minerals

Review

Investigations of Chemical Element Distributions in Soil, North Macedonia—A Review

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Abstract: This review article considers the following aspects: naturally distributed chemical elements and their enrichments, and the increased occurrence of PTEs due to anthropogenic and urban activities, as well as due to the geochemical uniqueness of certain geochemical landscapes, depending on the lithological environment. The review article is the result of many years of successful cooperation between the Geological Survey of Slovenia and the Faculty of Natural Sciences in Skopje, Ss. Cyril and Methodius University in Skopje, as well as several other institutions from North Macedonia, Russia and Romania but, also, through the voluntary and enthusiastic work of Prof. Trajče Stafilov's PhD and Master's students. To create the Geochemical Atlas, the territory of North Macedonia was covered with 995 sampling locations, but 16 separate areas with soil contamination were additionally sampled. The total sum of all collected soil samples was 3983 from 2449 different sampling sites in the period from 2006 to 2017. The analyses were performed at the Institute of Chemistry, Faculty of Natural Sciences in Skopje, at the Ss. Cyril and Methodius University in Skopje, North Macedonia, at the Research Institute for Analytical Instrumentation (ICIA), Cluj-Napoca, Romania, at the Joint Institute for Nuclear Research in Dubna, Moscow Region, Russia, and at Acme Labs in Vancouver, Canada. The sum of all analysed soil samples in all four mentioned laboratories was 7991 from 2006 to 2017. Using advanced mathematical methods such as multivariate statistical methods (HCA, FA, PCA) and artificial neural networks–multilayer perceptron (ANN-MP), predictions were made about the concentrations of potentially toxic elements (PTEs) and their distribution in real space. In less than two decades (2007–2023) of fruitful collaboration, a large number of scientific works have been published: 188 scientific publications, 8 geochemical atlases and 23 chapters in monographs.

Keywords: chemical elements; distribution; pollution; soil; North Macedonia

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1. Introduction

The impact of humans on the biosphere is extensive and complex and, in most cases, has led to irreversible changes. All human-induced changes disturb the natural balance of ecosystems as they have evolved over a long period. Therefore, in most cases, these changes lead to a degradation of the natural environment for humans. Although the human impact on the biosphere dates back to the Neolithic period, the problems of ecosystem degradation through pollution have intensified in the last few decades of the 20th century. Most of the chemical elements necessary for life on Earth are mainly supplied from the soil above the lithosphere. The content of elements in plants often correlates with their presence in the surrounding soils. Most of the chemical elements that are essential for human life are also essential for plants. However, the concentrations of most elements that can be harmful to humans are not toxic to plants, as they have adapted to such concentrations [1,2]. The consumption of energy and mineral resources leads to the contamination of the biosphere with potentially toxic elements (PTEs). Anthropogenic environmental changes, especially those associated with contamination, lead to environmental degradation. The most potentially hazardous PTEs for the biosphere are As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Se and Zn. However, elements, such as Ag, Au, Be, Mn, Sb, Sn, Tl, U and V, can be hazardous to the environment if they are released in excessive quantities [3–5].

Soil is crucial for the survival of humanity, which is closely linked to its productivity. Soil acts as a filtering, buffering, storage and transformation system and protects against the effects of heavy metal pollution in groundwater. Soil is the most important source of chemical elements for plants, both in the form of micronutrients and pollutants [2]. Due to geological and climatic influences, soils have very different properties. Soils have a unique structural feature that distinguishes them from pure earth materials and serves as the basis for their classification: a vertical sequence of layers formed by the combined action of percolating water and living organisms [1].

The problem of the destruction of ecosystems through pollution became increasingly acute towards the end of the 20th century. The rapid increase in PTE concentrations in the environment is usually accompanied by the development of utilisation technologies. Soils contain chemical elements of different origins: lithogenic elements, which originate directly from the lithosphere; geogenic elements, which are of lithogenic origin but whose concentration and distribution in the soil layers are altered by paedogenetic processes; or anthropogenic elements, which originate from direct or indirect anthropogenic activities. The behaviour of chemical elements in the soil and, thus, their bioavailability differ depending on their origin and soil conditions as well as their chemical and physical properties. Regardless of the chemical form of the anthropogenic elements in the soil, their availability to plants is significantly higher than that of elements of geogenic origin. In several regions of the world, soils are exposed to increasing mineral fertilisation, pesticide use, waste disposal and industrial pollution. All these human activities affect both chemical and physical soil properties and lead to changes in the behaviour of chemical elements in soils [1,6–9]. The behaviour of elements during weathering and paedogenetic processes, the basic soil-forming processes, is closely related to their geochemical properties. Most elements have a lithophilic character [10,11]. Paedogenetic processes occur simultaneously with weathering processes; usually, these different processes are closely related.

