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Assessment of Atmospheric Deposition of Potentially Toxic Elements in Macedonia Using a Moss Biomonitoring Technique

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Abstract: This study aims to investigate the changes in atmospheric deposition trends in Macedonia, using a moss biomonitoring technique. This technique has been used to assess the content of potentially toxic elements in Macedonia in 2002, 2005, 2010, and 2015, within the framework of the International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops. The content of 42 elements was analyzed using instrumental neutron activation analysis (INAA), inductively coupled plasma–atomic emission spectrometry (ICP–AES), and atomic absorption spectrometry (AAS), on 72 moss samples collected in the summer of 2015. The median values of the elements studied were compared with data from previous years and with median values obtained from comparable studies in Norway and the neighboring countries. Through factor and cluster analysis, three geogenic factors were identified: Factor 1, which includes the elements Al, Ce, Fe, Hf, La, Li, Na, Sc, Sm, Tb, Ti, Th, V, and U; Factor 4, which includes As, Cl, and I; and Factor 5, which includes the elements Ba and Sr. In addition, one geogenic-anthropogenic factor containing Co, Cr, and Ni (Factor 2), was identified, and one anthropogenic factor containing Cd, Pb, Sb, and Zn (Factor 3). The lead and zinc mines near the towns of Kriva Palanka, Probištip, and Makedonska Kamenica in the eastern region of the country, the former lead and zinc smelter in the town of Veles, and the ferronickel smelter near Kavadarci, have continuously had the greatest anthropogenic impact on the atmospheric deposition of potentially toxic elements during the time period of the study. In addition to the human influences, the lithology and the composition of the soil continue to play a significant role in the distribution of the elements.

Keywords: moss; biomonitoring; air pollution; potentially toxic elements; Macedonia

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1. Introduction

Since the late 1960s, mosses have been used in terrestrial ecosystems as passive bioindicators of metal accumulation by atmospheric deposition [1,2]. They are commonly used in biomonitoring surveys, since wet and dry deposition is the primary method of collecting important nutrients. The absence of vascular tissue ensures that nutrients are not transferred internally among the plant's organs, and the absence of an advanced root system justifies limited uptake of the substrate [3,4]. The moss cell walls' high cation exchange capacity is a significant advantage over traditional bulk precipitation collectors, where

problems with sample contamination and measurement can appear [5,6]. High-density networks can be used to monitor element depositions from the atmosphere on a global scale due to mosses' widespread geographic distribution, abundance, and distinctive morphological and physiological characteristics [7,8]. Within the framework of the International Cooperation Project on Impacts of Air Pollution on Natural Vegetation and Crops (ICP Vegetation), European-scale moss surveys have been carried out since 1990 every five years. By analyzing the regional and temporal patterns of atmospheric deposition of Al, As, Cd, Cr, Cu, Fe, Ni, Pb, Sb, V, and Zn on naturally occurring moss bioindicators [6–11], the program aims to estimate transboundary air pollution. The International Cooperative Programme on Modelling and Mapping of Critical Levels and Loads and Air Pollution Effects, Risks, and Trends uses the data to validate air pollution models and reports the results to the Working Group on Effects of the United Nations Economic Commission for Europe (UNECE n.d.), Convention on Long-Range Transboundary Air Pollution (UNECE Air Convention). The program's standardized sampling protocol establishes a list of appropriate moss species that can be used as biomonitors, specifies the minimum distances between sampling locations and local emission sources, specifies conditions for the samples' transportation and storage, and gives preferred analytical techniques and standard reference materials to ensure data comparability [12,13].

Air pollution with potentially toxic elements poses severe risks to both environmental integrity and human health. Their release into the atmosphere leads to widespread contamination with lasting effects. The effects on the environment include the contamination of soil and water, the disruption of ecosystems, and threats to biodiversity. Potentially toxic elements can accumulate in the environment, persisting for extended periods and entering the food chain, posing threats to plants, animals, and aquatic life [14–17]. The impact of air pollution with potentially toxic elements on the corrosion and soiling effects on materials has been also the focus of many investigations. Heavy metals, released into the atmosphere from industrial activities and vehicle emissions, contribute significantly to the degradation of materials. Corrosion, a common consequence of heavy metal pollution, accelerates the deterioration of structures, monuments, and surfaces. Metals with sulfur dioxide and nitrogen oxides react with moisture in the air, forming acidic compounds that corrode metals, causing structural weakening and aesthetic damage to buildings and cultural artifacts [18,19].

The objectives of this study are to present the results of the 2015 deposition survey in Macedonia based on terrestrial moss analyses, to compare these results with those of the 2010 survey, to investigate the stability of element deposition over time, to explore whether specific regions consistently exhibited higher or lower levels of certain elements, highlighting potential contamination hotspots or natural enrichment zones, to compare these results with those of similar surveys conducted in 2015 in other Balkan countries and Norway, to differentiate between natural and anthropogenic sources, and to identify deposition patterns across the entire study area using different statistical methods, as well as Geographic information systems (GIS) technology. By comparing some of these aspects across the survey years, the study sought to provide insights into the evolution of elemental deposition, aiding in the development of effective environmental management strategies and targeted interventions to mitigate potential risks associated with these elements' atmospheric deposition.

2. Materials and Methods

2.1. Study Area

The Republic of Macedonia is a landlocked country in southeastern Europe (Figure 1). It borders Serbia to the north, Kosovo to the northwest, Albania to the west, Greece to the south, and Bulgaria to the east. The total area of the country is 25,713 km^2, which makes it one of the smallest countries in Europe. The country's topology is characterized by a mixture of mountainous regions, valleys, and plains. The country is divided into three major regions: the mountainous region in the north, the hilly region in the center, and the

flat plain in the south. The country has several mountain ranges, including 16 mountains higher than 2000 m, although most of the country's area is between 500 and 1000 m. The longest river in Macedonia is the river Vardar, whose central valley clearly defines the investigated area [20].

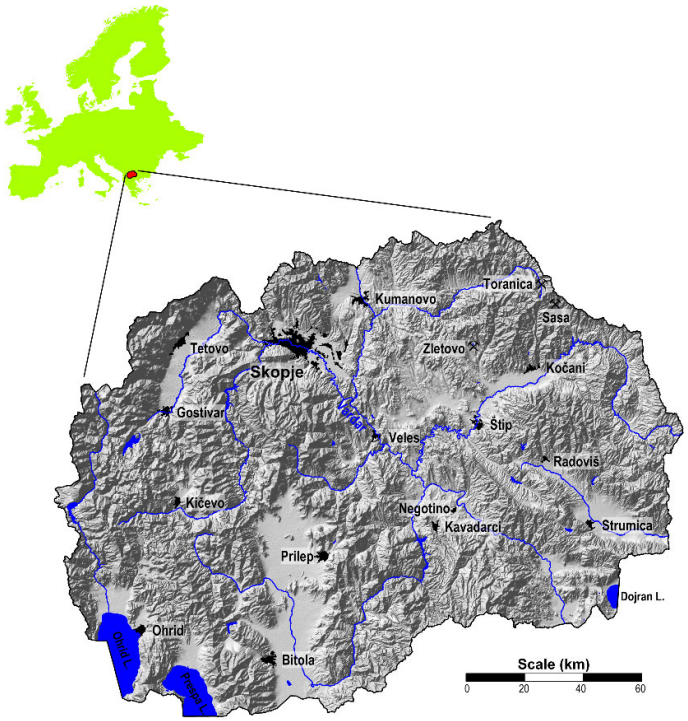


Figure 1. Position and map of the Republic of Macedonia.

The climate in the Republic of Macedonia is predominantly continental. However, due to the country's diverse topography, there are some regional variations in climate. In the lowland areas of the country, such as the Vardar River Valley, the climate is typically Mediterranean, characterized by temperatures often reaching over 30 °C in the summer. In the mountainous regions of the country, the climate is mountainous and characterized by more precipitation and longer winters. The higher elevations receive significant snowfall in the winter months, which can last from December to March. In the northern part of the country, the mildly continental climate dominates. Overall, Macedonia has a relatively dry climate, with an annual rainfall of 500–800 mm in most areas. The wettest period is typically from November to February, while the driest period is from June to August. However, there can be significant variations in precipitation from year to year. The majority of the population (1.837 million) lives in urban areas and about a quarter of them live in the capital Skopje [21,22].

The country has a long history of mining and mineral resource exploitation, dating back to ancient times. The country is rich in various mineral resources, and among the most important ones are copper (Macedonia has several copper deposits, including the Bučim copper mine, which is one of the largest copper mines in Europe), lead and zinc (there are several lead and zinc deposits in Macedonia, including the Zletovo, Toranica, and Sasa mines), chromium (Macedonia has one of the largest chromium reserves in the world, located in the central part of the country), nickel (nickel is primarily found in the region of Kavadarci), coal (Macedonia has several coal mines, including the REK Bitola lignite mine, which is the largest coal mine in the country), and gold (there are several gold deposits in Macedonia, including the Plavica and Zlatica gold mines). In addition to these minerals, Macedonia also has deposits of iron, manganese, and silver. The mining industry is an important sector of the country's economy, contributing significantly up to 30% to its GDP. The presence of both operational and abandoned industrial sites in the

mentioned areas inevitably results in environmental contamination with various heavy metals, in both nearby and remote regions. This has been documented in various research papers (references [23,24]).

2.2. Geological Characteristics of the Country

The country is located at the boundary between several major tectonic plates, which has resulted in the formation of diverse geological structures over millions of years. The Pelagonian Massif (PM) is the largest and oldest geotectonic unit in Macedonia, covering most of the western and central parts of the country. It consists of crystalline rocks, such as gneisses, schists, and granites, and was formed over 300 million years ago. The Vardar Zone (VZ) is the geotectonic unit that runs through the central and eastern part of the country and consists of a complex series of rocks, including metamorphic rocks, sedimentary rocks, and volcanic rocks. The Vardar Zone was formed through a series of tectonic collisions and subductions and is younger than the Pelagonian Massif. The Serbo-Macedonian Massif (SMM) is the geotectonic unit located in the northeastern part of the country and is characterized by a series of metamorphic and igneous rocks. The Serbo-Macedonian Massif was formed during the late Paleozoic and early Mesozoic periods. The Western Macedonian Zone (WMZ) is a geotectonic unit located in the western part of the country. This geotectonic unit consists mainly of metamorphic rocks, such as schists and gneisses, and is characterized by a series of thrust faults and folds. It was formed during the Mesozoic era. A simplified lithological map of Macedonia, where principal tectonic units are marked, is given in Figure 2 [25–28].

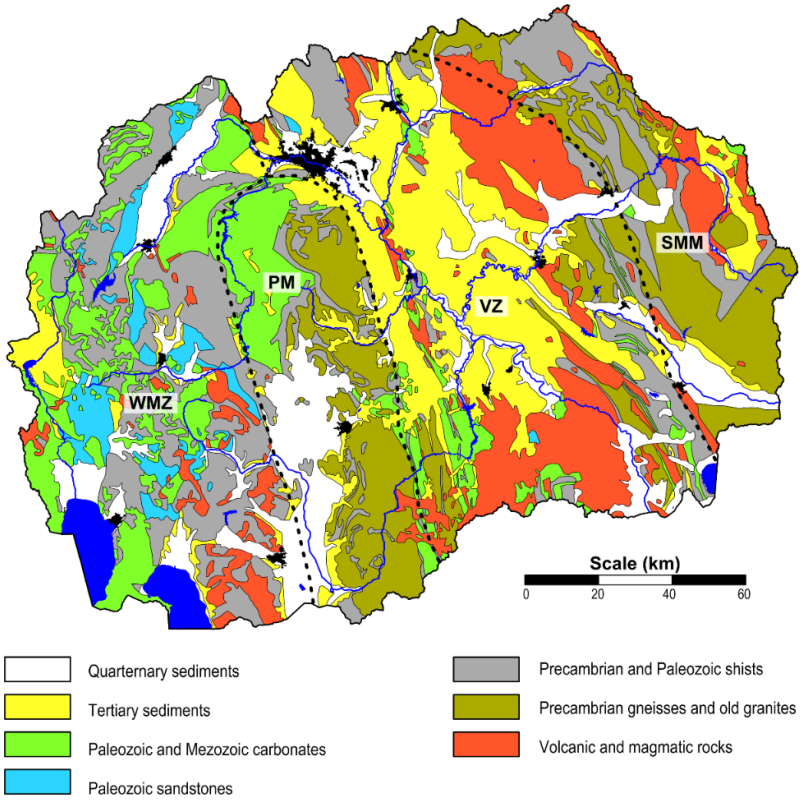


Figure 2. Simplified lithological map of Macedonia (according to geological map of SFR Yugoslavia, 1970). The areas of the principal tectonic units are separated by dashed lines: Western Macedonian zone (WMZ), Pelagonian Massif (PM), Vardar Zone (VZ), and Serbo-Macedonian Massif (SMM).

2.3. Moss Biomonitoring in Macedonia

For the purpose of assessing the atmospheric deposition of potentially toxic elements and discovering the potential sources of their emission on the territory of the Republic of Macedonia, the moss biomonitoring technique was used in 2002. Samples of three carpet-

forming moss species—*Hypnum cupressiforme*, *Homalothecium lutescens*, and *Homalothecium sericeum*—were the preferred species for analysis, since the mosses were collected in a range of habitats and different climate conditions. Samples were collected in August and September from 72 sites (2.8 samples were taken per 1000 km^2), outside urban areas, according to the sampling procedure previously described (references [29–32]). The amount of 42 elements in each sample were determined either by instrumental neutron activation analysis (INAA), inductively coupled plasma–atomic emission spectrometry (ICP–AES) or by atomic absorption spectrometry (AAS). In some locations, two or three types of the mentioned moss species were collected, and interspecies comparisons showed equal contents of elements within the error estimates [24]. The following survey was conducted during the August and September of 2005 at the same 72 locations using samples of *Hypnum cupressiforme* and *Homalothecium lutescens* [33]. Thirty-eight elements were determined in each sample using the aforementioned analysis methods [24]. The same 72 locations were used for the third moss study, which was undertaken in August and September 2010, and the same moss species (*Hypnum cupressiforme* and *Homalothecium lutescens*) were gathered. Using a combination of the analyzing techniques used in earlier surveys and atomic emission spectrometry with inductively coupled plasma (ICP–AES), the content of 41 elements was determined [24]. The fourth moss survey took place in August and September 2015, when 72 samples were collected over the territory of the Republic of Macedonia, using the same sampling network grid as for the previous three surveys. Using the three aforementioned analysis methods, a total of 42 elements (Al, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Fe, Hf, Hg, I, In, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, Pb, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, and Zn) were determined.

2.4. Sampling and Sample Preparation

Sampling sites practically overlapped, to allow for comparisons between the different surveys, and the same biotope conditions were applied (Figure 3). Sampling in 2002 was undertaken in accordance with the European moss surveys' guiding principles [31–33], and, in 2005, in accordance with the ICP Vegetation Programme's monitoring manual for the 2005/2006 survey as well [6]. In 2010 and 2015, sampling was conducted in accordance with the Convention on Long-Range Transboundary Air Pollution (CLRTAP) and the International Cooperative Programme on the Effects of Air Pollution on Natural Vegetation and Crops—Monitoring Manual for 2010/11 Survey [9], as well as in accordance with the methodology used in previous European moss surveys.

Regardless of the sampling year, samples were collected at least 3 m from the treetop, preferably on the ground or on the surface of decomposing trunks. According to the methodology, sample locations were situated outside of urban areas, at least 300 m from major roads, villages, and industry, and at least 100 m from smaller roads and houses. Five to ten subsamples were taken from each site throughout a 50 × 50 m area, from which a composite sample was created. In the composite sample, there was just one type of moss. Paper bags were used for collecting. One liter of moss was taken from one location. Powder-free gloves were used for each sample, to avoid contamination of the samples.

In the laboratory, samples were cleaned of extraneous material (litter and dead leaves) and dried at 30–40 °C for 48 h to constant weight. Green–brown parts of the moss shoots, which reflect the last three years of moss growth, were chosen for the investigation of pollutant content.

2.5. Analytical Measurements

Instrumental neutron activation analysis (INAA), atomic absorption spectroscopy (AAS), and inductively coupled plasma–atomic emission spectrometry (ICP–AES) were used to evaluate the elemental content of moss samples in each of the sampling surveys. INAA was carried out at the IBR-2 pulsed fast reactor's radioanalytical complex REGATA (Frank Laboratory of Neutron Physics, JINR, Dubna, Russia). Further information on the irradiation and measurement of moss samples can be found in ref. [24]. The Genie

2000 software from Canberra was used for the analysis of the spectra, with the interactive peak fit verification, and the concentration program was used for the element contents computation [34].

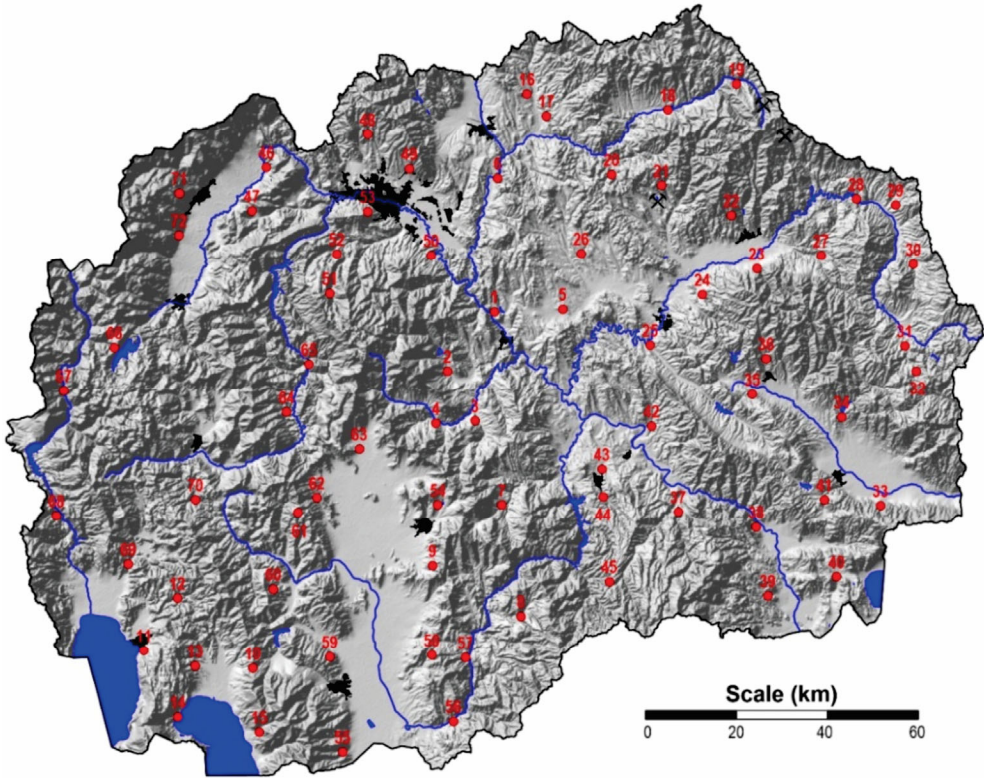


Figure 3. Location of the 72 sampling points.

