relationship between the two variables. In the final multivariate factor analysis, 50 elements or variables were considered (Table 3). The elements below detection limits and Hf, Nb, Sr, Ta, Ti, W, and Zr (MA digestion) were excluded because of the lack of significant associations with other chemical elements or because of their low commonalities.

Table 3. Factor analysis (n = 816).

	F1	**F2**	**F3**	**F4**	**F5**	**F6**	**F7**	**F8**	**Comm**
Ga	**0.80**	0.26	0.30	0.02	0.20	0.10	0.14	−0.09	87.3
Al	**0.80**	0.27	0.29	0.06	0.16	0.16	0.05	0.05	85.2
Rb	**0.77**	0.24	0.04	0.04	−0.01	0.01	0.03	−0.09	66.6
K	**0.76**	−0.01	−0.16	−0.09	−0.12	−0.05	0.39	−0.08	78.6
Cs	**0.75**	0.24	0.03	0.14	0.23	0.13	−0.30	−0.03	79.6
Li	**0.63**	0.48	0.15	0.07	0.30	0.04	−0.16	−0.09	77.5
Be	**0.62**	0.13	0.21	0.01	0.24	0.35	0.04	−0.04	63.8
Sc	**0.62**	0.56	0.24	0.08	0.14	0.26	0.08	0.03	84.9
Sn	**0.61**	−0.06	0.24	0.36	0.29	0.24	−0.05	−0.16	73.2
Th	**0.54**	0.04	0.36	0.00	0.50	0.38	−0.08	−0.22	86.2
Ni	0.15	**0.86**	0.13	0.09	0.06	0.16	−0.25	0.08	88.6
Cr	0.20	**0.84**	0.23	0.04	0.14	0.09	−0.13	−0.11	84.9
Co	0.16	**0.82**	0.19	−0.07	0.20	0.27	−0.01	−0.17	87.7
Cu	0.24	**0.75**	−0.07	0.32	−0.08	0.12	0.02	0.06	75.1
V	0.41	**0.65**	0.35	−0.02	0.37	0.05	−0.02	−0.03	86.2
Fe	0.55	**0.63**	0.27	0.10	0.15	0.17	0.13	−0.01	84.8
Mn	0.01	**0.61**	0.14	0.19	0.08	0.47	0.04	−0.16	69.1
$\text{Nb}_{(\text{AR})}$	−0.02	0.02	**0.80**	0.18	0.35	0.24	0.05	0.02	85.2
$\text{Ga}_{(\text{AR})}$	0.32	0.43	**0.75**	0.10	0.11	0.16	−0.08	−0.04	90.1
$\text{Cs}_{(\text{AR})}$	0.30	0.08	**0.74**	0.04	0.21	0.00	0.04	−0.17	71.7
$\text{Al}_{(\text{AR})}$	0.32	0.40	**0.73**	0.16	0.05	0.16	−0.15	0.02	86.9
$\text{Rb}_{(\text{AR})}$	0.24	0.30	**0.72**	0.08	0.01	0.11	0.00	−0.01	69.0
$\text{Ti}_{(\text{AR})}$	−0.12	0.01	**0.69**	−0.08	0.10	0.22	0.52	0.11	83.1
Ag	0.08	0.14	−0.01	**0.74**	0.04	−0.07	−0.04	0.21	62.6
$\text{S}_{(\text{AR})}$	−0.17	−0.03	0.11	**0.72**	0.06	0.00	−0.22	0.29	69.6
Pb	0.08	0.00	0.17	**0.69**	0.39	0.18	−0.10	−0.17	73.5
P	−0.07	0.14	0.07	**0.69**	−0.07	0.19	0.27	0.26	68.6
$\text{Hg}_{(\text{AR})}$	0.14	0.00	0.00	**0.64**	0.19	−0.02	−0.29	−0.22	60.5
Zn	0.30	0.41	0.09	**0.64**	0.14	0.19	−0.05	0.14	75.4
$\text{Sn}_{(\text{AR})}$	0.09	0.00	0.50	**0.59**	0.13	0.26	−0.31	−0.02	77.9
Cd	−0.20	0.11	0.05	**0.53**	0.31	0.32	−0.39	0.27	77.1
Bi	0.38	0.21	0.19	**0.51**	0.28	0.23	−0.36	−0.06	74.4
Mo	0.01	0.17	0.27	0.14	**0.76**	0.03	−0.23	0.10	75.9
As	0.27	0.31	0.11	0.26	**0.69**	0.20	−0.12	−0.05	78.5
U	0.27	−0.04	0.32	0.06	**0.68**	0.22	−0.20	−0.06	74.2
Sb	0.27	0.19	0.00	0.34	**0.67**	0.12	−0.05	−0.08	69.9
$\text{Tl}_{(\text{AR})}$	0.05	0.15	0.48	0.32	**0.55**	0.18	−0.34	−0.04	81.5
Y	0.13	0.31	0.18	0.20	0.11	**0.81**	−0.23	0.16	92.3
Er-Lu	0.24	0.33	0.19	0.17	0.13	**0.77**	−0.23	0.09	89.7
Sm-Ho	0.27	0.35	0.29	0.10	0.29	**0.74**	−0.08	0.06	92.2
La-Nd	0.32	0.25	0.40	0.00	0.48	**0.53**	−0.02	−0.13	86.1
$\text{Be}_{(\text{AR})}$	0.28	0.32	0.37	0.19	0.27	**0.50**	−0.32	0.07	78.4
Na	0.32	0.01	0.19	−0.11	−0.20	−0.03	**0.64**	0.02	59.0
Ba	**0.57**	0.08	0.16	−0.10	0.04	−0.03	**0.62**	−0.15	77.8
$\text{Zr}_{(\text{AR})}$	0.06	0.20	0.23	0.17	0.33	0.31	**−0.72**	0.06	84.8
$\text{Hf}_{(\text{AR})}$	0.05	0.20	0.14	0.24	0.17	0.30	**−0.74**	0.15	81.3
$\text{Sr}_{(\text{AR})}$	−0.17	−0.02	−0.09	0.14	−0.09	0.04	−0.18	**0.80**	74.7
Ca	−0.31	−0.08	−0.06	0.18	0.03	0.19	−0.20	**0.79**	84.1
Mg	0.01	0.06	−0.04	0.10	−0.01	0.09	−0.01	**0.77**	61.2
$\text{Na}_{(\text{AR})}$	0.09	−0.19	0.09	−0.04	−0.03	−0.20	0.23	**0.66**	58.1
Prp.Totl	14.6	12.4	11.1	9.5	8.5	8.1	7.5	6.1	77.7
EigenVal	18.58	6.63	3.28	2.93	2.80	1.97	1.43	1.22	
Expl.Var	7.28	6.20	5.54	4.74	4.27	4.05	3.73	3.03	

F1—F8—factor loadings; Comm—communality in %; Prp.Totl—total explained variance; Expl.Var—component variance; EigenVal—Eingen value; (AR)—aqua regia digestion. Values in bold indicate the factor values for the elements that belong to the corresponding factor.

To properly perform factor analyses, rare earth elements (REEs) were combined into three new variables, light REE (La, Ce, Pr, Nd), intermediate REE (Sm, Eu, Gd, Tb, Dy, Ho), and heavy REE (Er, Tm, Yb, Lu). During the analysis, the values of Al, Be, Cs, Ga, Hf, Hg, Na, Nb, Rb, S, Sn, Sr, Ti, Tl, and Zr, analyzed after AR digestion, were also considered because some were not analyzed after MA digestion (Hg, Tl, S), or some of the elements were excluded after MA digestion analysis (Hf, Nb, Sr, Ti, Zr). Also, in statistical data processing and distribution analysis, it was established that the elements Al, Be, Cs, Ga, Na, Rb, and Sn, analyzed after AR digestion, represent independent variables. Table 3 presents the factor loadings and the proportion of the factors to the total variance. These eight factors account for approximately 78% of the total variance.

3.4.3. Visual Representation of Chemical Elements Distribution

The universal kriging method with linear variogram interpolation was used to create spatial distribution maps for each factor value [114]. The base size of the grid cells for interpolation was 500 × 500 m. The seven classes were selected with the following percentile values: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100. A vertical bar plot was used for better visualization to compare the elemental contents and trends of determined factors according to different natural units, drainage areas, and geologic units (Appendix B, Figures A1–A4).

4. Results and Discussion

The basic statistical functions (means, medians, ranges, standard deviations, standard errors of the means, coefficient of variation, skewness, and kurtosis) are presented in Appendix A (Tables A1 and A2).

Slovenian median values, according to this study, were compared with European median values [52,54]. The highest concentration ratios (Slovenian vs. EU medians) were calculated for the following elements: As, Cd, Cu, Co, Ni Sb, Zn (MA digestion), where they ranged from 1.9 to 3.7 and for As, Cd, Co, Hg, Ni, Pb, Sb, Tl (AR digestion), where they ranged from 1.9 to 3.1 (Table 2). These elements were grouped into independent groups using cluster and factor analyses, represented mainly by Factor 2, Factor 4, and Factor 5.