The content of chemical elements in soil materials from natural and contaminated sites shows great variability, both horizontally and vertically. The heterogeneity of soils, especially at the micro level, leads to considerable problems when taking representative soil samples. This affects the reproducibility and comparability of analytical data, which are very important for assessing the background content of chemical elements in soils. Although, today, there is no truly pristine state of PTEs in soils even in remote regions, some values of PTEs in “uncontaminated” soils are used as reference values for the assessment of soil contamination [2].

The terms contamination and soil pollution are used synonymously. Soil contaminated with PTEs is only considered polluted if a threshold concentration is exceeded, and biochemical and biological processes are adversely affected [12]. The main sources of inorganic substances are industrial activities, such as mining and smelting of metal-bearing ores, brick and pipe manufacturing, cement, ceramic and glass production, electricity generation, fossil fuel combustion, nuclear reactors, municipal waste incineration, agricultural practises, such as soil amendment by sewage sludge, manure, mineral fertilisers and pesticides, fumigation, traffic and urban pollution, cosmic particles and long-range transport of pollutants [2,3].

Soil has recently become the subject of numerous studies, some of which deal with large areas. For example, Salminen et al. [13] and De Vos et al. [14] produced the first Geochemical Atlas of Europe as part of the FOREGS (Forum of European Geological Surveys) Geochemical Baseline Programme, which contains data on 63 elements in about 800 topsoil and subsoil samples. In 2014, Chemistry of Europe’s Agricultural soils (in which North Macedonia participated) was published by Reimann and the GEMAS study group (Geochemical Mapping of Agricultural and Grazing Land Soil), which is based on the geochemical analysis of agricultural and grazing soils [15,16]. There are also numerous studies on soil pollution at the national or regional level [17–55].

Regional soil contamination occurs mainly in industrial regions and in the centres of large settlements, where factories, traffic and municipal waste are located [1]. Due to the heterogeneity and constant change of urban areas, it is necessary to understand the natural distribution of PTEs and the methods by which they can be distinguished from man-made anomalies in nature. The natural background of the content of PTEs in soil is variable, which means that higher levels of some elements may be normal in one region but abnormal in another. However, in cases where industrial enterprises, particularly mining and smelting operations, are located close to cities, pollution may increase. Recently published works have shown that mining and smelting activities lead to enormous soil pollution [56–75] and that the most serious soil pollution is a consequence of Pb-Zn mining and smelting activities [64,67,76–82] as well as similar activities for copper, arsenic and antimony [42,51–55,65,70–75,79–88] or coal-fired power plants [89].

North Macedonia first participated in the UNECE ICP Vegetation Programme–Heavy Metals in European Mosses [90,91] in 2002 (survey 2000/2001) and again in 2005, 2010, 2013, 2015 and 2020, in which the atmospheric deposition of trace elements was investigated using samples of terrestrial mosses. The results of these studies in North Macedonia indicate a deterioration in air quality with regards to PTE pollution [92]. The main emission sources are metallurgical activities, power plants and mining. Therefore, additional studies were conducted in the areas with the highest PTE pollution of various environmental media.

Despite conducting these studies in certain regions of the country, soil quality data are limited in terms of representing PTEs at the national level. Therefore, a soil geochemical survey was conducted throughout the country. This article provides an overview of all previous studies on the distribution of a large number of potentially toxic elements in the soils of North Macedonia. In addition to investigating their distribution in soils throughout the country, additional studies were conducted in areas where a higher occurrence of some elements is expected due to anthropogenic and urban activities, as well as due to the geochemical uniqueness of certain geochemical landscapes and depending on the geochemistry of the underlying lithology.