AAS and ICP–AES analysis was performed at the Institute of Chemistry, Faculty of Natural Sciences and Mathematics in Skopje, Macedonia. About 0.3 g of moss was placed in a Teflon vessel for AAS and ICP–AES analysis, and it was treated with 5 mL of concentrated nitric acid (HNO_3) and 1 mL of hydrogen peroxide (H_2O_2). Complete digestion of the moss samples was carried out using a microwave digestion system (Mars; CEM, USA). Further information about the sample preparation for AAS and ICP–AES techniques were previously given [24,35].

2.6. Quality Control of the Analysis

Quality control and the assurance of the INAA results involved the simultaneous analysis of samples and the following Standard Reference Materials (SRM), produced by the National Institute of Standards and Technology (NIST): NIST SRM 1633c-Coal Fly Ash, NIST SRM 1633b-Coal Fly Ash, NIST SRM 2710-Montana Soil, NIST SRM 1575a-Pine Needles, NIST SRM 1515-Apple Leaves (Table S1).

Quality control and assurance of the results obtained by AAS and ICP–AES was completed using the European Moss Survey's M2 and M3 standard moss reference materials [36]. The concentrations measured were within the recommended range. The differences between the measured and certified values were within 15%. The standard addition method was also used, and quantitative recoveries were reached for most elements (Table S2).

2.7. Statistical Methods

The statistical analysis software Statistica 13 (StatSoft, Inc., Tulsa, OK, USA) was used to perform both descriptive and multivariate statistics. The Box–Cox method of transformation was used to transform the data, since they were not normally distributed. The correlation degree, also known as the linear dependence between two random variables

or sets of random variables, was computed using the Pearson correlation coefficient. For values of the coefficient ranging between 0.7 and 1.0, a significant association was identified and, for values from 0.5 to 0.7, a good association between the elements was considered to exist [37,38].

To investigate the association of chemical elements and reduce variables, multivariate cluster analysis and R-mode factor analysis, were carried out, based on the matrix of correlation coefficients [39–42]. In this case, the values obtained in the matrix in the range of 0.7 to 1.0 were taken as a strong association, while values in the range of 0.5 to 0.7 were taken as a good association. The multivariate statistical cluster and factor analyses were performed on 26 elements (Al, As, Ba, Br, Co, Ce, Cr, Cd, Fe, Hf, I, La, Li, Na, Ni, Pb, Sb, Sc, Sm, Sr, Tb, Th, Ti, U, V, and Zn). Elements that did not show a reasonable connection with other chemical elements were excluded from the analysis. Based on the characteristics of the 26 elements, the five new variables were designed, Factor 1—F1 to Factor 5—F5, with a variability of the established elements of 78.8% of the total variability of the treated elements. It is considered that the variables significantly contributed to a given factor if their factor loadings were greater than 0.6.

Universal kriging with the linear variogram interpolation method was used to create maps exhibiting the spatial distribution of factor scores and the distribution of potentially toxic elements in the moss samples [39,40]. The fundamental grid cell size for the interpolation was 1 × 1 km. Additionally, seven classes of percentile values of the distribution values were defined: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90, and 90–100. Statistica 13 (StatSoft, Inc., Tuls, OK, USA), QGIS (#), and Surfer 17 (Golden Software, Inc., Golden, CO, USA) were used for the visualization of the data.

3. Results and Discussion

Table 1 shows the statistics for the 42 analyzed elements (Al, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Fe, Hf, Hg, I, In, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, Pb, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, and Zn) in the 72 moss samples collected over the study area. The values for Au, Hg, Ta, Tb, and W are given in µg/kg; Al, Ca, Fe, K, and Mg are given in %; and the values for the remaining 31 elements are given in mg/kg. For each element, the following parameters were calculated separately: arithmetic mean, median, arithmetic mean values transformed by Box–Cox transformation, minimum and maximum values, 10th, 90th, 25th, and 75th percentiles, standard deviation, median absolute deviation, kurtosis, skewness and values for kurtosis, and skewness obtained after Box–Cox transformation. The skewness coefficient or asymmetry for all elements suggests a positive skewness of the data set, which is further supported by higher arithmetic mean values than median values. The distributions of Au, Cr, Cs, Hf, Ni, Sr, Ta, Th, and U are strongly skewed. Some studies have shown that the high value of this coefficient reflects the presence of point pollution sources in the study area [41,42]. The results of the kurtosis or coefficient of distribution asymmetry indicate that the distribution is more pointed than the normal distribution for all elements, with an exception for As, In, and Zn.

Table 2 compares the average contents of the studied elements according to territorial regions (MKD-W—western part, MKD-C—central part, MKD-E—eastern part) and tectonic units (WMZ—Western Macedonian Zone, PM—Pelagonian Massif, VZ—Vardar Zone, SMM—Serbo-Macedonian Massif, and Ng–Pg—Neogene and Paleogene basins, which generally trend from northwest to southeast and were formed mainly within the Vardar zone and the Serbo-Macedonian tectonic units [27,28]). Some of the elements have relatively similar mean contents in the three territorial regions and the mentioned tectonic units and basins, indicating that their presence in the mosses is strongly influenced by the surface soil particles attached to the mosses and that they do not have an anthropogenic origin (Al, Br, Ce, Cs, Fe, Hf, Mg, Na, Sc, Se, Sm, Tb, Ti, and V). Some of the elements have higher values in the central part of the country, where most of the metallurgical facilities are located, and, at the same time, in the Neogene and Paleogene basins, indicating anthropogenic origin (As, Cd, Co, Cr, Mo, Ni, Pb, and Zn). The mean values for the other elements in

the different tectonic units differ, which can be explained by the lithogenic origin of these elements and their higher abundance in some of the rocks, for example, Ba, Cl, Li, Mn, Th, and U [25].

Table 1. Descriptive statistics for all elements contents in the 72 moss samples collected from Macedonia.

	Unit	X	Md	X_{BC}	Min	Max	P_{10}	P_{90}	P_{25}	P_{75}	S	MAD	A	E	A_{BC}	E_{BC}
Al	%	0.23	0.20	0.20	0.085	0.68	0.14	0.34	0.16	0.28	0.11	0.044	1.94	4.89	−0.00	0.36
As	mg/kg	0.71	0.72	0.64	0.079	1.7	0.16	1.3	0.27	1.0	0.43	0.40	0.21	−0.95	−0.20	−1.16
Au	µg/kg	1.4	0.85	0.80	0.14	14	0.21	3.1	0.37	1.6	1.9	0.56	4.17	23.47	0.02	−0.60
Ba	mg/kg	60	50	52	13	180	27	110	34	78	34	20	1.20	1.54	−0.01	−0.36
Br	mg/kg	2.5	2.3	2.4	1.3	5.3	1.7	3.5	2.0	2.8	0.74	0.40	1.28	2.52	−0.00	0.14
Ca	%	0.66	0.66	0.65	0.28	1.2	0.45	0.85	0.52	0.76	0.17	0.11	0.45	0.41	−0.00	0.09
Cd	mg/kg	0.25	0.21	0.21	0.018	0.88	0.040	0.49	0.10	0.39	0.19	0.13	1.04	1.19	−0.10	−0.66
Ce	mg/kg	2.9	2.6	2.5	1.1	9.8	1.6	5.0	2.0	3.3	1.6	0.58	2.23	6.30	−0.01	0.31
Cl	mg/kg	110	84	86	44	390	61	170	67	120	68	19	2.49	6.61	0.11	−0.36
Co	mg/kg	0.89	0.78	0.77	0.19	3.4	0.47	1.5	0.60	0.98	0.53	0.19	2.68	9.34	−0.03	1.76
Cr	mg/kg	7.1	5.7	5.7	2.1	35	3.2	10	4.4	8.1	5.3	2.0	3.27	13.35	−0.01	0.21
Cs	mg/kg	0.28	0.22	0.21	0.067	1.4	0.12	0.44	0.16	0.28	0.25	0.057	3.08	9.96	−0.06	1.13
Cu	mg/kg	4.7	4.6	4.6	3.0	8.3	3.5	6.1	4.1	5.2	1.1	0.58	1.03	1.27	0.01	−0.16
Fe	%	0.17	0.16	0.16	0.050	0.37	0.093	0.29	0.13	0.20	0.072	0.038	0.91	0.48	−0.00	0.03
Hf	mg/kg	0.20	0.18	0.16	0.041	1.2	0.094	0.28	0.13	0.21	0.18	0.044	4.55	23.28	−0.08	2.49
Hg	µg/kg	85	84	79	20	250	20	150	53	120	47	33	0.55	0.70	−0.11	−0.49
I	mg/kg	1.2	1.2	1.1	0.45	2.3	0.74	1.8	0.90	1.4	0.39	0.25	0.64	0.11	−0.01	−0.33
In	mg/kg	0.22	0.23	0.18	0.025	0.52	0.046	0.42	0.067	0.34	0.15	0.15	0.24	−1.28	−0.17	−1.55
K	%	0.70	0.69	0.67	0.39	1.5	0.49	0.94	0.59	0.78	0.19	0.098	1.37	3.14	−0.00	0.17
La	mg/kg	1.6	1.3	1.4	0.48	5.1	0.80	2.5	1.1	1.7	0.85	0.34	2.24	6.28	−0.02	0.64
Li	mg/kg	0.90	0.79	0.78	0.32	3.1	0.51	1.4	0.59	1.0	0.48	0.22	2.35	7.36	−0.00	0.18
Mg	%	0.22	0.21	0.21	0.096	0.37	0.16	0.31	0.19	0.23	0.058	0.025	0.84	0.36	−0.00	0.74
Mn	mg/kg	170	130	130	36	540	48	320	73	240	120	78	1.08	0.76	−0.01	−1.06
Mo	mg/kg	0.39	0.27	0.28	0.020	2.4	0.080	0.81	0.16	0.51	0.37	0.12	2.87	12.58	0.01	0.31
Na	mg/kg	260	220	220	130	890	160	450	180	280	140	51	2.25	5.85	0.13	−0.61
Nd	mg/kg	1.2	0.96	0.97	0.015	4.3	0.39	2.1	0.59	1.4	0.94	0.38	1.87	3.40	0.11	1.28
Ni	mg/kg	7.7	4.4	4.3	0.96	79	2.4	10	2.8	6.4	12	1.7	4.27	19.64	−0.07	1.06
Pb	mg/kg	5.3	4.8	4.8	2.2	14	3.0	8.4	3.3	6.9	2.4	1.6	0.92	0.81	0.01	−0.90
Rb	mg/kg	8.9	7.5	7.6	2.7	39	4.2	15	5.8	9.9	5.4	2.1	3.00	13.41	−0.01	0.38
Sb	mg/kg	0.13	0.11	0.11	0.045	0.52	0.065	0.22	0.080	0.14	0.081	0.031	2.67	9.20	0.03	−0.23
Sc	mg/kg	0.52	0.45	0.46	0.13	1.7	0.28	0.83	0.35	0.61	0.28	0.13	2.03	5.43	−0.02	0.89
Se	mg/kg	0.20	0.18	0.19	0.030	0.50	0.11	0.36	0.14	0.25	0.093	0.044	1.19	1.37	0.04	1.09
Sm	mg/kg	0.29	0.26	0.25	0.076	0.99	0.15	0.47	0.20	0.31	0.16	0.060	2.34	6.94	−0.03	1.07
Sr	mg/kg	42	32	34	11	240	19	80	26	45	32	10	3.76	20.05	−0.02	0.50
Ta	µg/kg	180	50	50	11	4300	15	310	24	120	530	33	6.78	51.29	0.10	−0.70
Tb	µg/kg	39	32	32	11	140	19	64	24	43	24	8.9	2.37	6.75	−0.01	0.28
Th	mg/kg	0.43	0.35	0.36	0.14	1.8	0.21	0.68	0.28	0.51	0.27	0.094	3.02	12.03	−0.02	0.46
Ti	mg/kg	150	130	130	49	570	87	220	100	180	78	39	2.69	11.58	−0.01	0.43
U	mg/kg	0.13	0.11	0.11	0.046	0.68	0.070	0.18	0.094	0.15	0.079	0.024	5.01	33.86	−0.07	1.27
V	mg/kg	3.7	3.3	3.4	1.0	8.3	2.4	5.7	2.7	4.3	1.4	0.68	1.28	1.79	−0.00	1.13
W	µg/kg	100	85	87	25	380	49	160	63	120	58	26	2.46	8.71	−0.01	0.60
Zn	mg/kg	33	32	32	15	59	21	47	26	39	10	6.8	0.38	−0.44	−0.02	−0.58

X—arithmetic mean; Md—median value; X_{BC}—mean value (Box–Cox transformed data); Min—minimum value; Max—maximum value; P_{10}—10th percentile; P_{90}—90th percentile; P_{25}—25th percentile; P_{75}—75th percentile; S—standard deviation; MAD—median absolute deviation, A—skewness; E—kurtosis; A_{BC}—skewness; and E_{BC}—kurtosis (Box–Cox transformed data).

Table 3 shows the median values and the interval ranges for the contents of all 42 elements used for the comparison between the moss surveys measurements. A detailed analysis and the comparison of the results from 2002, 2005, and 2010 are given in [24]. It was found that the medians of elements decrease, according to the sampling campaign, with some exemptions from this rule.

Table 2. Comparative statistics between the mean values obtained for different territorial regions and major tectonic units.

	Unit	MKD-W	MKD-C	MKD-E	Ng–Pg	WMZ	PM	VZ	SMM
Al	%	0.21	0.20	0.20	0.21	0.21	0.22	0.19	0.19
As	mg/kg	0.42	0.92	0.76	0.86	0.47	0.51	0.76	0.75
Au	µg/kg	1.0	0.71	0.64	0.66	1.5	0.62	0.52	0.74
Ba	mg/kg	55	52	47	70	56	46	39	44
Br	mg/kg	2.6	2.2	2.3	2.4	2.7	2.2	2.4	2.2
Ca	%	0.67	0.74	0.56	0.69	0.69	0.67	0.66	0.50
Cd	mg/kg	0.19	0.31	0.17	0.26	0.20	0.21	0.14	0.22
Ce	mg/kg	2.6	2.5	2.5	2.5	2.6	2.6	2.7	2.3
Cl	mg/kg	78	100	86	93	83	82	94	81
Co	mg/kg	0.68	1.0	0.74	1.0	0.64	0.70	0.85	0.76
Cr	mg/kg	5.4	8.9	4.6	8.4	5.3	5.6	5.9	4.3
Cs	mg/kg	0.21	0.21	0.23	0.26	0.20	0.20	0.21	0.20
Cu	mg/kg	5.1	3.9	4.5	4.2	5.0	4.6	4.7	4.4
Fe	%	0.15	0.18	0.16	0.19	0.15	0.16	0.17	0.16
Hf	mg/kg	0.16	0.17	0.16	0.17	0.16	0.19	0.13	0.17
Hg	µg/kg	71	80	89	100	72	57	82	87
I	mg/kg	0.99	1.2	1.3	1.3	0.99	1.1	1.2	1.3
In	mg/kg	0.20	0.14	0.19	0.17	0.19	0.20	0.14	0.21
K	%	0.65	0.72	0.66	0.64	0.64	0.72	0.69	0.68
La	mg/kg	1.5	1.4	1.2	1.3	1.5	1.6	1.2	1.3
Li	mg/kg	0.76	1.0	0.69	0.96	0.77	0.83	0.79	0.61
Mg	%	0.21	0.23	0.20	0.23	0.21	0.22	0.21	0.19
Mn	mg/kg	140	93	160	110	170	87	95	230
Mo	mg/kg	0.28	0.34	0.25	0.46	0.27	0.28	0.19	0.22
Na	mg/kg	210	230	230	210	200	244	240	230
Nd	mg/kg	1.0	0.88	0.97	0.91	0.80	1.5	0.87	0.99
Ni	mg/kg	3.5	8.3	3.8	7.6	3.1	3.9	6.2	3.6
Pb	mg/kg	3.9	5.9	5.5	5.7	4.1	4.3	5.1	5.5
Rb	mg/kg	8.7	6.6	7.2	7.1	9.0	7.7	6.1	7.8
Sb	mg/kg	0.09	0.13	0.11	0.14	0.10	0.09	0.11	0.10
Sc	mg/kg	0.43	0.48	0.47	0.50	0.44	0.43	0.49	0.44
Se	mg/kg	0.18	0.18	0.20	0.18	0.21	0.18	0.17	0.20
Sm	mg/kg	0.26	0.25	0.26	0.25	0.27	0.25	0.23	0.25
Sr	mg/kg	31	37	35	54	31	27	32	31
Ta	µg/kg	36	53	74	60	35	56	48	66
Tb	µg/kg	32	31	33	31	32	33	31	34
Th	mg/kg	0.36	0.39	0.33	0.37	0.34	0.45	0.33	0.32
Ti	mg/kg	140	120	140	130	140	120	130	140
U	mg/kg	0.11	0.13	0.11	0.12	0.10	0.14	0.10	0.11
V	mg/kg	3.4	3.5	3.4	3.7	3.3	3.5	3.6	3.1
W	µg/kg	91	86	84	95	85	84	87	85
Zn	mg/kg	30	38	31	38	29	30	36	30

MKD-W—western regions; MKD-C—central regions; MKD-E—eastern regions; Ng–Pg—Neogene and Paleogene basins; WMZ—Western Macedonian Zone; PM—Pelagonian Massif; VZ—Vardar Zone; SMM—Serbo-Macedonian Massif.