Very low concentration ratios (<0.5) were calculated for Ag, Hf, and Zr (MA digestion) (Tables 1 and 2). In general, low concentrations of Ag are characteristic of European soils. The surface enrichment in Ag is found in well-known Pb-Zn-Ag and U mining districts in the southwest and northwest Massif Central, the Harz Mountains, Lavrion in Greece, and Erzgebirge in Germany/Czech Republic. Similar to Ag, there is no pronounced accumulation of Hf in sedimentary rocks, and with the exception of carbonates, all sedimentary rock types contain comparable concentrations of Hf. The high concentrations of Hf in Europe are related to felsic rocks, especially an intrusive massive [87]. The surface enrichment in Zr is found in felsic igneous rocks. By contrast, the level of Zr in sedimentary rocks is related only to the presence of heavy minerals, i.e., zircon and sphene [87,115].

A comparison between the median values for chemical elements from the previous study [56] with the median values from this study (after MA digestion) has been performed as well. Both analytical results coincide with each other, except for Co and W. This anomaly occurred due to contamination during the preparation method in 1993, when the use of a vibrating mill resulted in elevated concentrations of W and Co.

High concentration ratios for MA vs. AR (Table 2) were established for the elements generally grouped in independent clusters (Figure 6) or in factors 1, 3, and 7 according to multivariate analyses. At the same time, low correlation coefficients for MA vs. AR (<0.7) were determined for the mentioned groups. For other elements, generally grouped into factors 2, 4, 5, 6, and 8, significant variations in concentration ratios have not been found; these elements have relatively high correlation coefficients for MA vs. AR (>0.7).

Based on these preliminary studies, the spatial distribution of concentration ratios (CRs) between the two digestion methods (MA vs. AR) shows the greatest differences for Rb, Ga, Cr, Al, V, Nb, Cs, Ti, Sn, and K in relation to clastitic rocks. However, there are no significant differences in terms of geographical units or catchment areas. For the second group of elements (Zn, Cu, Ni, Co, Li, and Fe), the highest CRs are associated with carbonate areas. As for the first group, there are no significant differences between the geographical units or catchments. The highest CR for Ca, Sr, Ba, Hf, and Zr are associated with igneous and metamorphic rocks. As expected, significant differences can be observed, especially in the area of the Eastern Alps, the Pannonian Plain, or in the Drava catchment. The last group (Ce, Th, La, Y, Sc, Mn) shows no clear CR differences between the lithological and geographical units and the catchment areas.

Seven natural and one mixed natural/anthropogenic geochemical group were identified based on (a) factor analyses (FA) (Table 3); (b) hierarchical cluster analysis (HCA) results (Figure 6); (c) visually indicating the similarity of the geographic distribution of element patterns; (d) comparisons of basic statistical functions (Appendices A and B); and (e) concentration ratios and correlation coefficients (Table 2). For a description in the manuscript, as well as in figures and tables, the analyses performed by AR digestion are marked with the additional subscript (AR), and elements analyzed by MA digestion have no additional subscript.

Factor 1 describes c. 15% of the total variance and is characterized by strong positive loadings of Al, Be, Cs, Ga, K, Li, Rb, Sc, Sn, and Th. These elements represent the group that is little affected by anthropogenic activities and whose existence is confirmed by both the HCA and FA, respectively. The Slovenian median values for Factor 1, calculated for both chemical digestion methods (AR and MA digestions), are at the European level or slightly exceed them. Comparing the spatial distribution of elements after using these two digestion methods, some important differences can be observed. The ratio between MA and AR has an average value of 4.2 and varies from 2.2 to 12.7. This group is characterized by a relatively low correlation coefficient (Table 2). It can be observed that high levels of these elements are characteristic of district cambisols, formed on the Paleozoic and Triassic clastic rocks of the Posavske gube (Eastern Alps, Western and Eastern Prealps). Some increases in the levels of these elements can be found in areas of outcropping Magmatic and Metamorphic rocks. However, their lowest levels are found on the outcropping Mesozoic Carbonate rocks of the Alps and Dinarides. As expected, the low values of these elements are found in the Quaternary sediments of the Adriatic Basin (Figures 7 and A1).

The second strongest geochemical association is the assemblage of the following eight elements: Co, Cr, Cu, Fe, Mn, Ni, Sc, and V, grouped in Factor 2, which describes c. 12% of the total variance. The existence of this group is confirmed by both HCA and FA. The main characteristic of this group is that Slovenian median values are 50–100% higher than European ones, with the exception of Fe (MA), which is 10% higher than EU averages, regardless of which digestion method is used (MA or AR). This trend is especially true for Cu, Co, and Ni. Consequently, the correlation coefficient between the digestion methods is high (Table 2). The changes in the concentration of these elements according to the main drainage areas and the main geological units are provided in Figures 8 and A1. The highest levels of these elements are found in cambisol developed in the Karstic area of W Dinarides. They were released in the soil by the weathering processes of the Paleogene and Cretaceous flysch and later transported to the alluvial sediments of the Adriatic Basin. Fairly high levels are also found in the metamorphic complex of NE Slovenia. By contrast, the lowest values are characteristic of soils developed on igneous rocks, such as outcropping Mesozoic Carbonates and Paleozoic Clastic rocks (Figures 8 and A1).

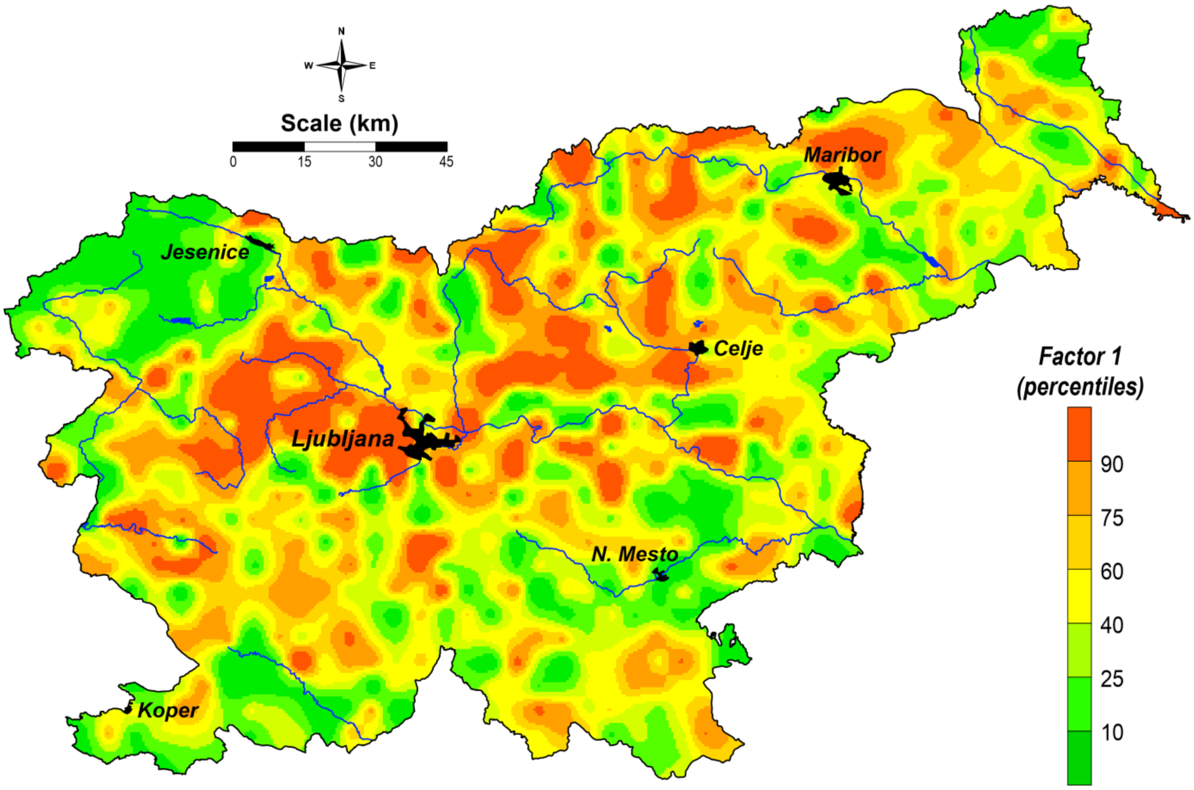

Figure 7. Spatial distribution of Factor 1 scores (Al, Be, Cs, Ga, K, Li, Rb, Sc, Sn, Th).