2. Geographic Description of North Macedonia

North Macedonia is a landlocked country in the central part of the Balkan Peninsula between 40°50′ and 42°20′ north latitude and between 20°28′ and 23°05′ east longitude (Figure 1), with an area of about 25,700 km^2. According to the 2022 census, North Macedonia has a total population of 1,830,000 (2022 census). North Macedonia is divided into eight statistical regions: Skopje, Pelagonia, Polog, Vardar, eastern, southeastern, northeastern and southwestern.

North Macedonia is geographically bounded by a central valley formed by the Vardar River and framed by mountain ranges, and the terrain is mostly rugged.

About two-thirds of the country's territory is mountainous; they belong partly to the old Rodope Group in the eastern part and to the young Dinaric Group in the western part of the country. The eastern mountains are generally lower than 2000 m, while the Dinaric Group over 2500 m high, with Golem Korab, 2764 m, as the highest peak in North Macedonia.

Valleys and plains cut through the mountainous relief structures and cover about a third of the country. The most pronounced valleys are those along the Vardar River, including the Skopje Valley (1840 km^2), while the largest plain in North Macedonia is the Pelagonian Plain in the southwest, which covers an area of about 4000 km^2 at an average altitude of 600 m. North Macedonia also has scenic mountains, belonging to two different mountain ranges: the Šar Mountains (Dinaric Mountains) and the Osogovo–Belasica mountain chain (Rhodope Mountains) [28].

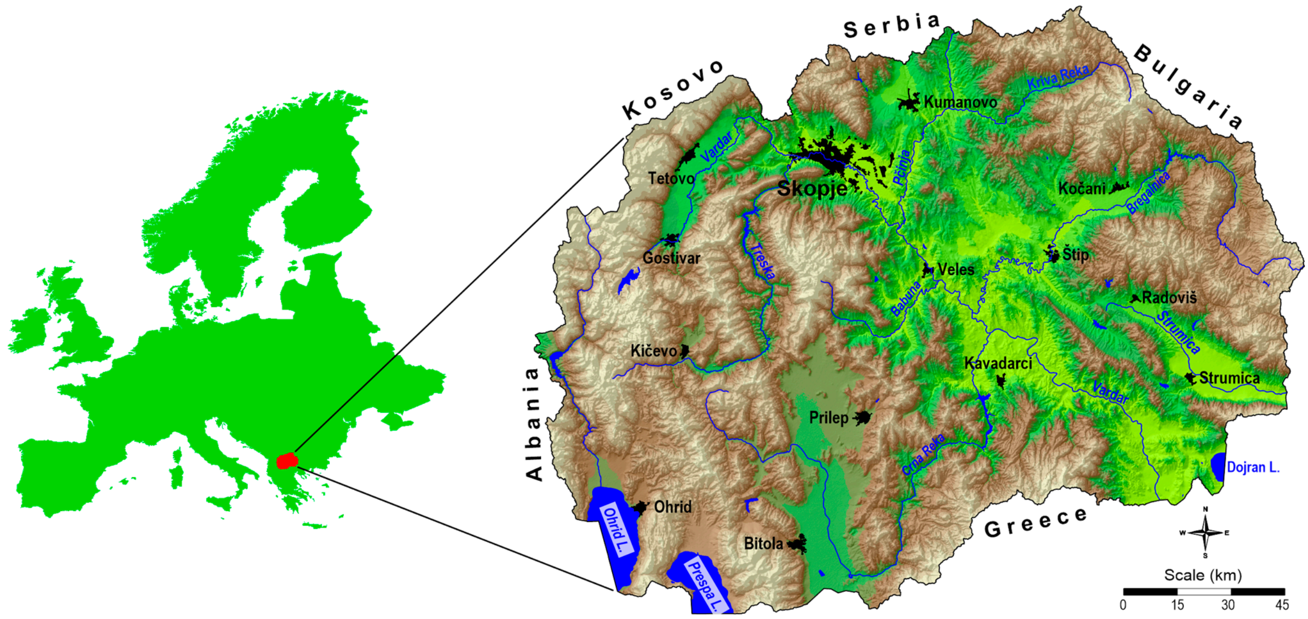

Figure 1. Topographic map of North Macedonia.