From the comparison of the median values for the content of the elements in the mosses in 2010 and 2015, it can be seen that the median values for most of the elements obtained in the survey in 2015 are lower than the results obtained in the 2010 sampling campaign. These elements are Al, Ba, Br, Ca, Cl, Co, Cr, Fe, Hg, I, In, La, Li, Mg, Mn, Nd, Sc, Tb, Ti, V, and W. Most of these elements are related to the lithological origin of the soil, and the low values are probably the result of comprehensive cleaning of the mosses and the presence of low soil contaminants in the moss samples. The amount of precipitation in the periods before sampling can also have some influence on the results obtained. In this case, according to [43,44], the average annual precipitation in the year of the sampling campaign in 2010 was lower than the average annual precipitation before the sampling campaign in

2015. The same stands for the amount of precipitation in the first 6 months of 2010 and 2015. For the final conclusion, further investigations should be conducted. In the case of Cr, the lower values can be explained by the preventive measures carried out during this period at the slag dump located near the formerly active ferrochromium smelter near the town of Tetovo [24].

Table 3. Comparative values for the median and range of minimum–maximum for the biomonitoring surveys in the Republic of Macedonia carried out in 2002, 2005, 2010 and 2015. (All values are given in mg/kg).

	This Study (2015)		Moss Survey in 2010 [24]		Moss Survey in 2005 [24]		Moss Survey in 2002 [24]	
Element	**Md**	**Min–Max**	**Md**	**Min–Max**	**Md**	**Min–Max**	**Md**	**Min–Max**
Al	2000	850–6800	2400	1100–6800	3600	1500–26,000	3736	825–17,600
As	0.72	0.079–1.7	0.48	0.23–1.9	0.68	0.18–4.3	0.80	0.12–8.0
Au	0.0085	0.00014–0.014	0.005	0.003–0.031	-	-	0.0061	0.001–0.034
Ba	50	13–180	50	14–360	53	18–190	54	14–256
Br	2.3	1.3–5.3	4.4	2.0–16	1.9	0.9–7.0	2.16	0.06–7.7
Ca	6600	2800–12,000	8300	3200–13,900	8500	5200–16,000	5593	1207–23,640
Cd	0.21	0.018–0.88	0.23	0.068–2.24	0.29	0.015–3.0	0.16	0.016–2.95
Ce	2.6	1.1–9.8	2.6	0.66–21	4.5	1.5–17	5.60	0.83–42
Cl	84	44–390	90	46–310	91	45–510	149	43–693
Co	0.78	0.19–3.4	0.83	0.26–2.9	1.1	0.41–5.3	1.09	0.24–13.6
Cr	5.7	1.1–35	6.46	2.46–35	6.8	2.1–82	7.47	2.33–122
Cs	0.22	0.067–1.4	0.20	0.09–0.90	0.32	0.13–2.3	0.39	0.097–1.7
Cu	4.6	3.0–8.3	3.5	2.0–10.6	6.7	0.68–21	22	3–83
Fe	1600	500–3700	1900	890–5400	2200	1000–8100	2458	424–17,380
Hf	0.18	0.041–1.2	0.17	0.085–0.70	0.21	0.076–1.1	0.26	0.05–3.8
Hg	0.084	0.020–0.25	0.093	0.01–0.60	0.068	0.01–0.42	0.056	0.018–0.264
I	1.2	0.45–2.3	1.6	0.51–2.9	1.7	0.64–3.7	1.18	0.36–2.8
In	0.23	0.025–0.52	0.0074	0.001–0.064	-	-	0.043	0.0032–0.16
K	6900	3900–15,000	6600	3600–10,000	7500	4700–14,000	8615	2861–18,190
La	1.3	0.48–5.1	1.4	0.62–9.0	2.3	0.97–9.1	2.32	0.50–22
Li	0.79	0.32–3.1	1.05	0.29–5.1	-	-	-	-
Mg	2100	960–3700	2400	1200–4400	1300	660–4000	2377	674–7421
Mn	130	36–540	140	35–440	190	55–600	186	37–1475
Mo	0.27	0.002–2.4	0.15	0.039–0.44	0.16	0.065–1.1	0.19	0.03–1.12
Na	220	130–890	190	89–1000	360	140–2000	419	118–8673
Nd	0.96	0.015–4.3	1.7	0.43–8.3	-	-	-	
Ni	4.4	0.96–79	4.3	1.0–55	5.8	1.8–43	2.4	0.09–24
Pb	4.8	2.2–14	4.6	1.9–22	7.6	0.1–47	6.0	1.5–37.2
Rb	7.5	2.7–39	6.6	2.2–21	9.8	4.0–29	10.9	5–47
Sb	0.11	0.045–0.52	0.09	0.044–0.22	0.15	0.044–0.92	0.2	0.039–1.4
Sc	0.45	0.13–1.7	0.44	0.016–1.9	0.67	0.3–4.6	0.81	0.12–6.79
Se	0.18	0.030–0.50	0.14	0.021–0.35	0.1	0.015–0.61	0.18	0.013–0.61
Sm	0.26	0.076–0.99	0.27	0.11–1.5	0.35	0.14–2.0	0.46	0.07–3.4
Sr	32	11–240	34	12–120	34	13–140	31	11.8–136
Ta	0.050	0.011–0.430	0.040	0.018–0.17	0.077	0.031–0.33	0.09	0.013–0.79
Tb	0.032	0.011–0.140	0.04	0.01–0.19	0.053	0.015–0.25	0.06	0.01–0.56
Th	0.35	0.14–1.8	0.36	0.17–2.1	0.58	0.26–3.3	0.67	0.12–7.6
Ti	130	49–570	150	33–470	220	86–1200	163	12–1365
U	0.11	0.046–0.68	0.11	0.058–0.61	0.21	0.08–1.1	0.21	0.03–1.45
V	3.3	1.0–8.3	3.8	1.5–14	6.4	2.5–32	6.9	1.79–43
W	0.085	0.025–0.380	0.11	0.024–0.50	0.7	0.19–3.2	1.21	0.25–3.9
Zn	32	15–59	29	13–94	36	16–91	39	14–203

From the data presented in Table 3, it can be seen that most of the potentially toxic elements (Cd, Ni, Sb, and Zn) have practically the same content in the moss samples collected in 2010 and 2015. This is mainly due to the fact that, despite the operation of all mining and smelting plants at the same capacity for a five-year period, government regulations requiring

the installation of waste/gas cleaning systems and new pollution control regulations were implemented. The operation of ferronickel in Kavadarci (with Ni and Cr) in the southern part, the lead and zinc mines in Kriva Palanka, Makedonska Kamenica, and Probištip in the eastern part, and the former Pb–Zn smelter in Veles and the steel plant in Skopje (with Cd, Pb, and Zn) in the northern part, continued to cause the highest anthropogenic air pollution with potentially toxic elements in the period of 2010–2015.

In this group, with approximately the same content of elements in the mosses collected in 2010 and 2015, are some of the elements normally associated with a lithological origin (Ce, Hf, Sm, Sr, Th, and U). A slight increase in median values for the As, Au, Cs, Cu, K, Mo, Na, Rb, Se, and Ta content in the moss samples collected in 2010 and 2015 can be observed. An increase in median values in the last five years was observed for Cu, which is probably due to increased mining activities in the Bučim copper flotation plant near Radoviš.

When compared with data from its neighboring countries (Albania, Bulgaria, Northern Greece, and Serbia [45–48]) from the 2015 survey (Table 4), Macedonia has the highest median values for Au, Cd, Ce Hf, Hg In K, Li, Mo, Sm, Ta, and Tb. The data obtained from Macedonia for Au, Hf, Hg, In Li, Mo, and Ta were higher in comparison than only one of the aforementioned countries, because these elements were not determined in all countries. Compared to Albania, Macedonia had higher median values for Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Hg, K, La, Li, Mg, Na, Nd, Ni, Pb, Rb, Sb, Sc, Sm, Sr, Tb, Th, Ti, U, V, and Zn, and lower median values for Mn and Se. Bulgaria had lower median values for As, Ba, Cd, Ce, Cl, Co, Cr, Cs, Fe, Hf, K, La, Ni, Rb, Sb, Sc, Sr, Tb, V, and Zn, and higher median values for Al, Br, Ca, Cu, I, Mg, Mn, Na, Nd, Pb, Se Th, Ti, and U. Compared to Northern Greece, Macedonia had higher median values only for Au, In K, Mo, and Sm. Compared to Serbia, Macedonia had higher median values for Al, Ca, Fe, Ni, Pb, Sb, V, and Zn, and lower median values for As, Cr, and Cu. The differences in the median values of elemental content between Macedonia and its neighboring countries may be influenced by various factors. Geological variations play a significant role, as different regions possess distinct geological formations, mineral compositions, and soil characteristics that impact elemental content in the environment. Natural geological processes, including weathering, erosion, and soil formation, contribute to varying elemental concentrations in different regions. Human activities and industrialization significantly affect elemental deposition. Differences in industrial operations, mining activities, and emission regulations between Macedonia and its neighbors can lead to distinct pollution profiles. The presence of specific industries, mining sites, and varying levels of pollution control measures significantly impact elemental content in the environment. The Norwegian results [49] are significantly lower for elements previously attributed mainly to mineral particles, but also for those elements commonly associated with pollution. Compared to Norway, Macedonia shows lower median values only for Mn and Se, which can be explained by the specific environmental conditions, such as a lower density of higher plants in Macedonia than in Norway and the influence of marine costs.

To identify potential correlations or associations between elements in the samples, bivariate statistics were used after the Box–Cox transformation of the data. For this purpose, the Pearson correlation coefficient r was calculated, which indicated the strength and direction of linear dependence (correlation degree) between two random variables or sets of random variables. Bivariate statistics highlight the relationships between pairs of elements and quantify the strength and direction of linear associations. In environmental studies, they reveal potential co-occurrences or patterns among elements. Strong correlations between elements suggest similar sources or behaviors in the environment. The results of bivariate statistics are shown in the matrix of correlation coefficients in Table 5. For better visibility, values or r in the range of 0.5–0.7, showing good association of the elements, are underlined and values in the range of 0.7–1.0, showing strong association, are bolded.

Table 4. Comparison of the results obtained in the present study with results obtained in the neighboring Balkan countries and Norway (values are given in mg/kg).

	Macedonia, 2015, *n* = 72; This Study		**Albania, 2015, *n* = 58 [45]**		**Bulgaria, 2015, *n* = 115 [46]**		**Northern Greece, *n* = 95 [47]**		**Serbia, 2015, *n* = 212 [48]**		**Norway, 2015, *n* = 228 [49]**	
Element	**Md**	**Min–Max**	**Md**	**Min–Max**	**Md**	**Min–Max**	**Md**	**Min–Max**	**Md**	**Min–Max**	**Md**	**Min–Max**
Al	2000	530–4300	460	100–3050	2310	569–10,900	5840	1350–46,100	1021	358–11,000	460	100–3050
As	0.72	0.079–1.7	0.13	0.04–4.72	0.45	0.20–10.8	1.45	0.52–17.9	0.73	0.16–71.1	0.13	0.04–4.72
Au	0.00085	0.00014–0.014	-	-	-	-	0.0007	0.0004–0.017	-	-	-	-
Ba	50	13–180	25	5.3–130	46	14.2–309	65.9	15.9–519	-	-	25	5.3–130
Br	2.3	1.3–5.3	-	-	2.8	1.2–9.4	5.84	1.69–15.0	-	-	-	-
Ca	6600	2800–12,000	3030	1820–7230	6630	606–14,200	8170	3960–23,400	-	-	3030	1820–7230
Cd	0.21	0.018–0.88	0.08	0.02–1.33	0.10	0.02–1.56	-	-	0.18	0.050–0.99	0.08	0.02–1.33
Ce	2.6	1.1–9.8	0.61	0.10–4.78	2.4	0.5–29.2	-	-	-	-	0.61	0.10–4.78
Cl	84	44–390	-	-	78.8	16.6–861	130	47–380	-	-	-	-
Co	0.78	0.19–3.4	0.2	0.06–23	0.59	0.197–3.29	1.69	0.43–20.3	-	-	0.2	0.06–23
Cr	5.7	2.1–35	0.7	0.2–17	2.73	0.219–25	11.5	2.04–222	3.21	0.006–60.8	0.7	0.2–17
Cs	0.22	0.067–1.4	0.16	0.02–1.63	0.207	0.0716–1.8	-	-	-	-	0.16	0.02–1.63
Cu	4.6	3.0–8.3	4.2	1.8–370	7.36	3.2–46.88	-	-	8.75	3.25–213	4.2	1.8–370
Fe	1600	500–3700	310	78–8125	1190	376–7240	3770	1010–38,700	1019	275–10,119	310	78–8125
Hf	0.18	0.041–1.2	-	-	0.16	0.04–1.44	-	-	-	-		
Hg	0.084	0.020–0.25	0.05	0.005–0.53	-	-	-	-	-	-	0.05	0.005–0.53
I	1.2	0.45–2.3	-	-	1.28	0.48–2.99	2.30	1.03–7.36	-	-	-	-
In	0.23	0.025–0.52	-	-	-	-	0.04	0.011–0.233	-	-	-	-
K	6900	3900–15,000	3560	1770–6400	5670	3250–14,200	5670	2160–17,200	-	-	3560	1770–6400
La	1.3	0.48–5.1	0.32	0.07–3.5	0.39	0.39–22.6	3.22	0.50–35.2	-	-	0.32	0.07–3.5
Li	0.79	0.32–3.1	0.16	0.04–2.02	-	-	-	-	-	-	0.16	0.04–2.02
Mg	2100	960–3700	1350	470–3280	2080	514–8550	5840	1350–46,100	-	-	1350	470–3280

Table 4. *Cont.*

	Macedonia, 2015, *n* = 72; This Study		Albania, 2015, *n* = 58 [45]		Bulgaria, 2015, *n* = 115 [46]		Northern Greece, *n* = 95 [47]		Serbia, 2015, *n* = 212 [48]		Norway, 2015, *n* = 228 [49]	
Element	**Md**	**Min–Max**	**Md**	**Min–Max**	**Md**	**Min–Max**	**Md**	**Min–Max**	**Md**	**Min–Max**	**Md**	**Min–Max**
Mn	130	36–540	400	40–1660	180	39–551	219	34–1090	-	-	400	40–1660
Mo	0.27	0.002–2.4	-	-	-	-	0.23	0.02–2.31	-	-	-	-
Na	220	130–890	210	60–800	225	79–1560	751	184–9210	-	-	210	60–800
Nd	0.96	0.015–4.3	0.23	0.01–2.24	1.3	0.2–24.1	-	-		-	0.23	0.01–2.24
Ni	4.4	0.96–79	1.1	0.4–550	2.1	0.45–13.5	7.26	1.72–90.2	3.12	0.62–90.6	1.1	0.4–550
Pb	4.8	2.2–14	0.05	0.001–0.4	10.72	3.72–102.8	-	-	4.31	0.36–460	0.05	0.001–0.4
Rb	7.5	2.7–39	1.4	1.4–81	7.38	2.24–50.7	15.5	5.11–82.9	-	-	1.4	1.4–81
Sb	0.11	0.045–0.52	0.07	0.007–0.38	0.11	0.04–0.51	0.20	0.02–3.23	0.078	0.02–2.2	0.07	0.007–0.38
Sc	0.45	0.13–1.7	0.09	0.02–1.4	0.41	0.10–3.13	1.44	0.29–8.92	-		0.09	0.02–1.4
Se	0.18	0.030–0.50	0.3	0.009–2	0.2	0.008–0.67	0.23	0.02–0.48	-	-	0.3	0.009–2
Sm	0.26	0.076–0.99	0.05	0.004–0.38	-	-	0.008	0.003–3.68	-	-	0.05	0.004–0.38
Sr	32	11–240	13.6	3.8–60	25	11.3–122	38.2	12.7–197	-	-	13.6	3.8–60
Ta	0.050	0.011–0.430	-	-	0.04	0.009–0.28	-	-	-	-	-	-
Tb	0.032	0.011–0.140	0.01	0.001–0.09	0.03	0.005–0.42	-	-	-	-	0.01	0.001–0.09
Th	0.35	0.14–1.8	0.03	0.007–1.5	0.39	0.09–2.8	0.99	0.28–13.6	-	-	0.03	0.007–1.5
Ti	130	49–570	24	6–152	143	46.4–764	327	97–1760	-	-	24	6–152
U	0.11	0.046–0.68	0.006	0.002–0.08	0.12	0.03–3.2	0.30	0.07–3.38		-	0.006	0.002–0.08
V	3.3	1.0–8.3	1.2	0.3–14	3.89	1.3–22.7	8.17	2.61–33.4	2.72	0.91–21.5	1.2	0.3–14
W	0.085	0.025–0.380	-	-	0.1	0.02–1.44	-	-	-	-	-	-
Zn	32	15–59	31	8–409	28	9–101	37.6	14.6–282	22.4	8.33–115	31	8–409

n—number of samples.

Table 5. Pearson correlation coefficient between element content in mosses (n = 72). Values in the range 0.7–1.0 (strong association) are bolded and the values in range 0.5–0.7 (good association) are underlined; Box–Cox transformed values were used.