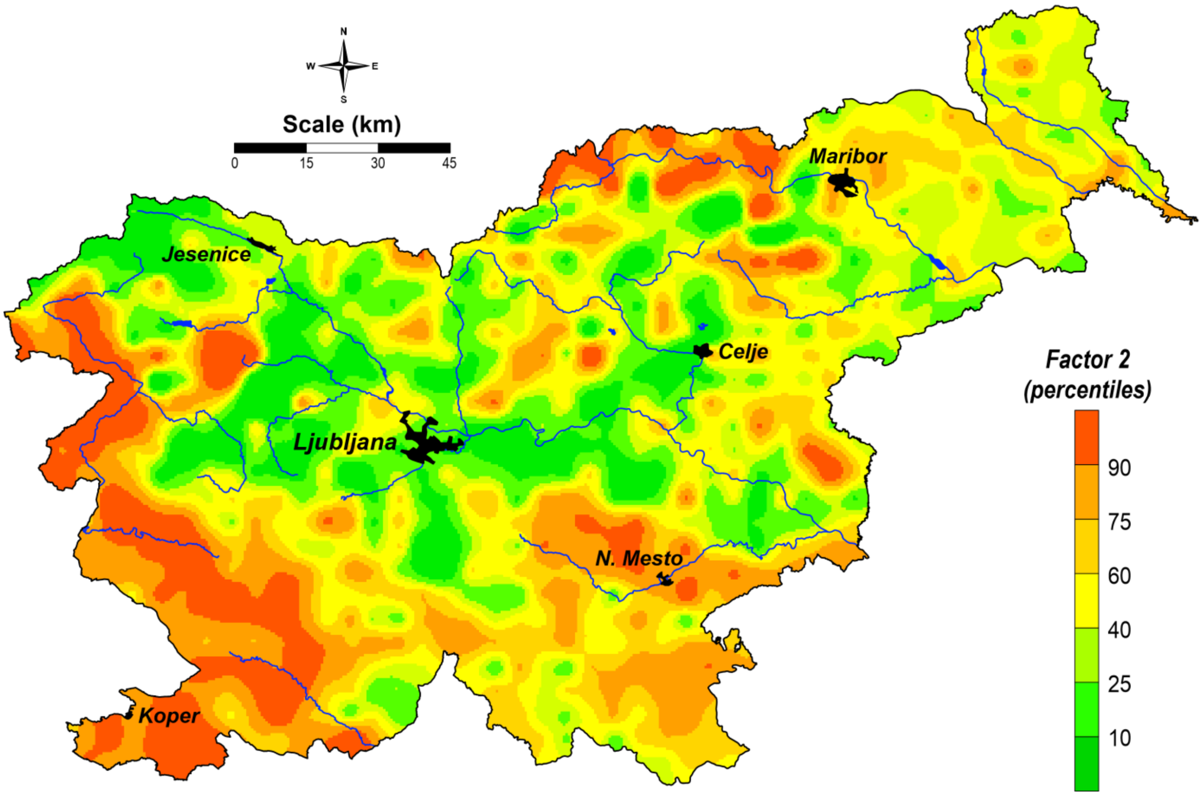

Figure 8. Spatial distribution of Factor 2 scores (Co, Cr, Cu, Fe, Mn, Ni, V).

The next group is the third strongest geochemical association, with 11% of the total variability. This group links the following six elements, $Al_{(AR)}$, $Cs_{(AR)}$, $Ga_{(AR)}$, $Nb_{(AR)}$,

$Rb_{(AR)}$, and $Ti_{(AR)}$, extracted using the AR digestion method. The HCA and FA isolate those elements in a separate group. Their spatial distributions differ significantly from the distributions obtained for elements extracted via MA digestion. The combination of these elements represented independent distribution and was treated accordingly. For most of these elements, it is significant that their Slovenian median values, calculated for both digestion methods, are similar to or above the European level. Like Factor 1, the ratio between MA and AR is about 4.2 but varies from 2.2 to 12.7. The correlation coefficient is relatively low. The highest values of elements belonging to this chemical association are found in district cambisols and rankers developed on igneous and metamorphic rocks in the E Alps. The main source of these high values could be the outcropping carbonate rocks of Paleogene, Cretaceous, and Jurassic in the E Dinarides. Clastic rocks contain rather low values of these elements; consequently, their release into the environment is very low (Figures 9 and A2).

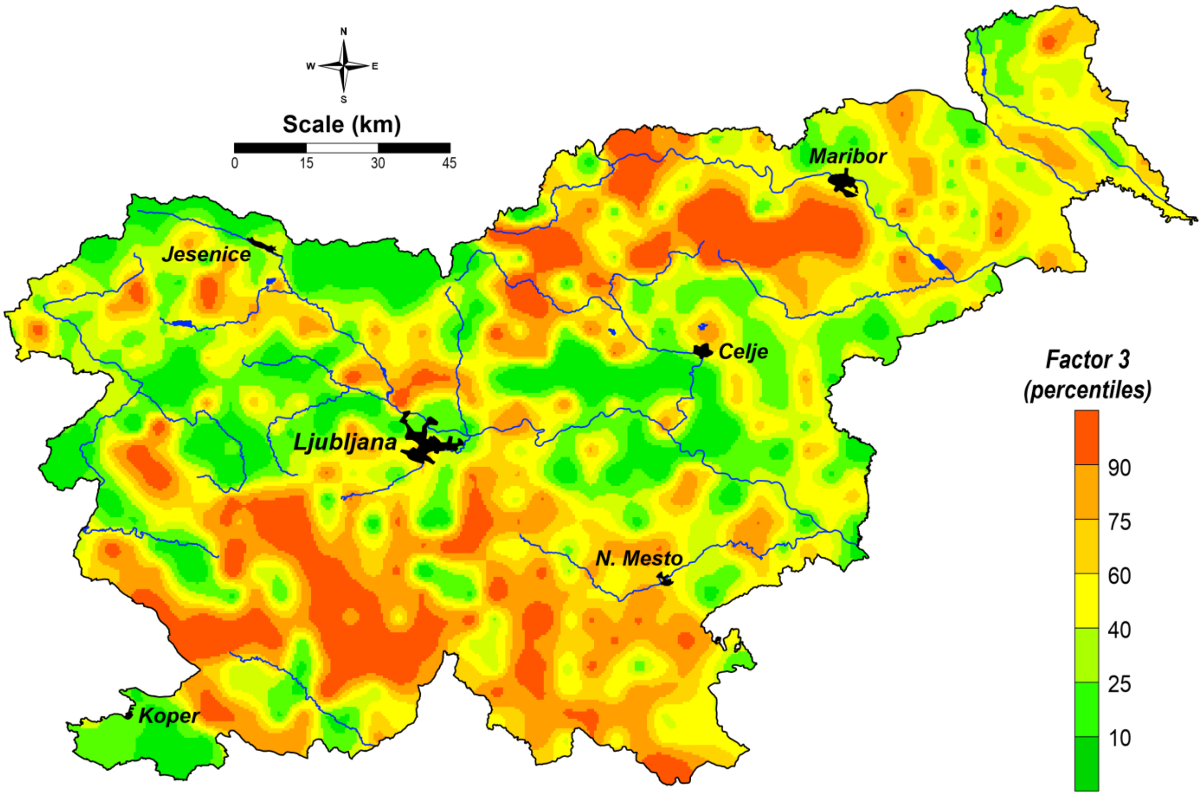

Figure 9. Spatial distribution of Factor 3 scores ($Al_{(AR)}$, $Cs_{(AR)}$, $Ga_{(AR)}$, $Nb_{(AR)}$, $Rb_{(AR)}$, $Ti_{(AR)}$).

Factor 4 is associated with Ag, Bi, Cd, $Hg_{(AR)}$, P, Pb, $S_{(AR)}$, $Sn_{(AR)}$, and Zn. This group represents a typical anthropogenic association combining toxic elements. They originate either as a result of natural erosion of ore-bearing rocks or as a consequence of mining and smelting activities in the past. This geochemical association represents an independent group after HCA and FA, described with 10% of the total variance. The Slovenian median values in this case—for both digestion methods—are about 70–90% higher than the European ones (except Ag). Since this group represents the anthropogenic group, consequently high concentrations can be found near mines and metallurgical centres such as Idrija [59], Mežica [63], Celje [62], Litija [64], and Jesenice (W Pre-Alps, Inner Basin). Past mining activities have left their traces, which are reflected in the high levels of these elements in the Quaternary sediments of the Sava watershed and the Adriatic Basin. Increased values of these elements are found in the Julian Alps (W Alps), the origin of which can be related to atmospheric deposition (Figures 10 and A2). In studying the regional distribution of Hg in the topsoil of Slovenia [60], it was found that the clearest Hg anomaly exists around the Idrija area as a result of former mining and ore processing.

The determined Hg median for the western part of Slovenia was almost twice as high as the value for eastern Slovenia and exceeded the Hg median for European soils [55] by four times. According to the natural geographical units of Slovenia, the highest Hg median was determined for the Western Prealps, where the Idrija mercury mine is located. This Hg anomaly can also be seen on the map of the spatial distribution of Factor 4 (Figures 10 and A2). In addition to the Idrija area, increased Hg concentrations were also observed in other mining areas (Litija [64], Podljubelj [116]), including the urban area of Ljubljana [117], and in areas with ironworks (Jesenice, Ravne [63]).

The HCA and FA isolated the fifth geochemical association. Factor 5 describes 9% of the total variance and is characterized by strong positive loadings of As, Mo, Sb, $Tl_{(AR)}$, and U. The main characteristic of this group is that Slovenian median values are about 50–70% higher than European ones, regardless of which digestion method is used. Consequently, the correlation coefficient between the digestion methods is high (Table 2). This geochemical association can be linked to the chromic cambisol of the Dinaric Karst, especially the karstic area of the Ljubljanica River (E Dinarides). The highest released levels of these elements are characteristic of soils developed on Cretaceous and Jurassic limestone, but somewhat lower values are found on Paleogene limestone in E Dinarides. The lowest levels are associated with district cambisols developed on Paleogene and Cretaceous flysch (Adriatic Basin) and the igneous rocks of NE Slovenia (Figures 11 and A3).