Due to the characteristic natural and geographical conditions, North Macedonia has two distinct climatic zones: a modified Mediterranean climate and a temperate continental climate. It also features two distinct seasons: cold, wet winters and dry, hot summers, associated with the transitional seasons of spring and autumn [93]. The complex relief structure and differences in altitude significantly alter the Mediterranean influence on the climate. The average annual temperature depends mainly on the altitude of the respective areas; the average annual variation can be up to 20 °C. In the mountain regions, the average annual temperatures are relatively low and range between 4.7 °C (1750 m) and 8.2 °C (1230 m). The highest average annual temperature of 14.5 °C is found in the lower reaches of the Vardar, which is influenced by the Aegean Sea.

The annual rainfall in North Macedonia is very unevenly distributed, with the lowest amounts, often less than 500 mm, falling in the central part of the country. Areas with higher rainfall are Skopje, Kumanovo and the Kočani-Radoviš valleys, with an average rainfall of 500–550 mm. The highest amounts of precipitation were found in the Debar Valley (870 mm) and in the mountainous regions of Bistra and Šar Mountains with over 1000 mm.

North Macedonia is rich in minerals, with deposits of various metals (Cr, Cu, Fe, Pb, Zn, Ni and Mn). Based on these mineral deposits, three mines for lead–zinc ore, one for copper ore and mines for iron, nickel and chrome ore have been opened in the past. In addition, smelters have been built for the extraction of various metals: iron and steel in Skopje, ferronickel in Kavadarci, ferrochromium and ferrosilicon in Jegunovce, and lead and zinc in Veles. The country also has gypsum, limestone, marble, lignite and granite mines.

Based on previous studies, it has been established that North Macedonia has a complex geology, comprising many geological formations of different ages and geological composition, which has led to a great variety of soil types. From a tectonic point of view, North Macedonia comprises six major tectonic units (Figure 2A), including the Vardar Zone (VZ) (Figure 2, IV) in the central region, the Pelagonian Massif (PM) (Figure 2, III), West-Macedonian Zone (WMZ) (Figure 2, II), a small part of the Cukali-Krasta Zone (CKZ) (Figure 2, I) in the west, the Serbo-Macedonian Massif (SMM) (Figure 2, V) and the Kraishtide Zone (KZ) (Figure 2, VI) in the east of the country [28,94–97].