	Al	As	Au	Ba	Br	Ca	Cd	Ce	Cl	Co	Cr	Cs	Cu	Fe	Hf	Hg	I	In	K	La	Li	Mg	Mn	Mo	Na	Nd	Ni	Pb	Rb	Sb	Sc	Se	Sm	Sr	Ta	Tb	Th	Ti	U	V	W	Zn
Al	1.00																																								
As	0.21	1.00																																								
Au	−0.09	0.09	1.00																																						
Ba	0.30	0.11	−0.02	1.00																																					
Br	0.31	0.12	0.18	0.10	1.00																																				
Ca	0.31	0.21	0.15	0.04	0.25	1.00																																			
Cd	−0.03	0.22	0.08	0.15	−0.00	0.05	1.00																																		
Ce	**0.87**	0.32	−0.03	0.28	0.35	0.34	−0.06	1.00																																	
Cl	−0.15	0.32	−0.14	0.08	0.07	0.09	0.01	0.01	1.00																																
Co	0.59	0.49	−0.16	0.16	0.22	0.16	0.11	0.57	0.11	1.00																															
Cr	0.43	0.43	−0.10	0.15	0.10	0.39	0.17	0.43	0.13	**0.73**	1.00																														
Cs	0.65	0.32	−0.06	0.31	0.28	0.24	0.10	0.66	−0.06	0.40	0.34	1.00																													
Cu	−0.10	−0.65	0.00	−0.05	0.19	−0.15	−0.20	−0.08	−0.15	−0.30	−0.33	−0.07	1.00																												
Fe	**0.78**	0.59	−0.07	0.28	0.25	0.35	0.09	**0.78**	0.15	**0.82**	0.69	0.61	−0.33	1.00																											
Hf	**0.83**	0.37	0.02	0.28	0.27	0.26	0.08	**0.82**	−0.07	0.48	0.40	0.61	−0.18	**0.73**	1.00																										
Hg	0.29	0.18	0.05	0.01	0.25	0.13	0.03	0.29	−0.08	0.29	0.08	0.31	0.05	0.30	0.29	1.00																									
I	0.45	0.53	−0.02	0.00	0.41	0.20	0.08	0.37	0.13	0.53	0.22	0.39	−0.36	0.51	0.38	0.37	1.00																								
In	0.05	−0.01	0.09	0.04	0.20	−0.07	−0.02	0.10	0.04	−0.01	−0.12	0.09	0.33	0.01	0.08	0.17	−0.10	1.00																							
K	−0.21	0.31	−0.08	0.09	−0.20	0.14	0.06	−0.12	0.57	−0.19	−0.01	−0.04	−0.00	−0.01	−0.02	−0.06	−0.10	0.11	1.00																						
La	**0.90**	0.24	−0.01	0.28	0.26	0.29	−0.01	**0.91**	−0.11	0.57	0.41	0.60	−0.09	**0.77**	**0.86**	0.22	0.32	0.10	−0.17	1.00																					
Li	**0.73**	0.37	−0.11	0.21	0.18	0.53	0.06	0.69	−0.00	0.52	0.50	0.55	−0.35	**0.70**	0.64	0.30	0.40	−0.09	−0.05	0.68	1.00																				
Mg	0.44	0.15	−0.07	0.21	0.18	0.53	−0.04	0.35	0.23	0.24	0.34	0.17	−0.14	0.37	0.36	0.15	0.23	−0.16	0.17	0.30	0.38	1.00																			
Mn	0.03	−0.16	0.10	0.24	0.23	−0.34	0.07	0.02	−0.19	−0.01	−0.35	−0.03	0.12	−0.10	0.00	0.15	0.09	−0.00	−0.20	0.06	−0.18	−0.25	1.00																		
Mo	0.01	0.03	−0.05	0.10	0.08	0.13	0.11	0.01	0.21	0.22	0.26	0.04	−0.20	0.15	0.07	−0.05	−0.06	−0.22	−0.05	0.08	0.11	0.22	−0.09	1.00																	
Na	0.64	0.48	−0.09	0.17	0.08	0.04	0.02	0.67	0.22	0.50	0.38	0.42	−0.21	0.68	**0.72**	0.10	0.32	0.14	0.19	0.63	0.44	0.28	−0.13	−0.06	1.00																
Nd	0.50	0.01	0.07	0.13	0.17	0.08	−0.09	0.44	−0.27	0.25	−0.02	0.40	0.09	0.34	0.44	0.24	0.27	0.11	−0.11	0.51	0.24	0.14	0.18	−0.01	0.31	1.00															
Ni	0.41	0.33	−0.21	0.11	0.17	0.16	0.14	0.37	0.00	**0.86**	**0.71**	0.29	−0.23	0.60	0.30	0.23	0.40	−0.12	−0.22	0.35	0.42	0.20	−0.04	0.19	0.34	0.15	1.00														
Pb	−0.03	0.51	0.10	0.03	0.14	0.05	0.28	0.07	0.15	0.18	0.08	0.01	−0.23	0.24	0.21	0.25	0.28	0.04	0.25	0.02	0.06	−0.07	0.10	0.12	0.23	0.12	0.14	1.00													
Rb	0.08	0.13	0.20	0.30	0.22	−0.01	−0.07	0.20	−0.00	−0.11	−0.11	0.33	0.18	0.02	0.26	0.16	−0.00	0.30	0.31	0.21	−0.03	−0.08	0.28	−0.03	0.14	0.22	−0.13	0.13	1.00												
Sb	0.28	0.61	0.04	0.05	0.24	0.46	0.50	0.30	0.14	0.41	0.49	0.39	−0.25	0.56	0.34	0.29	0.40	−0.00	0.21	0.22	0.40	0.16	−0.20	0.16	0.25	−0.09	0.37	0.53	0.06	1.00											
Sc	**0.87**	0.52	−0.04	0.18	0.33	0.32	0.04	**0.84**	0.03	**0.72**	0.59	0.64	−0.29	**0.90**	**0.82**	0.32	0.59	−0.03	−0.09	**0.82**	**0.72**	0.44	−0.04	0.05	**0.70**	0.36	0.49	0.14	0.04	0.47	1.00										
Se	−0.31	0.26	0.11	−0.08	−0.07	0.13	0.16	−0.22	0.08	−0.29	−0.18	−0.05	−0.29	−0.15	−0.14	−0.04	−0.06	−0.17	0.23	−0.21	−0.07	−0.11	0.01	0.23	−0.20	−0.11	−0.34	0.30	0.16	0.19	−0.19	1.00									
Sm	**0.86**	0.36	0.08	0.18	0.35	0.28	0.06	**0.87**	−0.04	0.57	0.41	0.63	−0.16	**0.78**	**0.86**	0.36	0.46	0.08	−0.13	**0.91**	0.67	0.33	0.06	0.11	**0.62**	0.41	0.33	0.11	0.18	0.37	**0.89**	−0.11	1.00								
Sr	0.42	0.08	−0.11	0.68	0.18	0.21	0.00	0.39	0.16	0.33	0.22	0.35	−0.03	0.36	0.31	0.19	0.27	−0.11	−0.10	0.32	0.36	0.42	0.11	0.20	0.17	0.14	0.30	−0.13	0.00	0.07	0.33	−0.22	0.28	1.00							
Ta	0.16	0.08	0.04	0.15	−0.22	0.03	0.07	0.13	−0.01	0.05	−0.07	0.23	−0.09	0.21	0.19	0.07	0.01	−0.05	0.02	0.15	0.12	0.05	−0.01	0.08	0.12	0.27	−0.06	0.23	−0.10	0.00	0.11	0.12	0.14	0.20	1.00						
Tb	**0.86**	0.37	−0.03	0.18	0.31	0.23	−0.03	**0.89**	−0.01	0.57	0.37	0.59	−0.20	**0.79**	**0.85**	0.31	0.48	0.09	−0.17	**0.92**	0.68	0.31	0.10	0.05	**0.66**	0.42	0.33	0.08	0.16	0.29	**0.89**	−0.17	**0.93**	0.31	0.14	1.00				
Th	**0.85**	0.38	−0.07	0.35	0.15	0.33	0.00	**0.86**	0.05	0.56	0.47	0.65	−0.19	**0.82**	**0.82**	0.21	0.32	0.10	0.00	**0.90**	**0.76**	0.30	−0.09	0.09	**0.67**	0.41	0.38	0.09	0.25	0.33	**0.78**	−0.21	**0.81**	0.39	0.23	**0.85**	1.00			
Ti	**0.83**	0.18	−0.15	0.22	0.30	0.13	−0.09	**0.72**	−0.07	0.49	0.29	0.55	−0.07	0.67	**0.74**	0.27	0.42	0.07	−0.21	**0.71**	0.57	0.27	0.15	−0.00	**0.63**	0.44	0.30	0.02	−0.03	0.22	**0.78**	−0.21	**0.73**	0.35	0.17	**0.78**	0.65	1.00		
U	**0.78**	0.43	−0.03	0.34	0.12	0.23	0.14	**0.75**	0.08	0.59	0.45	0.58	−0.20	**0.81**	**0.81**	0.31	0.37	0.14	0.09	**0.82**	0.65	0.25	−0.10	0.09	**0.69**	0.41	0.39	0.24	0.18	0.39	**0.75**	−0.17	**0.80**	0.35	0.31	**0.78**	**0.90**	0.61	1.00		
V	0.85	0.25	−0.16	0.21	0.38	0.35	0.00	**0.70**	−0.02	**0.71**	0.55	0.60	−0.06	**0.83**	0.62	0.30	0.53	0.02	−0.22	**0.71**	0.65	0.41	−0.05	0.07	0.54	0.34	0.57	0.03	−0.13	0.41	**0.83**	−0.30	**0.70**	0.43	0.16	**0.71**	0.69	**0.76**	0.69	1.00	
W	0.49	0.14	−0.07	0.15	0.11	0.25	0.08	0.44	0.03	0.23	0.28	0.47	−0.05	0.41	0.50	0.34	0.19	0.04	0.07	0.42	0.41	0.31	−0.22	0.08	0.37	0.12	0.13	−0.09	0.04	0.21	0.47	−0.12	0.53	0.22	0.08	0.40	0.43	0.41	0.50	0.39	1.00	
Zn	−0.22	0.08	−0.12	0.07	−0.02	0.15	0.21	−0.12	0.21	0.12	0.23	−0.08	0.14	0.02	−0.14	0.08	−0.13	0.08	0.31	−0.25	−0.09	0.06	−0.11	0.13	−0.03	−0.21	0.26	0.59	0.06	0.42	−0.13	0.03	−0.26	0.09	−0.10	−0.25	−0.13	−0.25	−0.09	−0.00	−0.18	1.00

Based on the correlation matrix, multivariate cluster and R-mode factor analyses were used to reveal associations of chemical elements and to reduce the number of variables for the obtained data [38–40]. Cluster analysis identifies natural groupings or clusters among elements, based on similarities in their concentrations in different samples. It helps with categorizing elements exhibiting similar spatial or temporal patterns and with providing insights into potential common sources or behaviors.

Multivariate analysis was used to examine all moss samples. This analysis of the results reduces the dimensionality of the data by the identifying underlying factors that explain the correlations among observed variables (elements). It helps in grouping elements that covary together, potentially indicating shared sources or similar environmental behavior. The factors derived from this analysis represent combinations of elements that often originate from similar geological, environmental, or anthropogenic sources. The multivariate statistical cluster and factor analyses were performed for 25 selected chemical elements (Al, As, Ba, Cd, Ce, Cl, Co, Cr, Fe, I, Hf, La, Li, Ni, Pb, Sb, Sc, Sm, Sr, Tb, Th, Ti, U, V, and Zn). Other elements were excluded from further analysis, because they tend to form their own clusters and do not have similarity linkage with other elements. Elements with a tendency to form independent factors and the elements with a low share of communality were also excluded. Before factor analysis (FA) was performed, variables were standardized to zero mean and unit standard deviation. The varimax method was used for orthogonal rotation [39,40]. With factor analysis, the characteristics of the 25 individual elements were reduced to five synthetic variables, named F1 to F5. Variables with factor loadings higher than 0.5 were assumed to contribute significantly to a given factor.

The results presented as a dendrogram (Figure 4), showing the results of the hierarchical cluster analysis of the 25 selected elements, and as a factor analysis, organizing the elements into five groups (Table 6). Comparing these two analyses, it was found that the tendency of categorization in the factor scores or clusters is the same. Due to the lack of similarity linkage, the other 17 elements were omitted from the grouping.

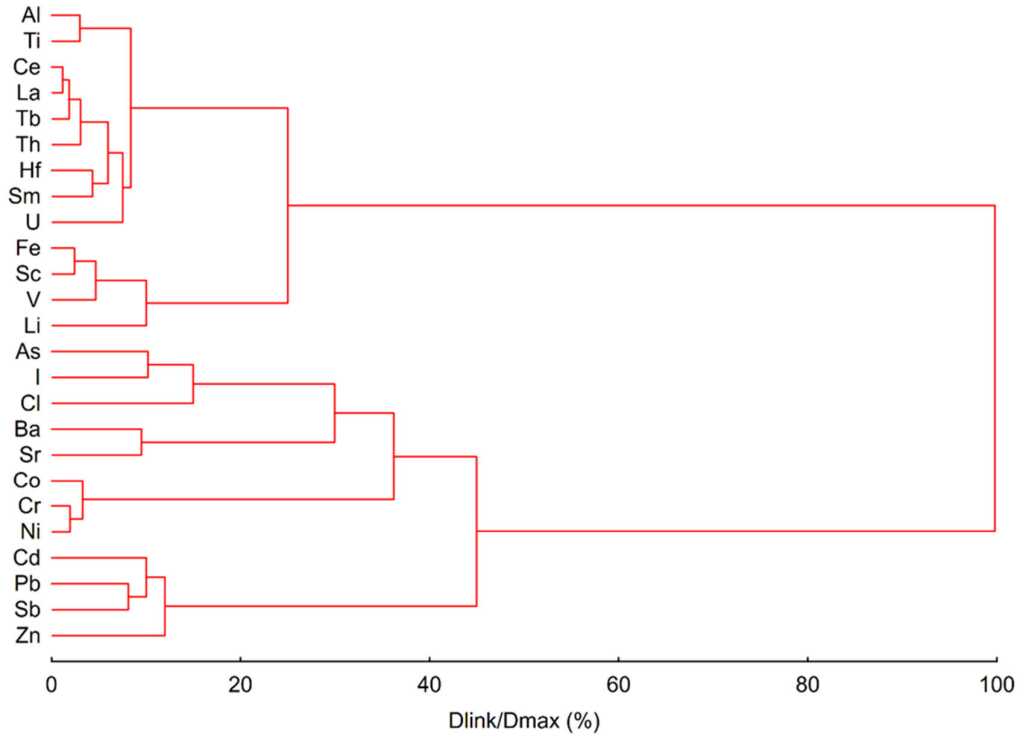


Figure 4. Dendrogram from the cluster analysis—Box–Cox transformed values (n = 72, 25 selected elements).

Table 6. Matrix of dominant rotated factor loadings—Box–Cox transformed values (n = 72, 25 selected elements).

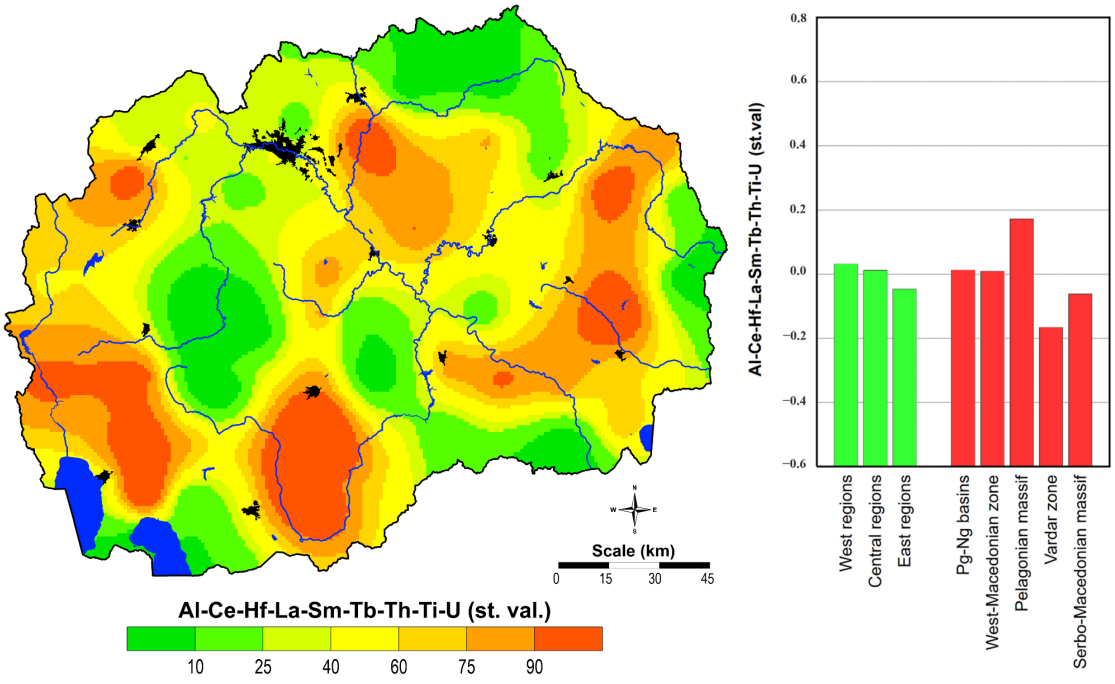
	F1	F2	F3	F4	F5	Comm
La	**0.95**	0.02	−0.06	−0.12	0.08	92.3
Ce	**0.95**	0.06	−0.03	−0.01	0.11	91.3
Tb	**0.94**	0.01	−0.10	0.14	0.05	90.7
Hf	**0.93**	−0.02	0.10	0.03	0.06	87.8
Al	**0.91**	0.12	−0.13	−0.04	0.21	91.3
Th	**0.90**	0.05	0.04	−0.04	0.17	84.3
Sm	**0.85**	−0.03	−0.01	0.21	0.10	78.6
Ti	**0.83**	0.04	−0.16	0.12	0.17	75.3
U	**0.81**	0.03	0.14	0.11	0.12	70.2
Na	**0.80**	0.03	0.11	0.20	−0.07	69.1
Sc	**0.77**	0.26	−0.02	0.48	0.14	90.6
V	**0.70**	0.42	−0.09	0.21	0.25	78.1
Fe	**0.69**	0.42	0.19	0.45	0.18	92.4
Li	**0.67**	0.20	0.09	0.24	0.22	60.7
Ni	−0.06	**0.96**	0.03	0.03	0.07	93.8
Cr	0.10	**0.92**	0.15	0.14	0.13	92.4
Co	0.26	**0.88**	0.01	0.27	0.08	92.6
Sb	0.08	0.08	**0.79**	0.29	0.03	72.3
Pb	−0.01	−0.08	**0.78**	0.29	−0.19	74.3
Cd	−0.06	0.02	**0.78**	−0.00	0.18	64.0
Zn	−0.11	0.46	**0.71**	−0.24	−0.03	74.3
I	0.21	0.20	−0.03	**0.77**	0.08	68.4
As	0.12	0.06	0.45	**0.77**	0.00	81.1
Cl	0.00	0.06	0.09	**0.70**	0.04	67.1
Sr	0.17	0.22	−0.09	0.23	**0.82**	81.6
Ba	0.27	0.01	0.10	−0.09	**0.81**	74.9
Prp.Totl	38.2	13.0	10.4	10.0	7.2	78.8
Expl. Var.	9.94	3.38	2.71	2.59	1.88	
Eigen Val.	11.24	3.91	2.45	1.59	1.31	

F1–F5—factor loadings; Comm—communality, given in %; Prp.Totl—total amount of the explained system variance given in %; Expl. Var.—particular component variance; Eigen Val.—Eigenvalues. Values that are greater than 0.5 are bolded.