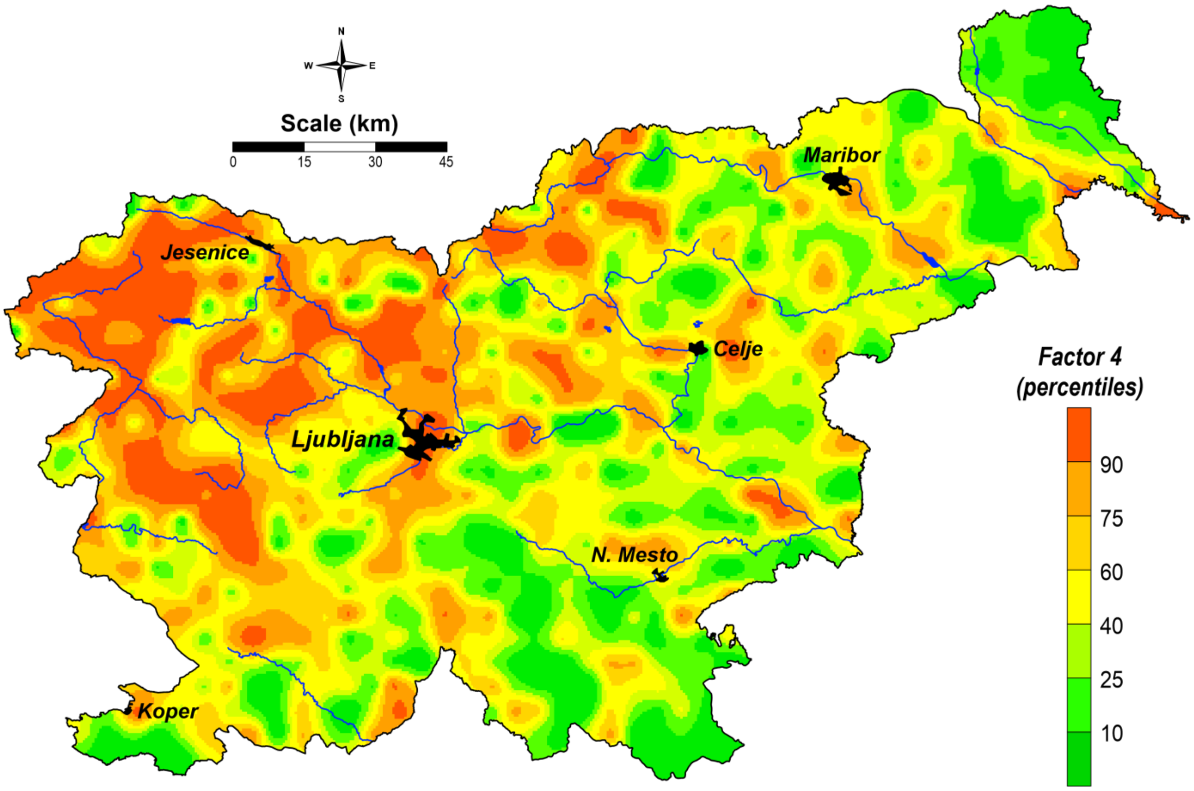

Figure 10. Spatial distribution of Factor 4 scores (Ag, Bi, Cd, $Hg_{(AR)}$, P, Pb, $S_{(AR)}$, Sn, Zn).

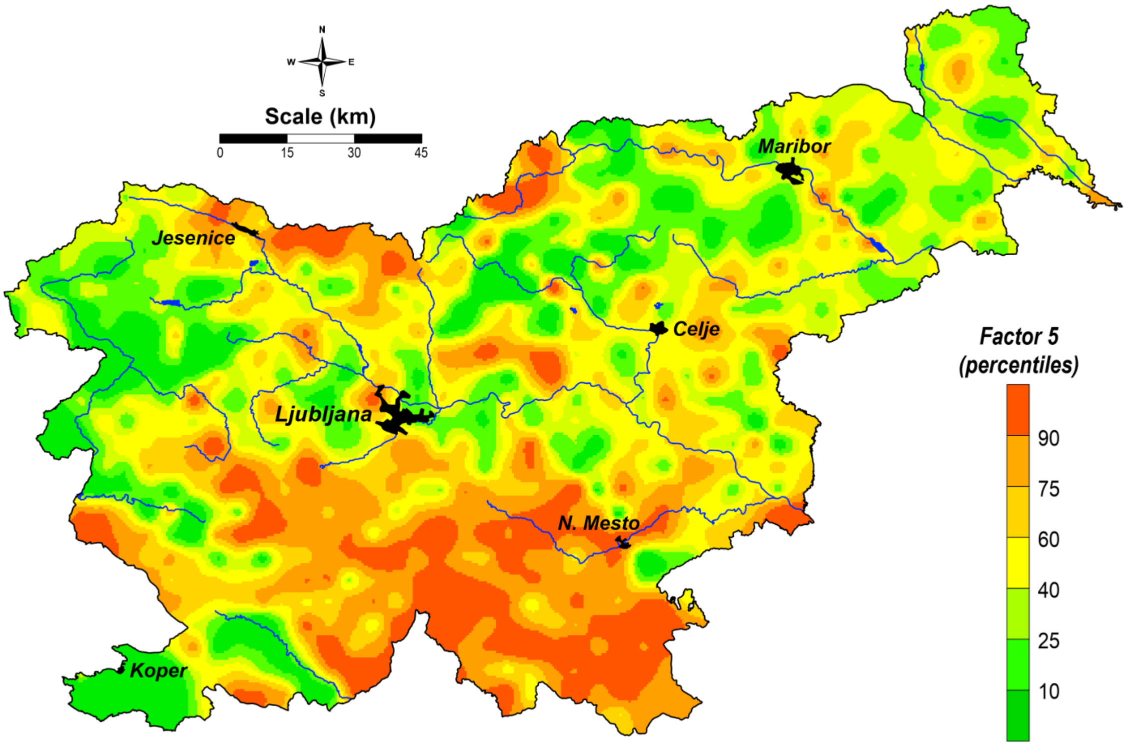

Figure 11. Spatial distribution of Factor 5 scores (As, Mo, Sb, $Tl_{(AR)}$, U).

High concentrations of As, Tl, and Sb can also be related to anthropogenic sources from mining, metallurgical activities, and fossil fuel combustion based on Pb, Zn, Cu, and Co, which are the main pollutants for soil, air, and water [49].

The next group, representing Factor 6, describes 8% of the total variance and associates the following rare earth elements (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb), $Be_{(AR)}$ and Y. This group has some similarities with the previous one, but the main differences between the factors are in their concentrations. A very interesting observation can be seen in Figures 12 and A3. The highest values are found in soils formed on Paleogene limestone and outcropping Cretaceous and Jurassic limestone. The lowest concentrations are found in the district cambisols developed on the Paleozoic, Paleogene, and Neogene clastites. This group shows no significant trend in the Quaternary sediments of the drainage areas.

The seventh group (Factor 7) is associated with high concentrations of Ba and Na with low concentrations of $Hf_{(AR)}$ and $Zr_{(AR)}$, which can be seen from the results of multivariate statistical methods, HCA and FA, respectively. This group differs from the previous geochemical associations by two characteristics: (a) the Slovenian median values for both digestion methods are higher ($Hf_{(AR)}$, $Zr_{(AR)}$) or lower (Ba and Na) than those at the European level. The ratio between MA and AR is 48 for Slovenian samples and ranges from 30 to 69, and (b) a very low correlation coefficient is detected between the digestion methods. Factor 7 provides the clearest chemical trends, which can be seen in Figures 13 and A4. It can be observed that the highest values of these elements are found in the district cambisol developed on the igneous and metamorphic rocks of NE Slovenia (E Alps and Pannonian Basin). The main causes of the high values are weathering processes in Neogene shales and sandstones, but also in igneous and metamorphic rocks. Consequently, the highest values of this factor are related to the Quaternary sediments of the Drava watershed. Contrary to this, the lowest values are characteristic of soils formed on the outcrops of Mesozoic carbonate rocks and Paleogene and Cretaceous flysch from SW Slovenia.

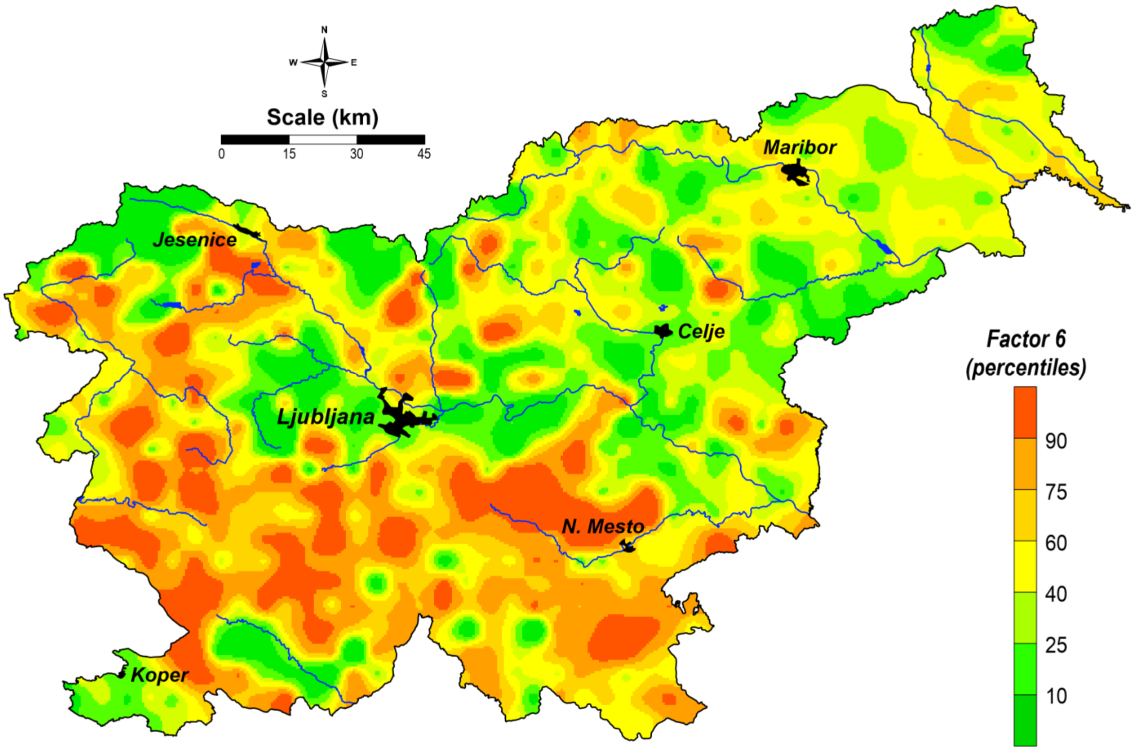

Figure 12. Spatial distribution of Factor 6 scores ($Be_{(AR)}$, REE, Y).