The five identified factors included 78.8% of the variability of the elements. Factor 1 (F1) represents the strongest factor, with 38.2% of the total variability. This group of elements represents the geogenic group of elements. Factor 2 (F2) is the second strongest factor and has 13.0% of the total variability. This factor is associated with the elements Ni, Cr, and Co, whose distribution can be both geogenic and anthropogenic. The third factor (F3), with 10.4% of the total variability, includes the elements Sb, Pb, Cd, and Zn, and represents the anthropogenic group elements. Factor 4 (F4) represents 10.0% of the total variability, including elements that show natural distribution (As, Cl, and I), while Factor 5 (F5), with only 7.2% of the total variability and including Ba and Sr, is also a geogenic factor. As can be seen from the results, geogenic factors play a crucial role in shaping the elemental composition of most of the elements reported in the paper. The distribution of certain elements, such as the elements that are present in F1, F2, F4, and F5, is intricately tied to geological phenomena and natural processes. These elements showcase distinct spatial patterns that are directly related to specific rock types, geological formations, and historical events in the study area.

Factor 1, which includes the elements Al, Ce, Fe, Hf, La, Li, Sc, Sm, Tb, Th, U, and V, is the strongest factor, representing 38.2% of the total variability. This group represents a geochemical association of elements that are naturally distributed and whose distribution is independent of industrialized and urban areas (Figure 5a,b). The content of these elements in mosses is influenced by mineral particles that enter the environment due to wind erosion of local sources or particles that adhere to the moss

(Figure 6). Aluminum and titanium are prevalent in the Earth's crust and are commonly occur in silicate minerals. The geology of Macedonia comprises a variety of rock types, some of which may contain aluminum- and titanium-bearing minerals. The existence of granite and basalt formations contributes to the availability of these components in the environment [25]. Thorium and uranium are often found in association with specific geological formations, most notably granitic rocks. The geological composition of Macedonia includes granitic intrusions in the Pelagonian Massif and the granite deposits near the town of Strumica, which also affect the presence of thorium and uranium in the moss samples [25]. To this group of elements, hafnium can be added, which is commonly found in granitic rocks and is commonly coupled with zirconium minerals. Rare earth elements, such as cerium, lanthanum, samarium, and terbium, exhibit complex geochemical behavior. These elements are commonly found in carbonatites and alkaline rocks. In Macedonia, there is no industry or mining exploration of these elements and their presence in the mosses is only due to natural geological processes [25]. The highest contents of the mentioned group of elements were found in moss samples collected in the southwestern part of the country, around the towns of Bitola and Prilep, which are rich in Proterozoic metamorphic rocks from the Pelagonian Massif, and in the region of the Galičica Mountains, due to the Mesozoic carbonate rocks occurring in southern part of the Western Macedonian Zone (Figure 5b). The highest contents of Fe, Sc, Li, and V are found in the mosses collected in the Vardar Zone, where the Ng–Pg basins are located (Figure 7a,b), and in the Pelagonian Massif. In these regions, alluvial and diluvial sedimentary rocks, as well as Ng and Pg sedimentary rocks, are present, which are within reach of the mentioned elements. The high Fe values near the city of Skopje and the town of Tetovo could be related to the previously active ferro smelter in Skopje and the ferrochromium smelter in Tetovo [25]. The spatial distributions of these elements are given in Figure 8.



(**a**) (**b**)

Figure 5. (**a**) Spatial distribution of F1 factor scores (Al, Ce, Hf, La, Sm, Tb, Th, Ti, and U) and (**b**) their distribution according to geographical regions and geological formations.

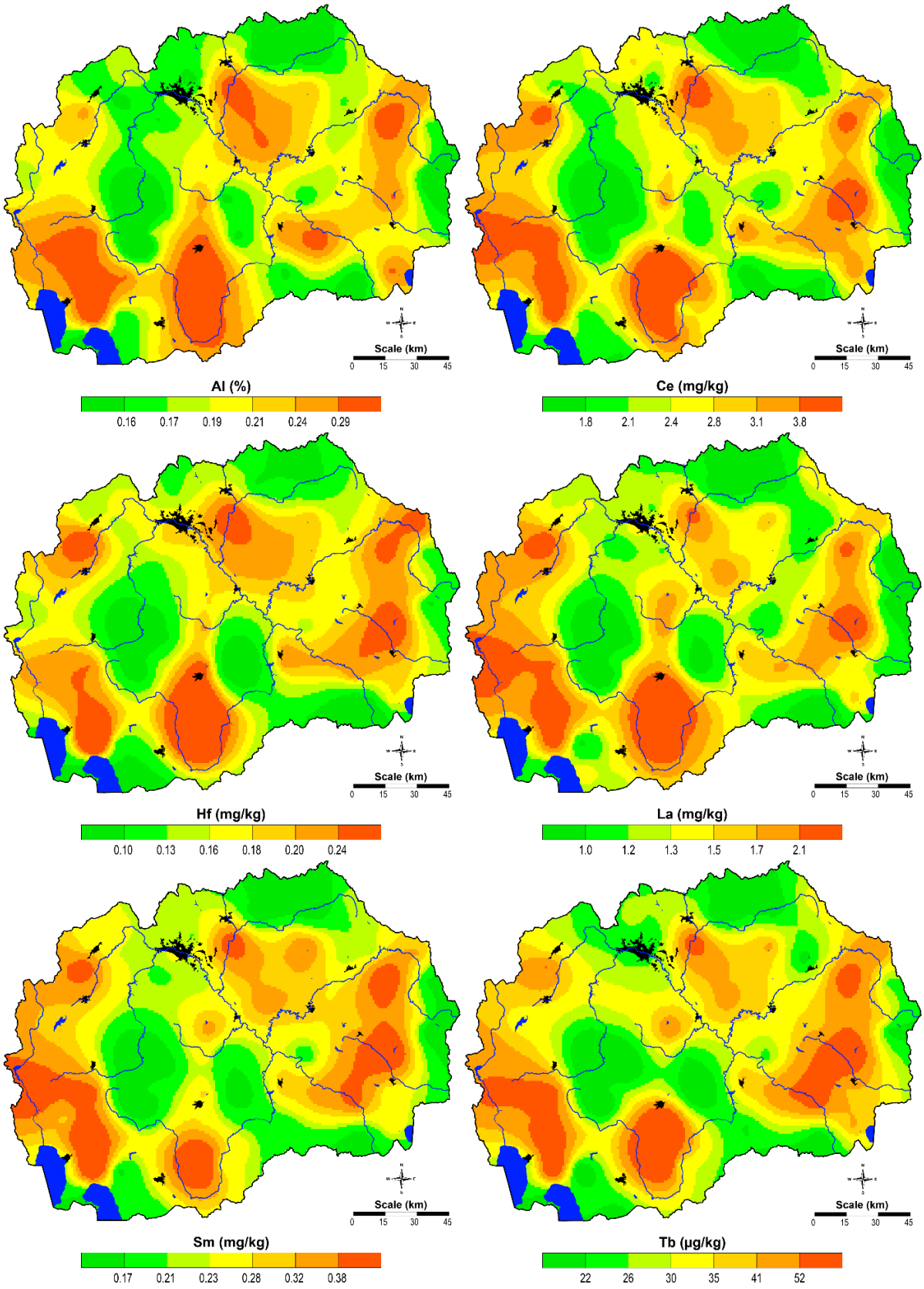


Figure 6. *Cont.*

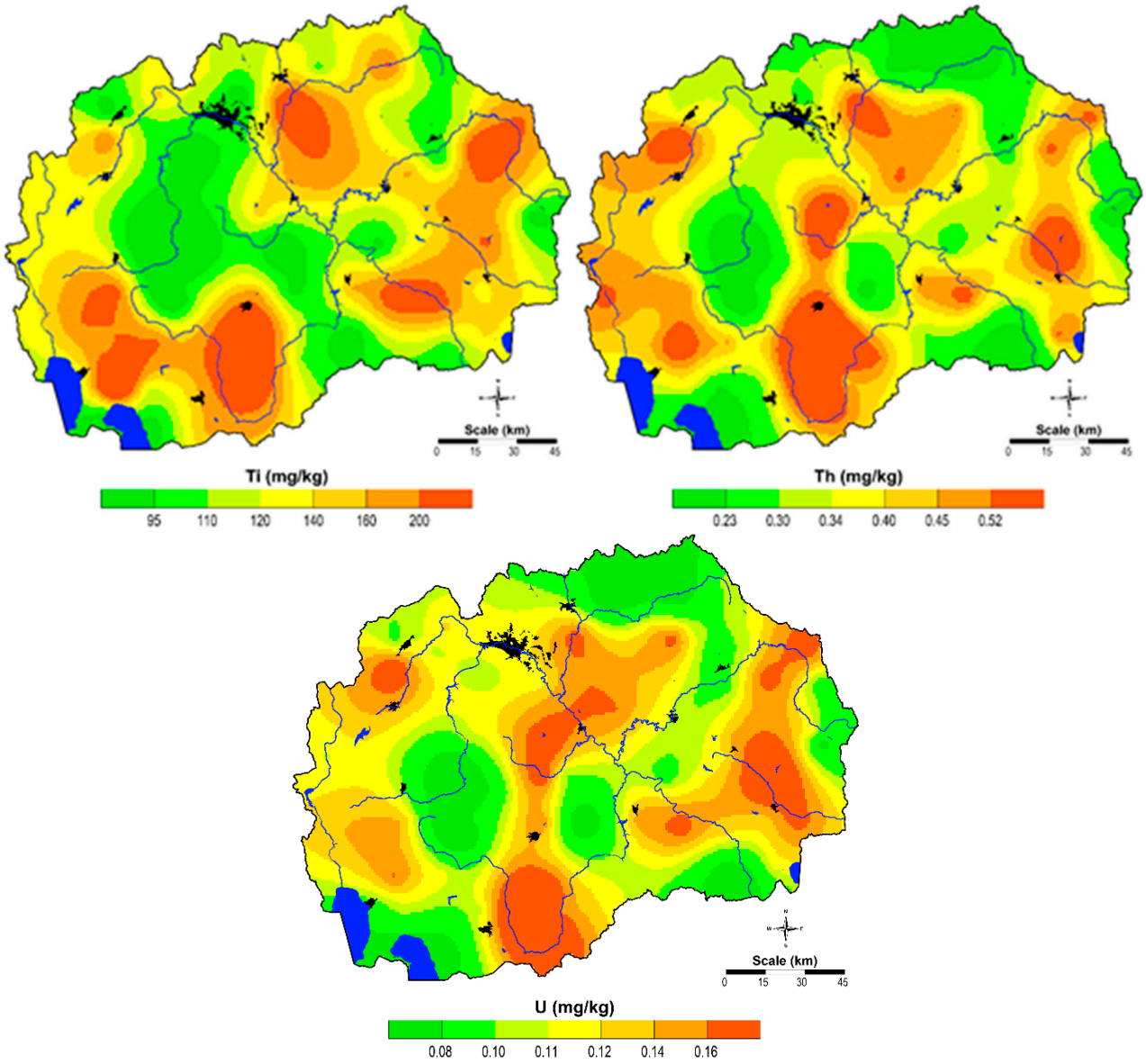
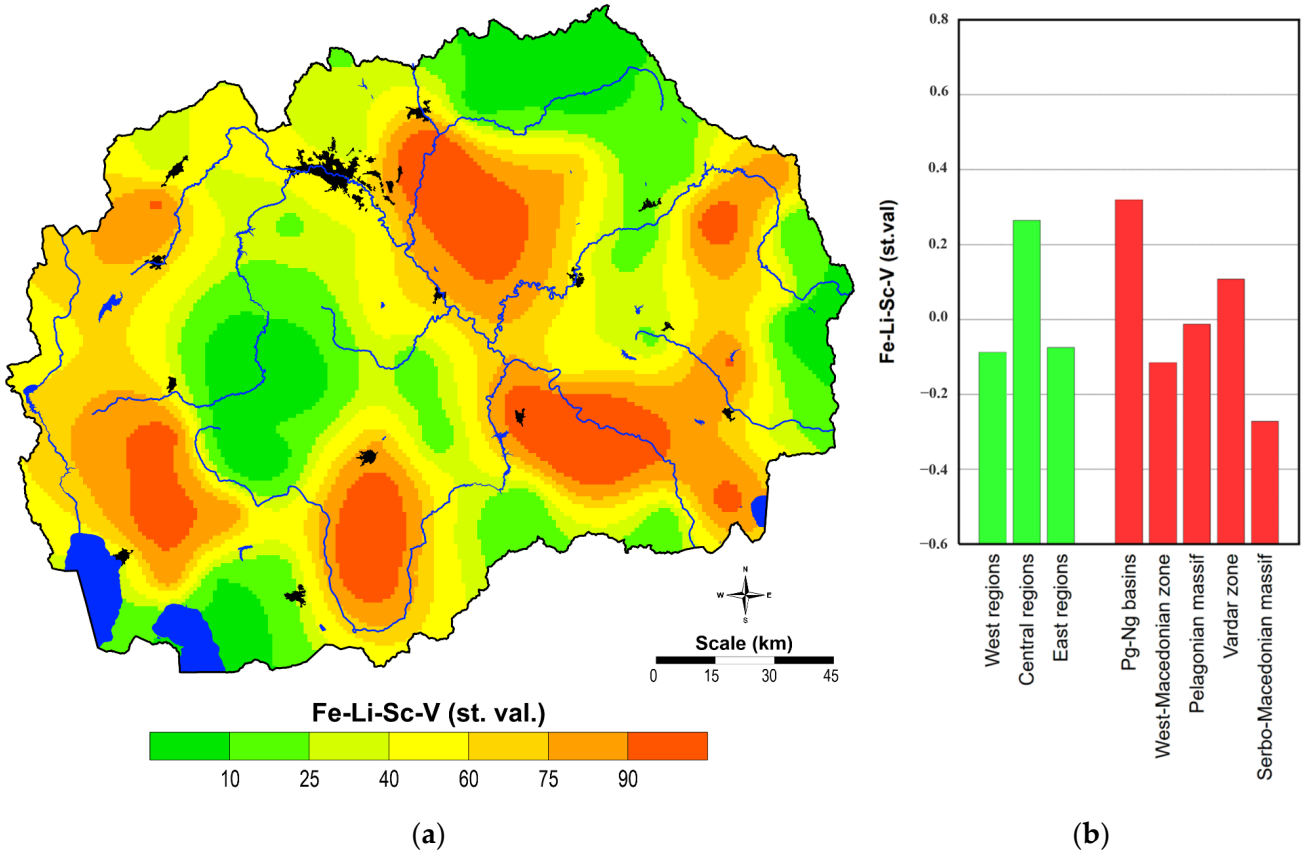


Figure 6. Spatial distribution of Al, Ce, Hf, La, Sm, Tb, Ti, Th, and U—elements included in F1.

Factor 2 includes Co, Cr, and Ni, all commonly associated with air pollution. These elements can be found in moss samples from various natural and anthropogenic sources. Local emissions, primarily from mines and smelters, are the main contributors to Co, Cr, and Ni release into the environment. These emissions are associated with industrial processes, and the distribution map of factor scores reveals higher levels of these elements in specific regions (Figure 9a,b). In particular, the Vardar and Crna river valleys, the Kavadarci region in the central southern part of the country, and the northern region, including Skopje and Tetovo, have elevated levels of these elements. The main sources of Co, Cr, and Ni in moss samples were identified as the ferronickel smelter and open pit mine near Kavadarci [24,25]. At the plant, which has been in operation since 1982, iron–nickel ore was used for ferronickel production in the smelter plant, resulting in relatively high contents of these elements. The elevated Cr contents in mosses collected near Tetovo are related to a nearby slag dump and the former operation of a ferrochromium smelter [25]. Mosses in the Vardar and Crna river valleys have higher concentrations of these elements, which is due to the continuous flow of air masses in both directions within these valleys [50], which allows the pollutants to be transported over larger areas. Previous studies have shown that these elements

occur mainly in silicate forms [25,26]. This suggests a connection with geological formations and possible release into the environment through weathering processes. The lithological background of the region has a significant impact on the observed patterns. The presence of certain mineral deposits and rock types, as well as geological characteristics, contribute to the environmental release and accumulation of Co, Cr, and Ni. The spatial distributions of Co, Cr, and Ni are given in Figure 10.



(**a**) (**b**)

Figure 7. (**a**) Spatial distribution of F1 factor scores (Fe, Li, Sc, and V) and (**b**) their distribution according to geographical regions and geological formations.

Factor 3 includes Cd, Pb, Zn, and Sb, which are commonly associated with air pollution and are less affected by geological factors. Notably, these elements have elevated levels in certain regions, including Veles, Skopje, Tetovo, and parts of Eastern Macedonia (Figure 11a,b). The main causes of these elevated levels are closely related to industrial activities, with the former lead and zinc smelter in Veles being the biggest contributor, despite its closure in 2003. The open slag dump near Veles, which contains significant amounts of slag and continues to release Cd, Zn, and Pb into the environment, contributes to the problem. The consistent airflow, facilitated by wind patterns such as Vardarec and Jugo, plays an important role in the dispersion of these elements in both directions, and contributes to their widespread distribution [50]. The reactivation of lead–zinc mines in Eastern Macedonia in 2010, including Sasa, Toranica, and Zletovo, has led to new concerns [24]. These mines are associated with huge amounts of waste materials, and, over time, weathering processes have led to increased element content in the surrounding soil. Airborne dust from these areas, carried by the wind, has been a major factor in the observed high metal contents in the moss samples. The spatial distributions of Cd, Pb, Sb, and Zn are given in Figure 12.

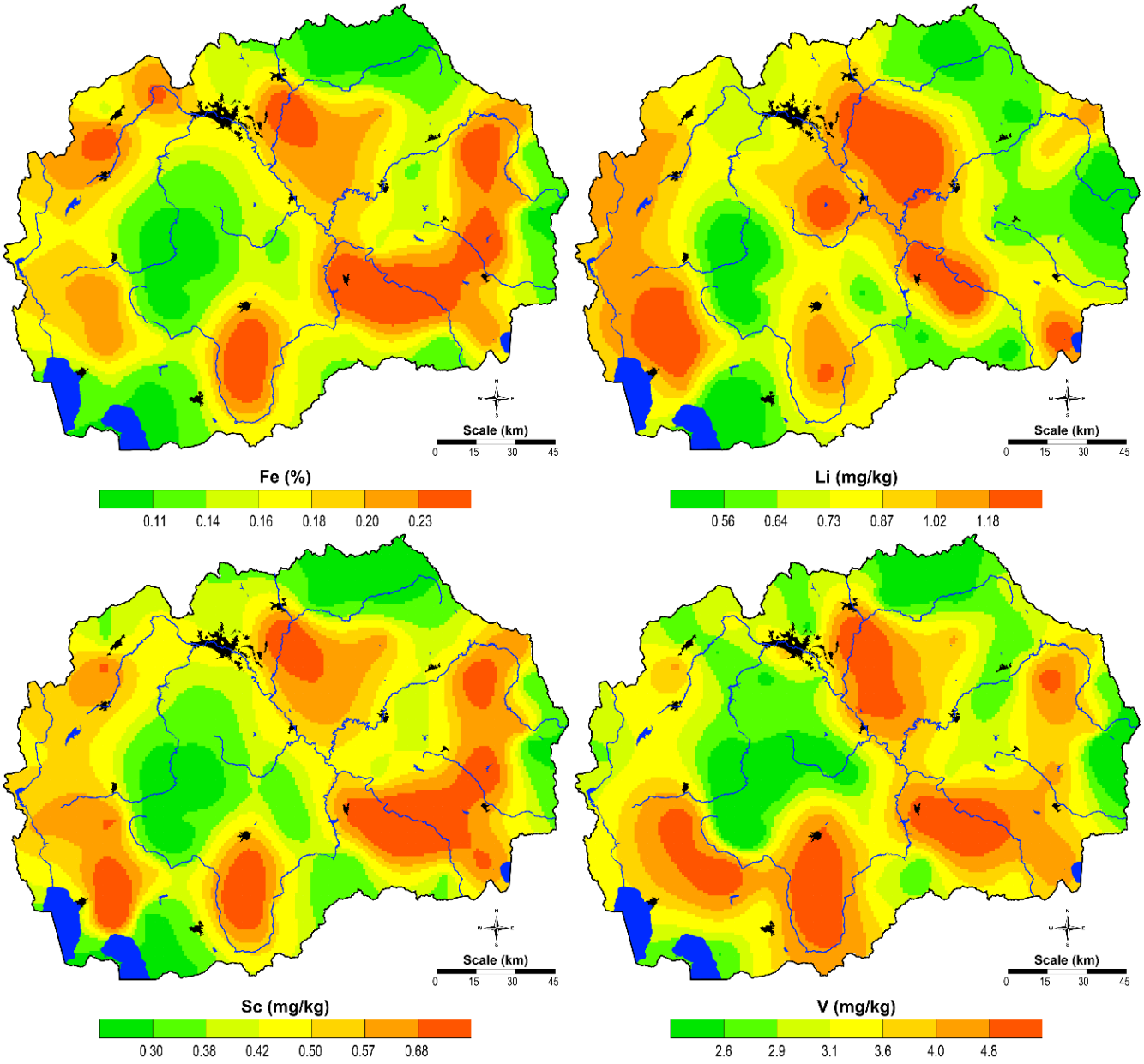


Figure 8. Spatial distribution of Fe, Li, Sc, and V—elements included in F1.

Factor 4 includes As, Cl, and I. This association of elements can be explained by different geological and environmental factors. Higher contents of these elements are found in the moss samples collected in the Vardar Zone, where Tertiary sediments are present, in the Serbo-Macedonian Massif, where Neogene and Paleogene magmatic rocks are found, and in the northwest of the country, where Quaternary sediments are present (Figure 13a,b). Although arsenic is commonly associated with anthropogenic sources like industrial activities or mining, its presence in the moss samples collected might have a natural origin as well. Elevated arsenic values in mosses are often related to the geological composition of the region, including different rock types such as sedimentary, shales, and volcanic rocks, as well as to the presence of ore deposits and hydrothermal activity. Areas where mining has occurred in the past or where ore deposits are present (e.g., the Radoviš and Probištip regions) have higher arsenic contents, due to mining activities associated with metal ores. Higher values of this element in the samples collected near Skopje may be caused by the former activity of the steel plant located in this town. The presence of chlorine and iodine in the

moss samples may be related to the geological and ecological conditions in Macedonia. Chlorine, which is relatively abundant in nature, may be influenced by the geological substrates and aquatic ecosystems in the region. On the other hand, iodine, which is associated with coastal areas, may be influenced by the country's proximity to the Aegean Sea (60 km air distance to the coast), leading to the dispersal of iodine and chlorine from coastal sources. Coastal environments are known sources of various halogen elements, including iodine and chlorine. The spatial distributions of As, Cl and I are given in Figure 14.

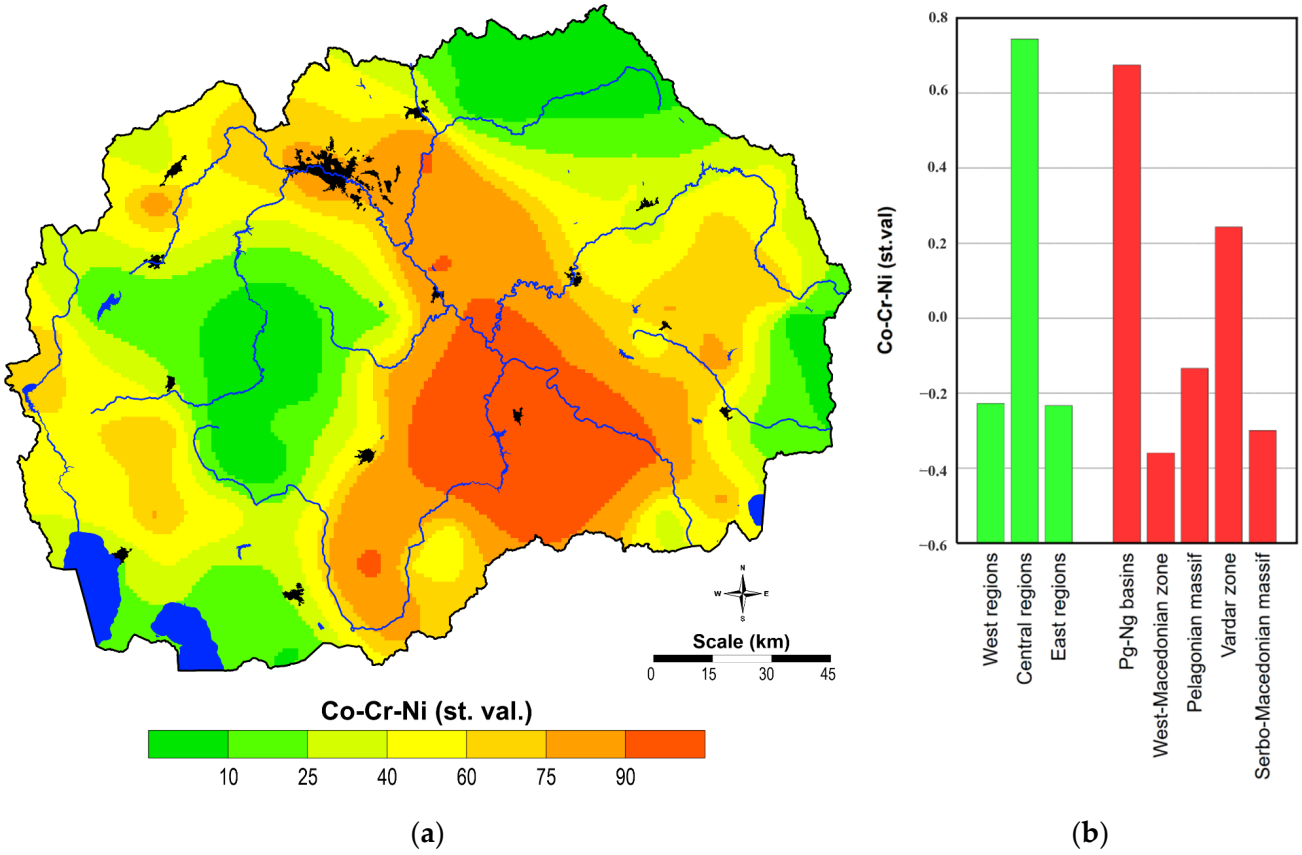


Figure 9. (**a**) Spatial distribution of F2 factor scores (Co, Cr, and Ni) and (**b**) their distribution according to geographical regions and geological formations.

Factor 5 (Ba and Sr) associates elements primarily influenced by the region's diverse lithology. Their distribution varies within the different lithological units. There are certain rock types and geological settings in the country where elevated Ba and Sr content is more common [25]. According to Figure 15a,b, the highest contents of Ba and Sr were found in the areas with occurrences of Neogene magmatic rocks and in areas with Paleogene cystitis occurrences. A slightly lower content of these elements in the moss samples was found in the samples collected in the areas with Quaternary alluvium and diluvium sediments. The spatial distributions of Ba and Sr are given in Figure 16.

The spatial distribution of various elements, including gold (Au), bromine (Br), calcium (Ca), cesium (Cs), copper (Cu), mercury (Hg), indium (In), potassium (K), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), neodymium (Nd), rubidium (Rb), selenium (Se), tantalum (Ta), and tungsten (W) in moss samples from Macedonia reflects a complex interplay of geological, environmental, and anthropogenic factors (Figure 17). The presence of these elements in mosses is often due to the geological characteristics of the region [25]. Certain elements such as Au and Cu may be naturally abundant in specific geological formations, resulting in their uptake

by mosses. In addition, areas with historical mining activities, industrial processes, and agricultural practices can significantly influence the element concentrations in the environment and, consequently, in the moss samples [24]. Of particular interest are elements such as Hg, which can originate from both geological and anthropogenic sources. The greatest anthropogenic impacts of mercury air pollution were found near the formerly active lead–zinc smelter in Veles, the lead and zinc mines Zletovo, Sasa, and Toranica in the country's northeast, the copper mine and flotation near Radoviš, and the ferronickel smelter near Kavadarci. Possible evidence of transboundary transport from Albania was found in the western part of the country [51]. Indium is another potentially toxic element. The presence of indium in moss samples collected in Macedonia indicates specific geological and industrial influences. Indium is often associated with zinc-rich geological formations. Indium is often found as a byproduct of zinc mining and refining. The highest values of In in moss samples collected near the former active lead–zinc smelter in Veles were also found in the eastern part of the country [24,25].

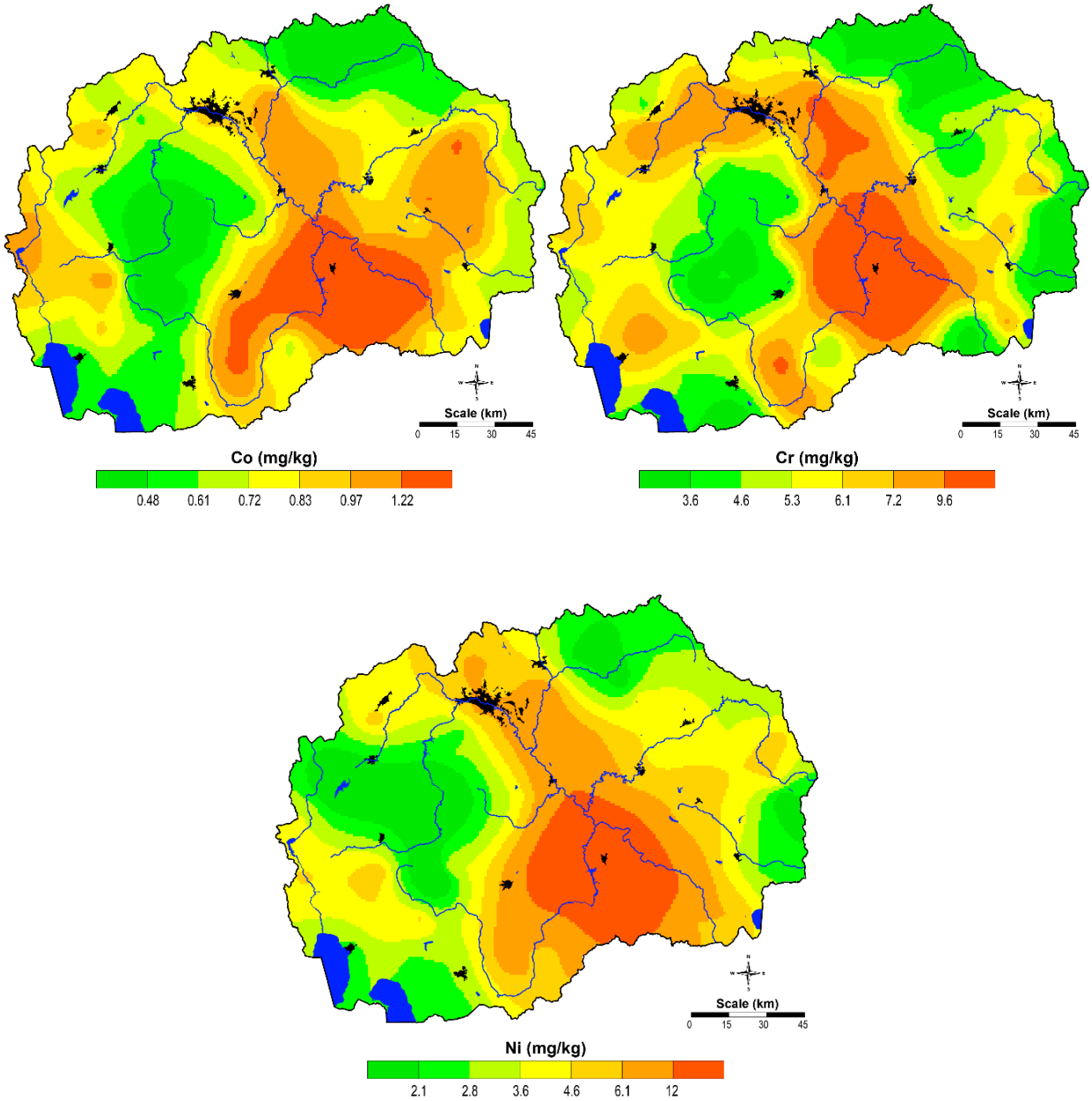
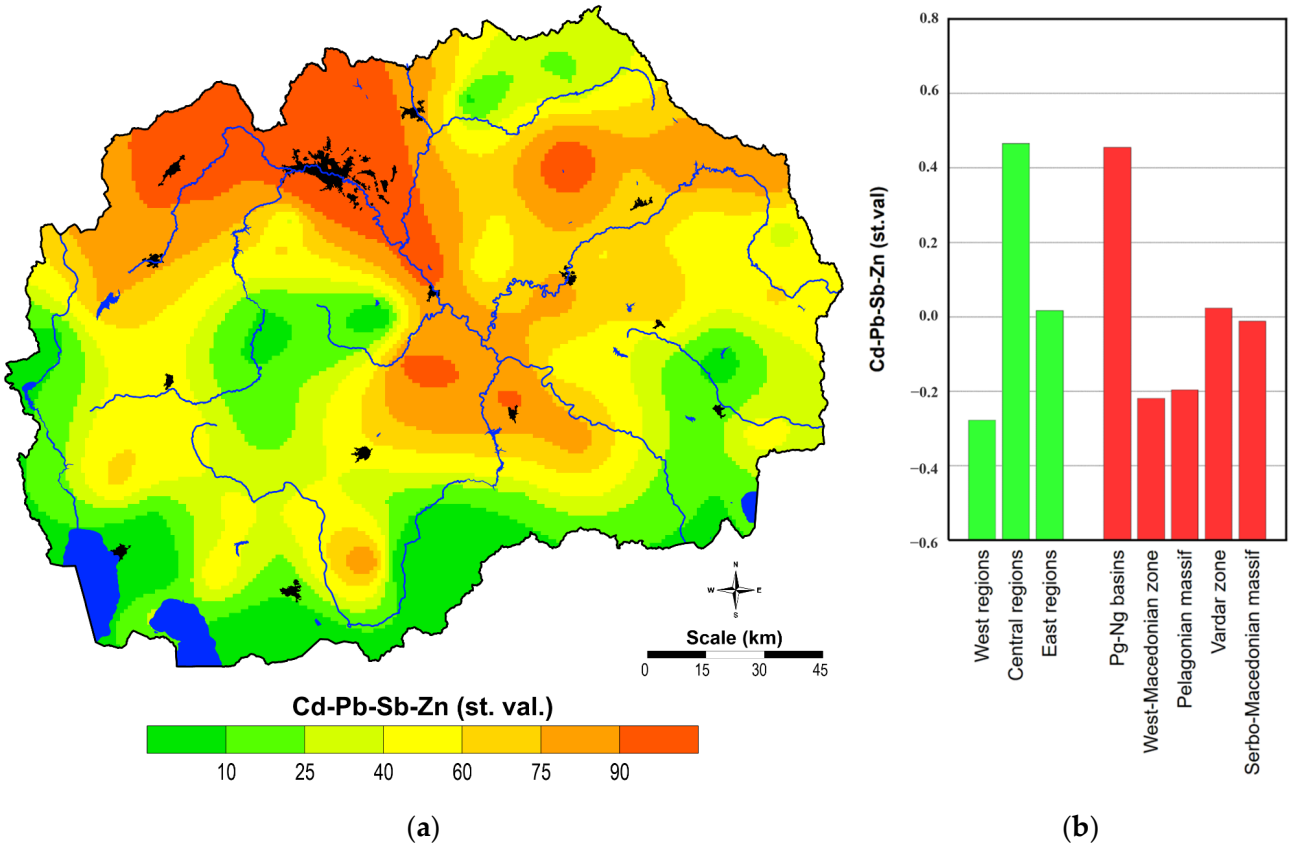


Figure 10. Spatial distribution of Co, Cr, and Ni—elements included in F2.