The last natural geochemical association (Factor 8) is described with the lowest total variance (6%) and is associated with the following four elements: Ca, Mg, $Na_{(AR)}$, and $Sr_{(AR)}$. It represents the geochemical association that could be related to the high mountain karst of the Julian Alps and Karavanke (W and E Alps) (Figures 14 and A4). Depending on the geological units, the highest values are found in soils from Triassic dolomites and Paleogene flysch, and the lowest values are found in soils generally developed on clastites.

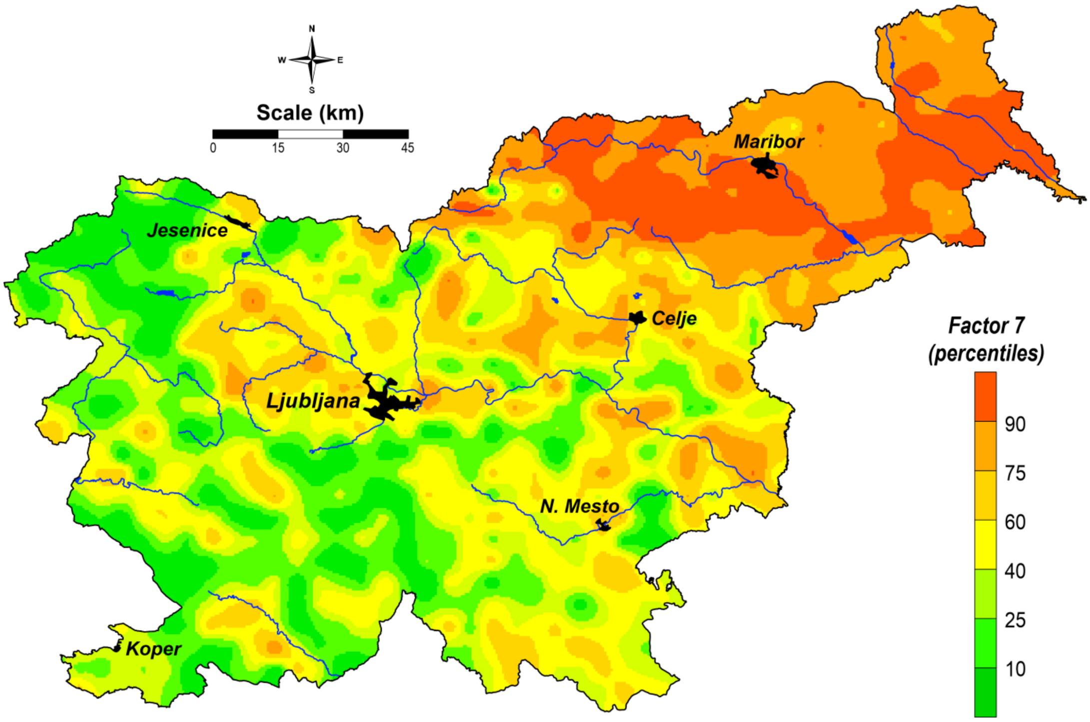

Figure 13. Spatial distribution of Factor 7 scores (Ba, Na, $-Hf_{(AR)}$, $-Zr_{(AR)}$).

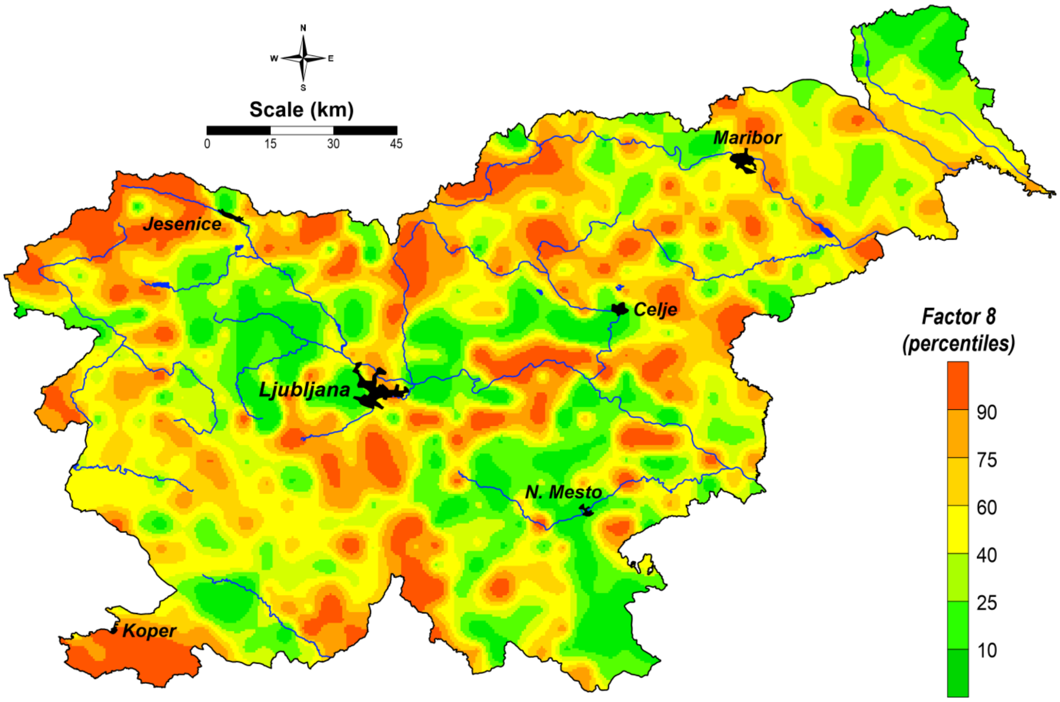

Figure 14. Spatial distribution of Factor 8 scores (Ca, Mg, $Na_{(AR)}$, $Sr_{(AR)}$).

5. Conclusions

The wide range of chemical elements analyzed based on multi-acid (MA) and aqua regia (AR) digestion and advanced multivariate statistical methods (factor and cluster analysis) have been used for the identification and isolation of the main geochemical trends in this country. In addition, the national levels of elements have been compared to the European soil levels to better understand contamination on the European level.

Because of the diverse Slovenian landscape, the geochemical baseline values are highly related to different characteristics of Slovenian natural units, drainage areas, and complex geological settings. Each natural unit has different geochemical characteristics due to the geological structure, lithology, relief, climate, and vegetation. Therefore, the regional distribution of 53 analyzed elements is presented according to the established geochemical associations. The first four geochemical associations are described with the highest percentage of total variance. High levels of the elements of the first geochemical association elements (Factor 1; Al, Be, Cs, Ga, K, Li, Rb, Sc, Sn, Th) have been found on district cambisol, developed on the Paleozoic and Triassic clastic rocks of Posavske gube (Eastern Alps, Western and Eastern Pre-Alps). The highest levels of the elements in Factor 2 (Co, Cr, Cu, Fe, Mn, Ni, Sc, V) are characteristic of soils formed on Cretaceous and Jurassic limestone in E Dinarides. The highest values of the elements in Factor 3 ($Al_{(AR)}$, $Cs_{(AR)}$, $Ga_{(AR)}$, $Nb_{(AR)}$, $Rb_{(AR)}$, $Ti_{(AR)}$) are formed in district cambisols and rankers formed on the igneous and metamorphic rocks of E Alps. Factor 4 (Ag, Bi, Cd, $Hg_{(AR)}$, P, Pb, $S_{(AR)}$, $Sn_{(AR)}$, Zn) represents an anthropogenic compound combining toxic elements. High concentrations of these elements are found in W Pre-Alps and the Inner Basin, especially in the vicinity of mines and metallurgic centers such as Idrija, Mežica, Celje, Litija, and Jesenice.

Important geochemical trends were determined using two digestion methods: the multi-acid method (MA) for total digestion and the partial method (sequential). The spatial distribution of most elements is not influenced by the digestion methods, but some elements are highly influenced by the treated digestion method, representing different (individual) geochemical trends.

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editing J.A., R.Š. and M.G.; Visualization, R.Š. and J.A.; data processing, R.Š. and J.A. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data are contained within the manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

Table A1. Descriptive statistics of measurements—multi-acid digestion (n = 816).