(**a**) (**b**)

Figure 11. (**a**) Spatial distribution of F3 factor scores (Cd, Pb, Sb, and Zn) and (**b**) their distribution according to geographical regions and geological formations.

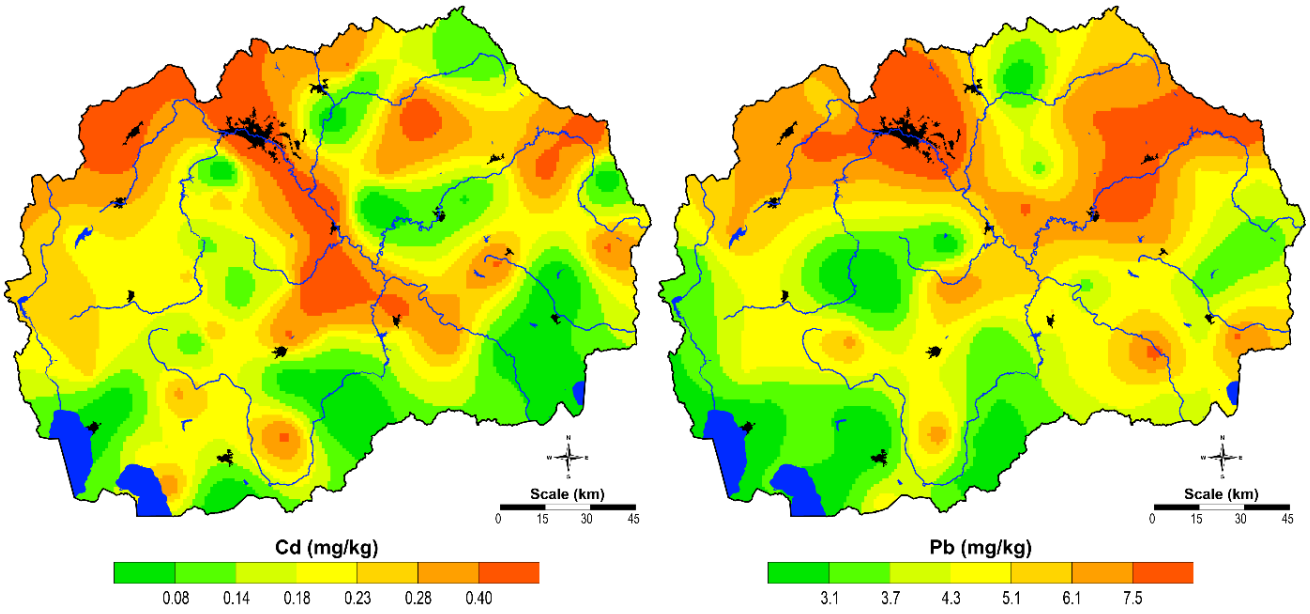


Figure 12. *Cont.*

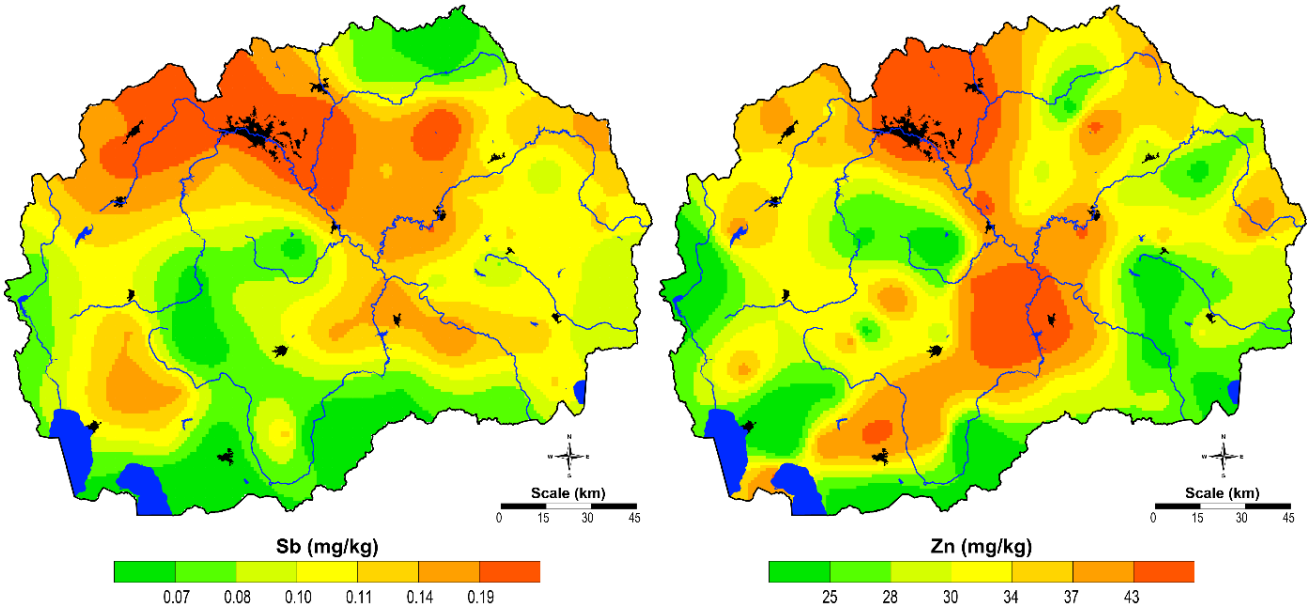
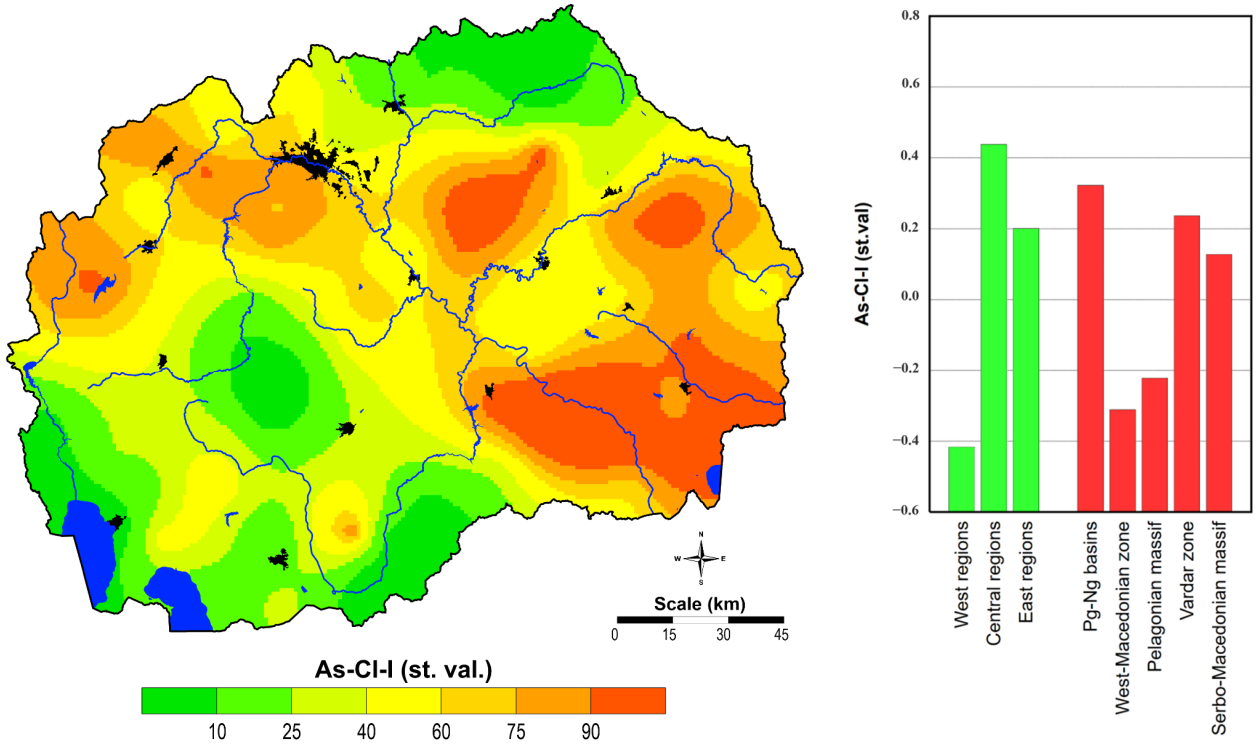


Figure 12. Spatial distribution of Cd, Pb, Sb, and Zn—elements included in F3.



(**a**) (**b**)

Figure 13. (**a**) Spatial distribution of F4 factor scores (As, Cl, and I) and (**b**) their distribution according to geographical regions and geological formations.

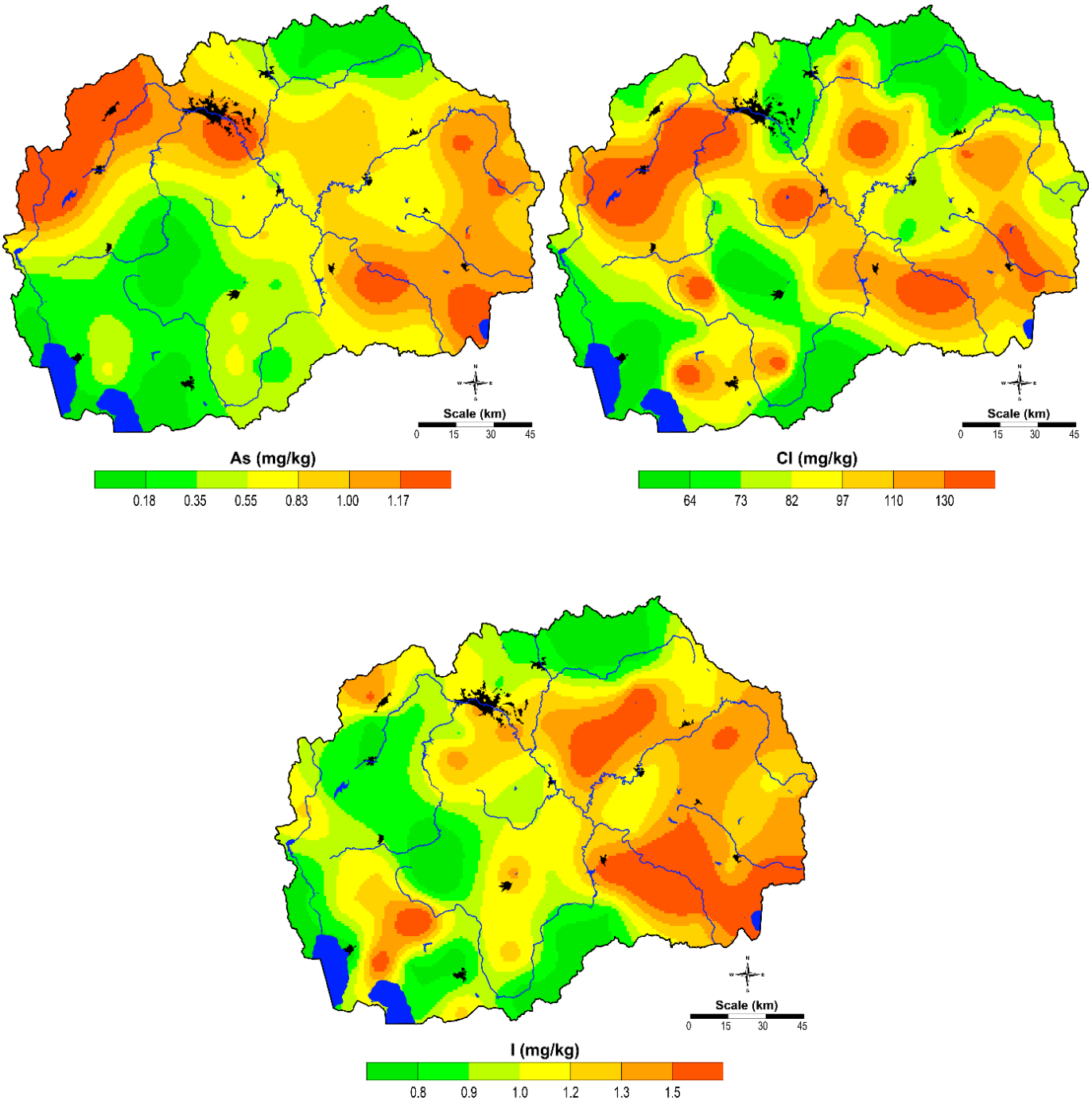


Figure 14. Spatial distribution of As, Cl, and I—elements included in F4.

Understanding the multiple influences on the spatial distribution of these elements in mosses is crucial for a comprehensive assessment of environmental conditions and potential sources of contamination in Macedonia. This information is crucial for environmental monitoring and management in the region, as well as for identifying areas where targeted mitigation measures may be needed to address potential risks.

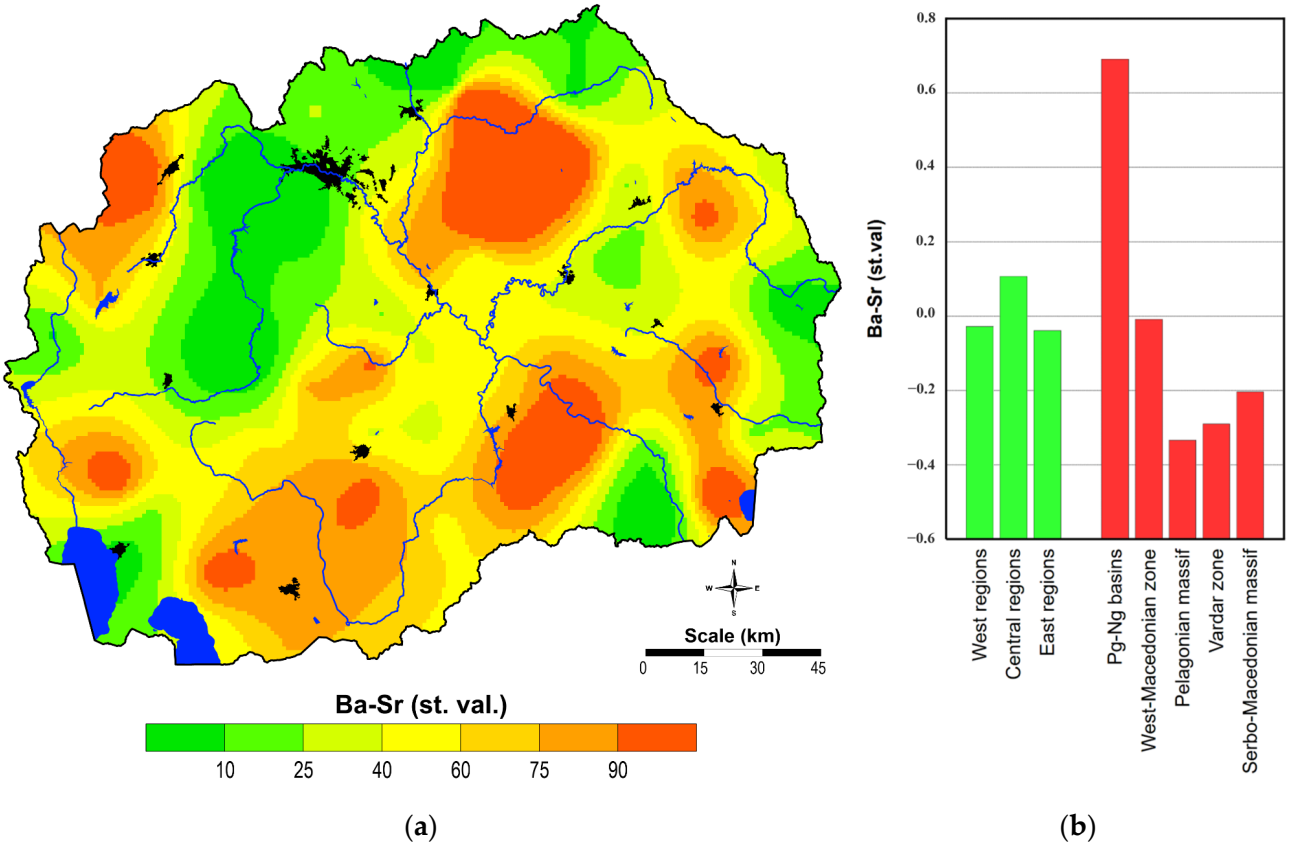


Figure 15. (**a**) Spatial distribution of F5 factor scores (Ba, and Sr) and (**b**) their distribution according to geographical regions and geological formations.