	$\overline{X}$	Md	Min	Max	P_{10}	P_{90}	S	$S_{\overline{X}}$	CV	A	E
Ag	95	82	<20	1200	33	160	73	2.6	77	6.05	74.72
Al	6.3	6.4	0.42	14	4.3	8.3	1.8	0.061	28	−0.28	1.46
As	15	14	0.70	150	6.9	24	10	0.36	67	4.86	44.90
Ba	340	330	16	1400	170	500	150	5.2	44	1.29	6.11
Be	2.1	2.0	<1.0	5.0	1.0	3.0	0.88	0.031	42	0.15	−0.07
Bi	0.43	0.40	0.060	1.3	0.23	0.70	0.19	0.006	43	1.13	1.84
Ca	2.5	0.67	0.020	28	0.18	8.2	4.3	0.15	174	2.76	7.92
Cd	0.96	0.56	0.040	13	0.19	2.1	1.2	0.042	125	4.02	24.32
Ce	72	70	4.0	180	41	110	27	0.93	37	0.42	0.72
Co	17	16	0.70	78	7.0	29	9.9	0.35	57	1.93	6.89
Cr	88	84	8.0	400	39	140	41	1.4	47	1.35	5.45
Cs	6.3	6.0	0.30	28	3.5	9.2	2.6	0.092	42	1.59	7.93
Cu	30	25	3.9	310	14	48	26	0.91	86	6.15	52.76
Dy	3.7	3.5	0.10	17	1.8	5.8	1.8	0.063	48	1.91	9.02
Er	1.9	1.7	0.20	9.8	0.90	3.0	1.0	0.035	53	2.30	11.44
Eu	1.2	1.1	<0.10	3.9	0.60	1.8	0.48	0.017	41	1.03	2.72
Fe	3.6	3.6	0.29	11	2.2	4.8	1.2	0.041	33	0.36	3.60
Ga	17	17	1.3	31	10	22	4.8	0.17	29	−0.58	0.75
Gd	4.6	4.4	0.20	18	2.4	7.1	2.0	0.071	44	1.51	6.34
Hf	1.5	1.5	0.12	5.8	0.52	2.5	0.82	0.029	54	0.80	1.35
Ho	0.72	0.7	<0.10	3.4	0.30	1.1	0.37	0.013	51	1.97	8.34
K	1.4	1.4	0.090	3.6	0.76	2.3	0.58	0.020	40	0.49	0.73
La	35	34	2.2	110	20	53	14	0.49	40	0.93	2.25
Li	50	48	1.9	240	29	73	21	0.74	42	2.16	15.13
Lu	0.27	0.20	<0.10	1.1	0.10	0.40	0.14	0.005	52	1.62	5.81
Mg	1.4	0.81	0.090	11	0.47	3.0	1.7	0.060	125	3.21	10.68
Mn	1100	920	39	6600	370	1900	690	24	65	2.09	9.05
Mo	1.7	0.91	0.14	39	0.46	3.4	2.7	0.093	158	7.24	80.11
Na	0.54	0.48	0.023	2.6	0.17	0.94	0.33	0.012	62	1.60	4.95
Nb	12	11	0.73	38	6.4	17	4.7	0.16	41	1.12	3.77
Nd	31	29	1.5	93	17	45	12	0.41	38	0.74	2.03
Ni	48	40	<0.10	560	18	92	35	1.2	72	4.89	60.03
P	0.078	0.066	0.012	0.56	0.034	0.13	0.051	0.002	65	3.16	17.80
Pb	46	40	8.9	840	24	66	37	1.3	79	13.11	268.61
Pr	8.4	8.2	0.50	24	4.8	13	3.2	0.11	37	0.62	1.40
Rb	92	93	4.2	210	55	130	30	1.1	33	−0.20	0.83
Sb	1.4	1.3	0.17	15	0.76	2.1	0.92	0.032	65	6.33	72.12
Sc	12	12	0.90	39	7.1	17	4.2	0.15	35	0.59	3.62
Sm	5.8	5.6	0.30	18	3.3	8.7	2.2	0.078	38	0.77	2.31
Sn	3.3	3.2	0.70	30	2.0	4.4	1.5	0.052	46	8.06	130.35
Sr	110	88	14	990	57	150	83	2.9	78	4.99	34.55
Ta	0.80	0.80	<0.10	2.4	0.40	1.2	0.32	0.011	40	0.85	2.51
Tb	0.71	0.70	<0.10	2.7	0.40	1.1	0.32	0.011	44	1.37	5.12
Th	11	11	0.50	26	6.2	16	4.0	0.14	35	0.12	0.48
Ti	0.39	0.38	0.023	1.7	0.20	0.54	0.16	0.006	43	2.13	13.23
Tm	0.29	0.30	<0.10	1.3	0.10	0.50	0.15	0.005	52	1.81	7.45

Table A1. *Cont.*

	$\overline{X}$	Md	Min	Max	P_{10}	P_{90}	S	$S_{\overline{X}}$	CV	A	E
U	2.9	2.6	0.30	9.6	1.6	4.7	1.4	0.048	47	1.59	3.36
V	110	100	8.0	300	54	160	46	1.6	43	0.99	2.27
W	1.6	1.5	0.10	12	0.80	2.2	0.71	0.025	45	4.45	57.35
Y	20	17	1.2	130	8.7	32	13	0.46	65	3.16	16.41
Yb	1.8	1.6	<0.10	8.2	0.90	2.8	0.87	0.030	48	2.03	9.30
Zn	110	97	17	1600	63	150	93	3.2	84	10.33	139.13
Zr	55	53	3.4	220	18	92	31	1.1	56	0.93	1.99

$\overline{X}$—mean; Md—median; Min—minimum; Max—maximum; P_{10}—10 percentile; P_{90}—90 percentile; S—standard deviation; $S_{\overline{X}}$—standard error of mean. CV—coefficient of variation; A—skewness; E—kurtosis; data rounded at two digits; units are the same as in Table 1.

Table A2. Descriptive statistics of measurements—aqua regia digestion (n = 817) [61].

	$\overline{X}$	Md	Min	Max	P10	P90	S	$S_{\overline{X}}$	CV	A	E
Ag	78	62	<2.0	1200	30	140	73	2.6	94	7.75	95.39
Al	1.9	1.8	0.090	5.7	0.98	2.9	0.78	0.027	41	0.53	0.74
As	13	11	0.85	140	5.3	20	9.5	0.33	76	5.67	56.73
Au	2.5	1.7	<0.20	110	0.70	4.1	5.0	0.18	199	14.62	274.70
B	2.8	2.0	<1.0	36	<1.0	6.0	2.8	0.099	99	3.90	31.11
Ba	83	75	3.2	820	37	130	51	1.8	62	5.36	61.52
Be	1.0	0.90	<0.10	3.5	0.50	1.8	0.54	0.019	53	0.98	0.86
Bi	0.36	0.33	0.020	1.3	0.18	0.59	0.17	0.006	47	1.28	2.53
Ca	2.0	0.44	<0.010	25	0.070	7.1	3.7	0.13	182	2.74	8.07
Cd	0.85	0.48	<0.010	11	0.15	1.9	1.1	0.039	131	3.86	21.40
Ce	39	38	1.8	130	14	63	19	0.68	50	0.50	0.61
Co	15	14	0.50	74	5.8	26	9.1	0.32	59	1.95	7.02
Cr	38	34	2.6	210	14	63	24	0.82	62	2.40	11.35
Cs	1.5	1.4	0.050	7.0	0.51	2.8	0.93	0.032	60	1.26	2.89
Cu	25	20	1.4	300	10	41	23	0.79	90	6.14	54.76
Fe	2.8	2.9	0.15	10	1.6	3.9	1.0	0.035	35	0.85	7.03
Ga	5.3	5.2	0.20	19	2.5	8.3	2.3	0.082	44	0.75	1.84
Hf	0.071	0.050	<0.020	0.37	<0.020	0.16	0.061	0.002	86	1.44	2.38
Hg	170	110	12	5300	0.050	310	320	11	185	10.38	135.24
In	0.039	0.040	<0.020	0.25	<0.020	0.060	0.022	0.001	57	2.31	15.37
K	0.13	0.11	<0.010	1.0	0.070	0.22	0.088	0.003	66	4.58	34.47
La	18	17	1.0	82	6.0	30	9.9	0.34	55	1.16	4.01
Li	20	19	0.30	150	8.1	31	12	0.43	61	4.27	37.31
Mg	0.98	0.46	0.030	9.9	0.21	2.4	1.6	0.054	159	3.40	12.11
Mn	960	790	17	7200	290	1800	680	24	71	2.42	12.41
Mo	1.4	0.72	0.070	38	0.32	3.0	2.4	0.085	173	7.83	92.88
Na	0.008	0.007	<0.001	0.057	0.003	0.014	0.006	0.001	74	3.03	16.49
Nb	0.75	0.60	<0.020	7.8	0.16	1.5	0.64	0.022	85	2.95	20.64
Ni	34	29	0.80	500	12	63	29	1.0	83	6.58	90.17
P	0.063	0.054	0.006	0.52	0.025	0.11	0.045	0.002	71	3.57	23.20
Pb	40	34	6.2	850	18	61	37	1.3	92	13.93	294.78
Rb	19	18	0.40	94	9.1	28	8.8	0.31	47	1.79	9.53
S	0.043	0.030	<0.020	0.37	<0.020	0.070	0.040	0.001	93	3.49	17.45
Sb	0.64	0.54	0.060	8.9	0.29	1.0	0.53	0.019	83	7.11	84.55
Sc	4.2	3.8	0.20	19	1.9	6.9	2.1	0.072	49	1.27	3.97
Se	0.44	0.4	<0.10	2.6	0.20	0.80	0.31	0.011	69	2.19	8.38
Sn	1.3	1.1	0.10	25	0.60	2.1	1.2	0.041	91	11.77	215.39
Sr	30	14	1.6	940	5.5	53	66	2.3	220	7.58	76.43
Te	0.049	0.040	<0.020	0.24	<0.020	0.11	0.040	0.001	81	1.39	2.18
Th	4.3	4.1	<0.10	17	1.5	7.2	2.2	0.076	50	0.59	0.91
Ti	0.012	0.006	<0.001	0.29	0.002	0.021	0.024	0.001	203	6.26	49.64
Tl	0.32	0.23	0.050	1.3	0.12	0.64	0.22	0.008	70	1.56	2.63
U	1.1	1.0	0.10	10	0.50	2.0	0.79	0.028	69	3.69	28.00
V	49	40	3.0	230	19	89	35	1.2	70	2.07	5.43

Table A2. *Cont.*

	$\overline{X}$	Md	Min	Max	P10	P90	S	$S_{\overline{X}}$	CV	A	E
Y	14	11	0.78	110	4.4	24	12	0.41	86	3.67	21.09
Zn	83	72	9.2	1400	42	120	82	2.9	100	11.10	152.99
Zr	2.4	1.8	<0.10	12	0.30	5.2	2.1	0.072	87	1.44	2.18

$\overline{X}$—mean; Md—median; Min—minimum; Max—maximum; P_{10}—10 percentile; P_{90}—90 percentile; S—standard deviation; $S_{\overline{X}}$—standard error of mean. CV—coefficient of variation; A—skewness; E—kurtosis; data rounded at two digits; units are the same as in Table 1.

Appendix B

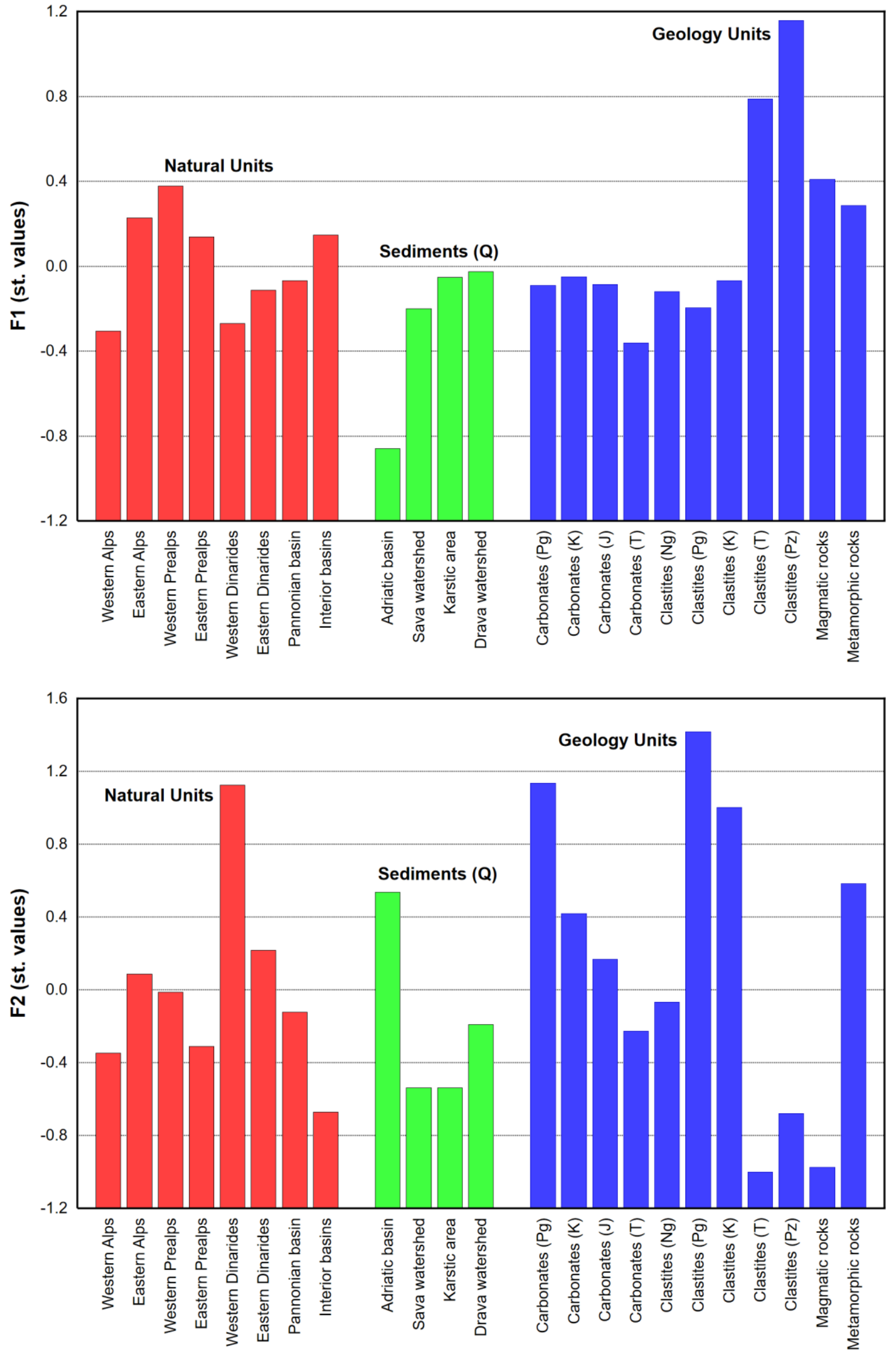


Figure A1. Distributions of Factor 1 scores (Al, Be, Cs, Ga, K, Li, Rb, Sc, Sn, Th)—above—and Factor 2 scores (Co, Cr, Cu, Fe, Mn, Ni, V)—below—according to the natural units, drainage areas and geological units.

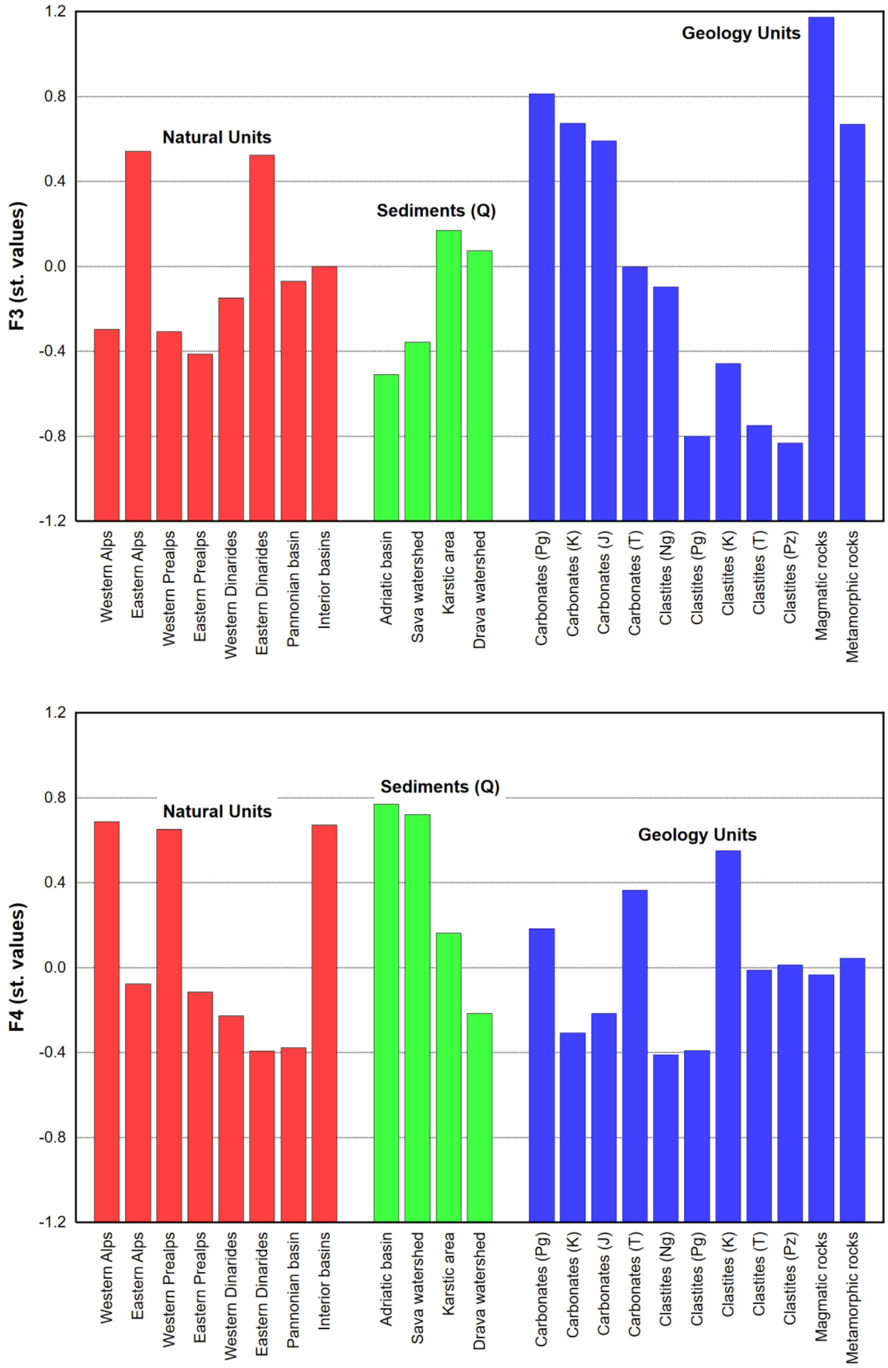
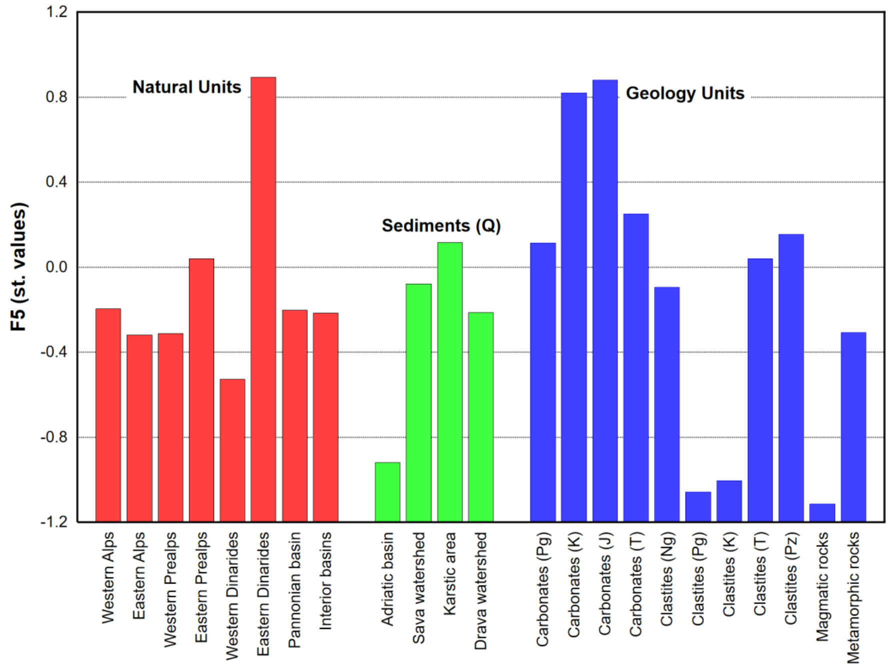