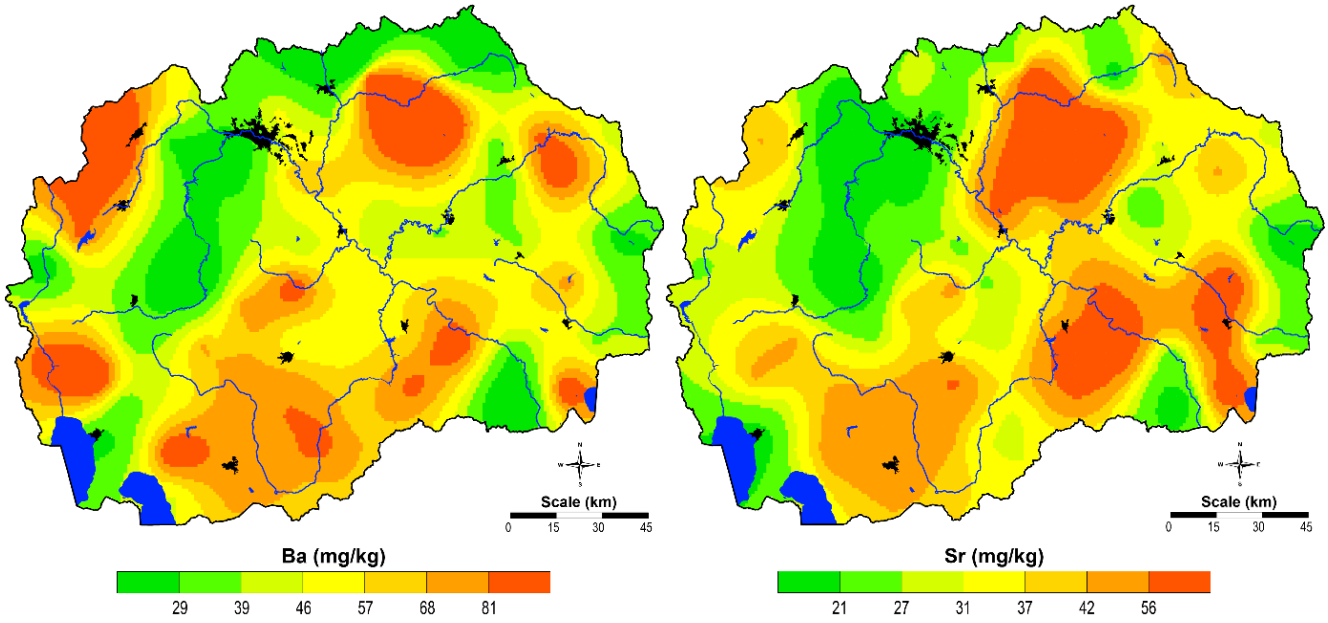


Figure 16. Spatial distribution of Ba and Sr—elements included in F5.

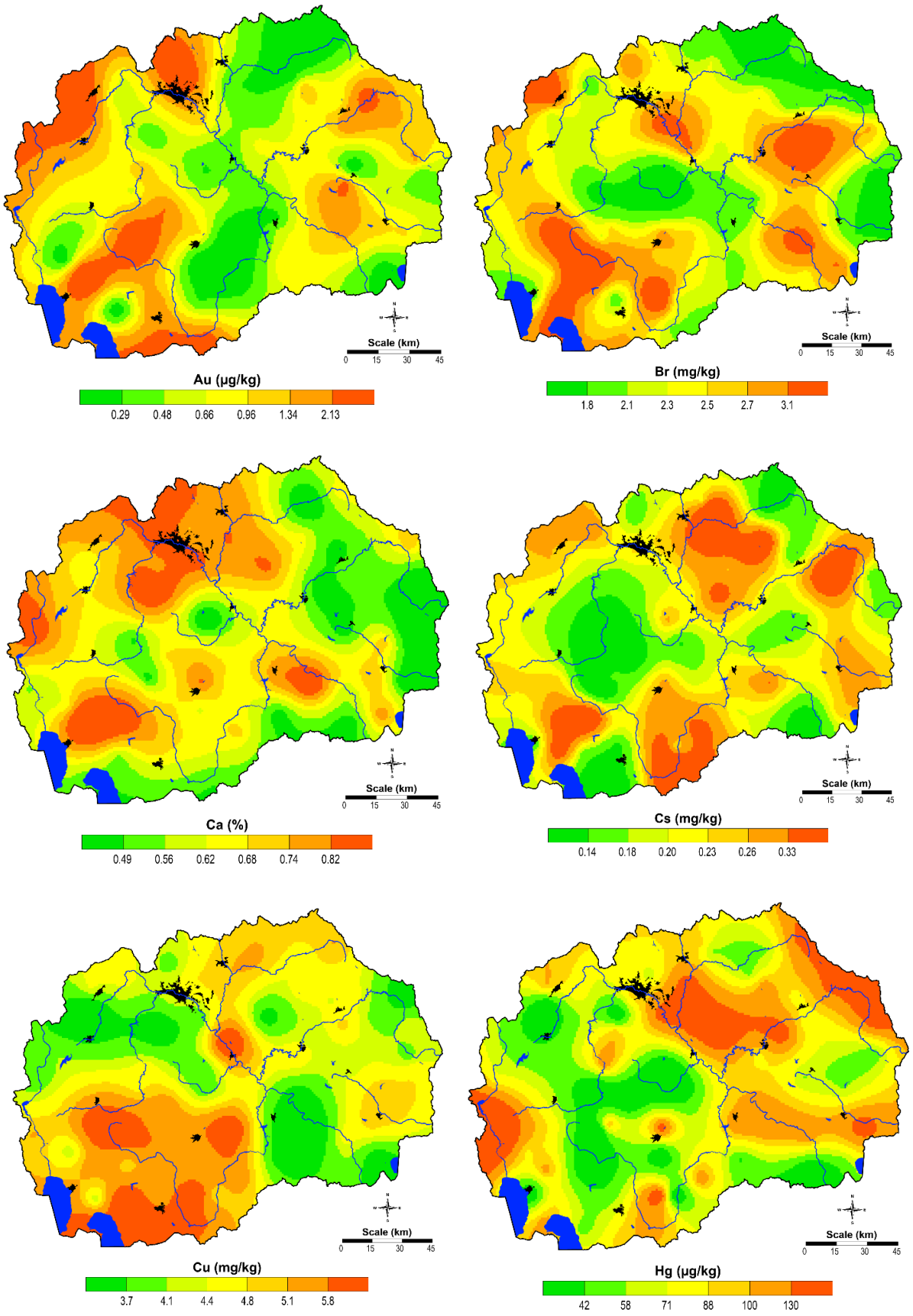


Figure 17. *Cont.*

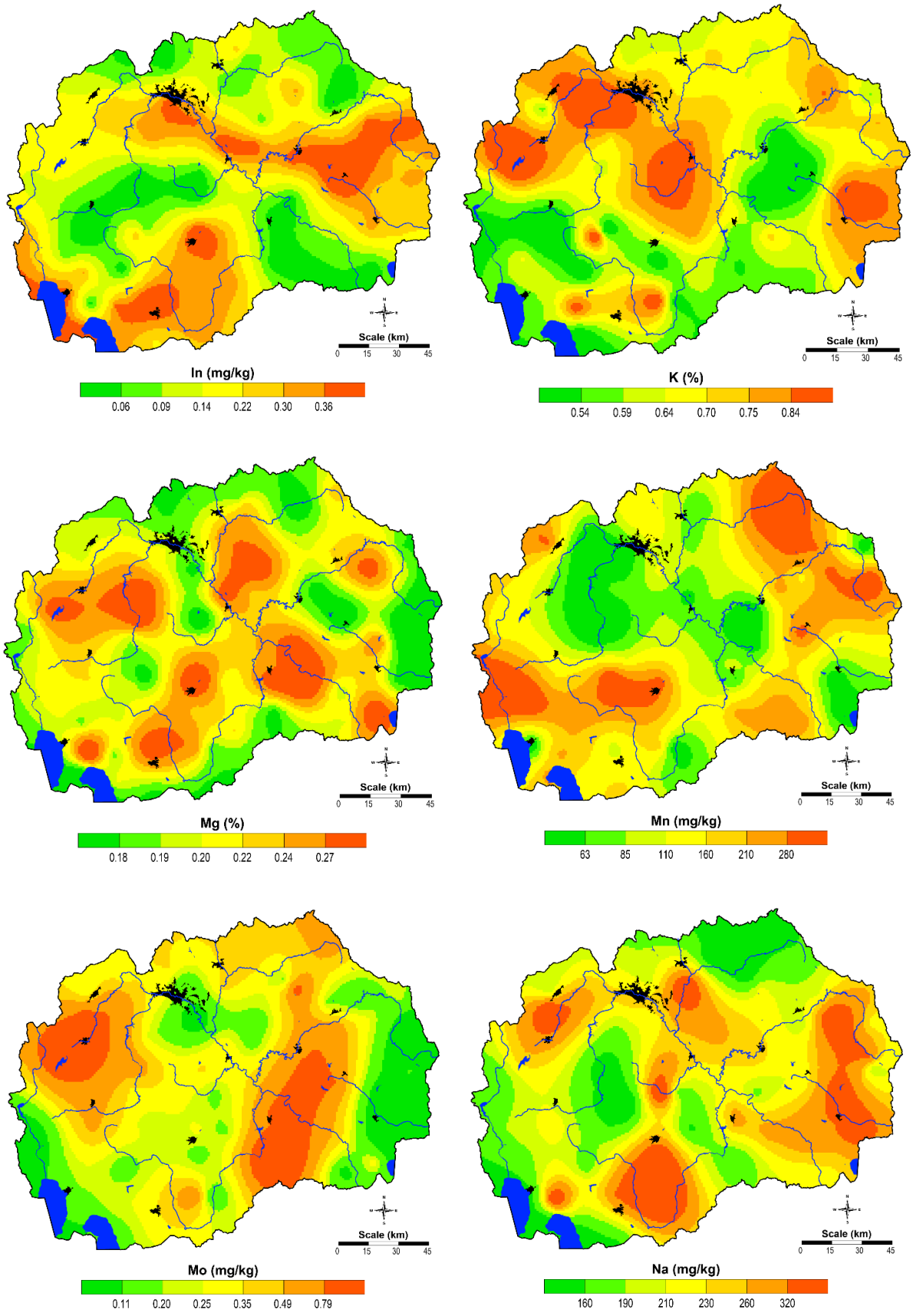


Figure 17. *Cont.*

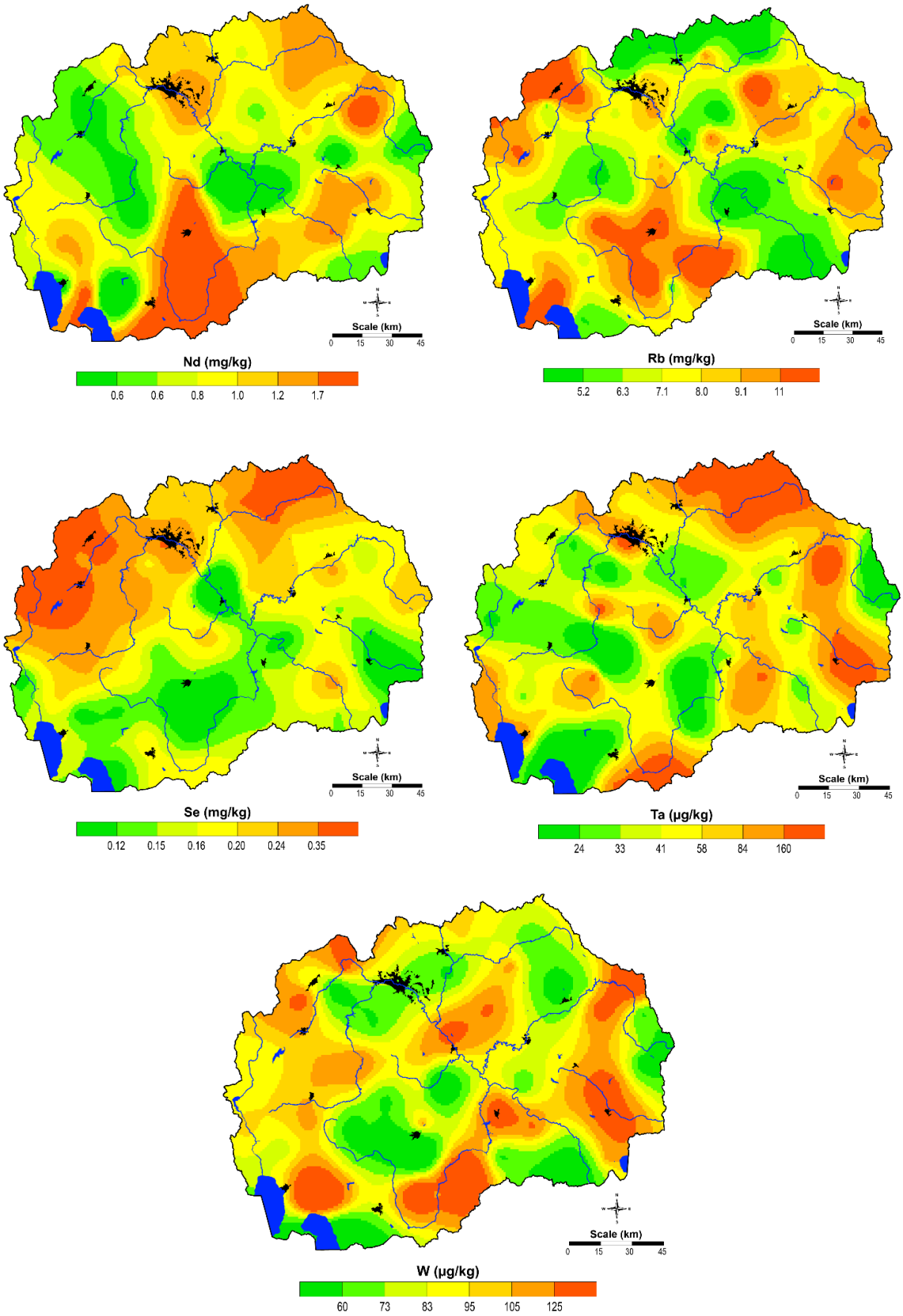


Figure 17. Spatial distribution of Au, Br, Ca, Cs, Cu, Hg, In, K, Mg, Mn, Mo, Na, Nd, Rb, Se, Ta, and W—elements that were eliminated from cluster and factor analysis due to their tendency to form their own clusters or their tendency to form independent factors.

4. Conclusions

The comprehensive analysis of moss samples collected in Macedonia in 2015 provides valuable insights into the distribution and sources of various elements in the environment. The study suggests that the presence of elements in mosses is influenced by a combination of geological, environmental, and anthropogenic factors. The identified factors, such as the geogenic groups of elements, the influence of industrial activities, and the effects of air pollution, shed light on the spatial patterns and sources of these elements. The study highlights the impact of past and present industrial activities on the concentration of certain potentially toxic elements, such as Cd, Cr, Ni, Pb, and Zn. These elements show higher concentrations in regions associated with past and present industrial activities, especially in Veles, Tetovo, Kavadarci, and the eastern part of the country. The former lead and zinc smelter in Veles, together with the waste dumps in the surrounding area, have left a lasting impact on the atmospheric deposition of these elements, despite the closure of the plant. The reactivation of lead and zinc mines in the eastern part of Macedonia in 2010 and the reactivation of a nickel smelter near Kavadarci contributed to the increase in the content of these elements, compared to the 2010 results. This study also reveals the role of geological formations in shaping the distribution of elements that are not considered to originate from anthropogenic activities. Overall, this research serves as a valuable resource for environmental monitoring and management, helping to identify areas where targeted interventions are needed to mitigate potential risks and protect the environment in the country. The findings can serve as a blueprint for robust monitoring strategies, allowing for the identification of hotspots and vulnerable areas impacted by both natural geological processes and anthropogenic activities. This knowledge will allow environmental authorities to allocate their resources efficiently and focus action on areas where they are most needed, such as implementing stringent regulations and pollution control measures in industrial zones, former smelting areas, and regions with ongoing mining activities. The research is also crucial for monitoring future trends and is a valuable resource for modelling atmospheric deposition fluxes.

Identified hotspot regions with elevated concentrations of potentially toxic elements, such as Veles, Tetovo, Kavadarci, Skopje, Radoviš, and areas around specific mining sites, require focused interventions. These could involve stricter regulatory measures, improved waste management practices, and the implementation of advanced pollution control technologies. Integration of these data with other environmental monitoring programs, such as soil and air quality assessment, can provide a comprehensive understanding of element distribution.

While mosses are reliable indicators, their specificity in pinpointing contamination sources remains a limitation. Sometimes a lack of specific source attribution to elevated element concentrations poses challenges in precisely identifying pollution origins. As avenues for future research, a continued, long-term monitoring program could reveal evolving trends in element deposition and assess the efficacy of mitigation strategies over time. Future studies focusing on conducting source attribution analyses would significantly contribute to advancing our understanding of element distribution dynamics and environmental remediation strategies.

This research significantly contributes to sustainability by shedding light on the intricate relationships between environmental factors and human activities, particularly concerning environmental elements' distribution. By delineating the sources of various elements, including those of anthropogenic and geogenic origins, our study aids in identifying regions affected by industrial activities, thus facilitating targeted interventions for mitigating environmental risks. Moreover, our findings can serve as a vital resource for policymakers and environmental agencies, enabling the formulation of evidence-based regulations and policies to control pollutant emissions and manage environmental contamination. Our research methodology offers a robust framework for monitoring environmental changes and identifying potential risks associated with

the atmospheric deposition of potentially toxic elements. The study serves as a fundamental tool for advancing sustainable development initiatives by providing insights into the interplay between human activities, geological factors, and their environmental impacts, supporting informed decision-making and policy development for a more sustainable future.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su16020748/s1, Table S1: Quality control and assurance of the elements determined by INAA; Table S2: Quality control and assurance of the elements determined by ICP_AES and cold vapor AAS. Reference [36] is cited in Supplementary Materials.

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