Figure A2. Distributions of Factor 3 scores ($Al_{(AR)}$, $Cs_{(AR)}$, $Ga_{(AR)}$, $Nb_{(AR)}$, $Rb_{(AR)}$, $Ti_{(AR)}$)—above—and Factor 4 scores (Ag, Bi, Cd, $Hg_{(AR)}$, P, Pb, $S_{(AR)}$, Sn, Zn)—below—according to the natural units, drainage areas and geological units.



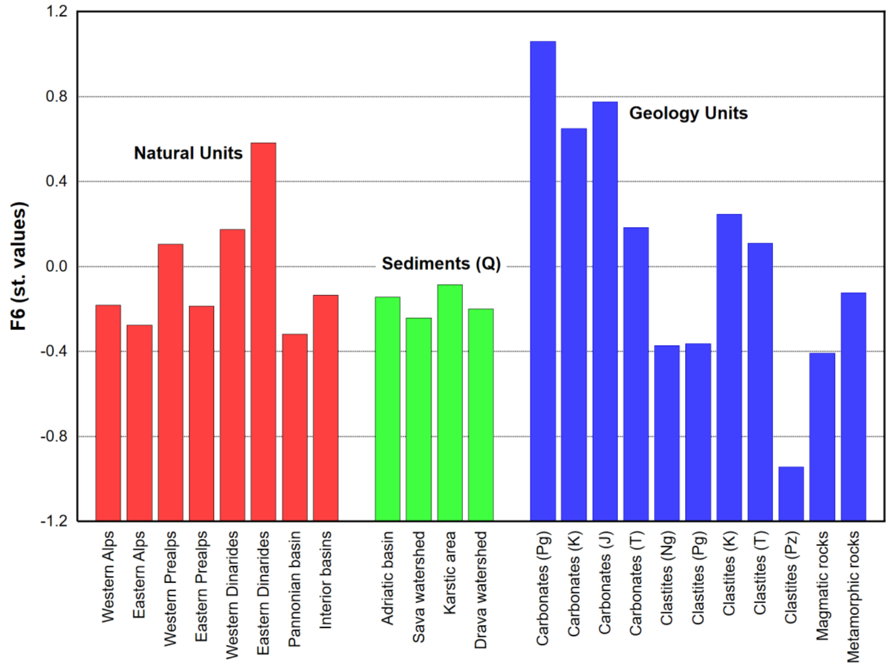
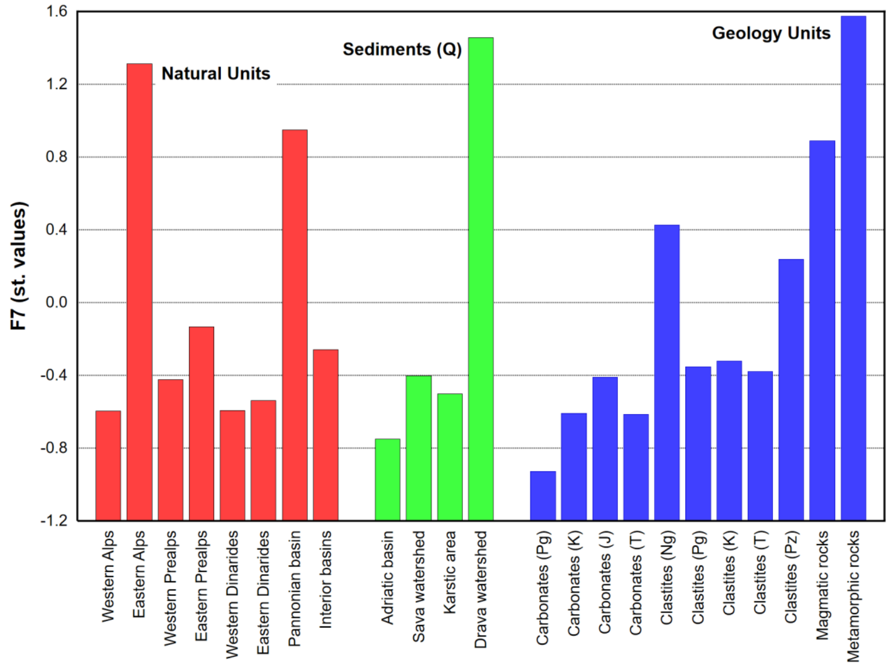


Figure A3. Distributions of Factor 5 scores (As, Mo, Sb, $Tl_{(AR)}$, U)—above—and Factor 6 scores ($Be_{(AR)}$, REE, Y)—below—according to the natural units, drainage areas and geological units.



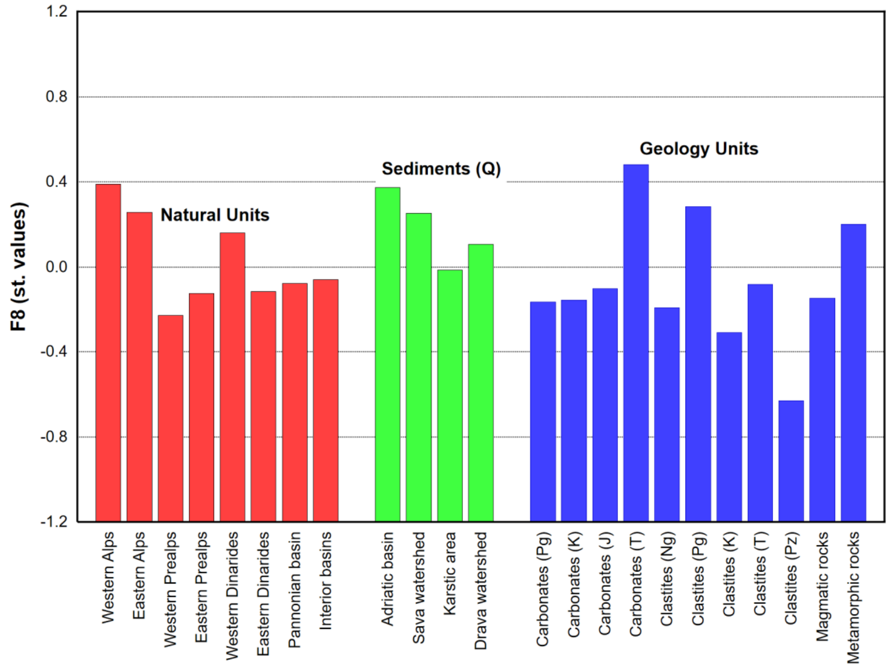


Figure A4. Distributions of Factor 7 scores (Ba, Na, -$\mathrm{Hf}_{(AR)}$, -$\mathrm{Zr}_{(AR)}$)—above—and Factor 8 scores (Ca, Mg, $\mathrm{Na}_{(AR)}$, $\mathrm{Sr}_{(AR)}$)—below—according to the natural units, drainage areas and geological units.

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