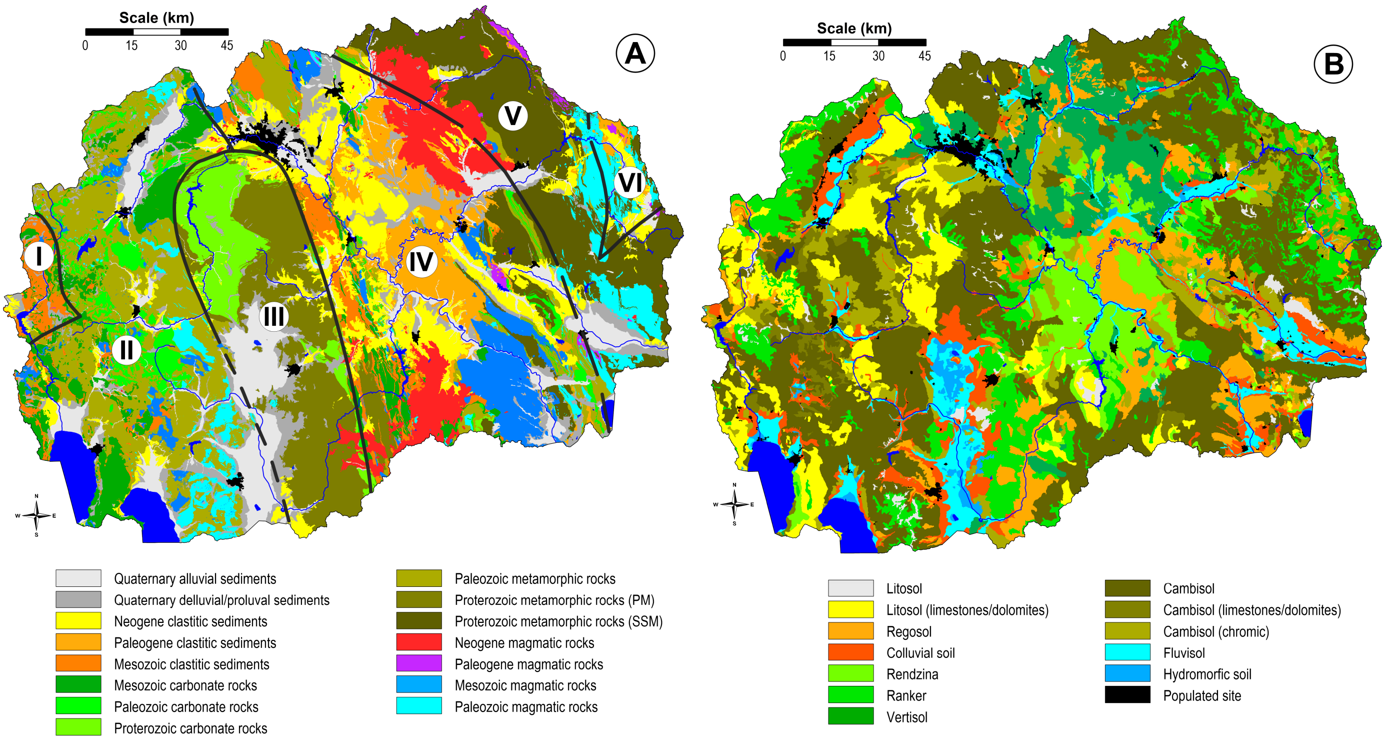

Figure 2. (**A**) Simplified geological map of North Macedonia. Tectonic units: I—Cukali-Krasta zone (CKZ), II—West-Macedonian zone (WMZ), III—Pelagonian massif (PM), IV—Vardar zone (VZ), V—Serbo-Macedonian massif (SMM), VI—Kraishtide zone (KZ) [28]; (**B**) generalized pedological map [28].

The Cukali-Krasta Zone (CKZ) is mainly distributed in Albania, with a small part in North Macedonia. This zone consists of Upper Cretaceous, conglomerates–sandstones, claystones and limestones with olistostromes and rudist limestones. Evaporites and minor Paleogene sediments can be found in this zone. The West-Macedonian Zone (WMZ) has an internal tectonic structure that was mainly formed during the Hercynian and Laramide compressions. The West-Macedonian Zone is lithologically composed of low-grade metamorphic rocks and anchi-metamorphic Paleozoic rocks and magmatites, Triassic and Jurassic sediments and magmatites, and Tertiary sediments. The Vardar Zone separates the Pelagonian Massif and the WMZ in the west from the Serbo-Macedonian massif in the east. It is an old structure that dates back to the Lower Palaeozoic. The Serbo-Macedonian Massif (SMM) is an accretionary wedge on the eastern edge of the Eurasian plate, which lies in the Carpatho-Balkanides and was pulled down over the Vardar Zone. The main mass consists of a complex of the lower or overthrusted Proterozoic and the Upper Riphean-Cambrian. The Kraishtide Zone (KZ) represents the southernmost segment of the Carpatho-Balkanides, which are part of the Serbo-Macedonian Massif. The largest part of the zone is located in Bulgaria and is characterised by a particular type of Alpine development.

The territory of North Macedonia is covered by the following 15 main geological units: Quaternary alluvium, Quaternary deluvium/proluvium, Neogene clastites, Paleogene clastites, Mesozoic clastites, Mesozoic carbonates, Paleozoic carbonates, Proterozoic carbonates, Paleozoic metamorphic rocks, metamorphic rocks from the Pelagonian Massif, metamorphic rocks from the Serbo-Macedonian Massif, Neogene, Paleogene, Mesozoic and Paleozoic magmatic rocks.

North Macedonia has a very heterogeneous land cover, consisting of many soil types and lower taxonomic units. According to the pedological map of the country [98,99], the following soil types are predominant: lithosol, lithosol (limestone/dolomite), regosol, colluvial soil, rendzina, ranker, vertisol, cambisol, cromic cambisol, cambisol (limestone/dolomite), fluvisol, hydromorphic soil and anthrosol (Figure 2B).

3. Materials and Methods

3.1. Soil Sampling and Preparation

The soil samples were taken in accordance with European guidelines but also in accordance with our many years of experience [13–15,28,100]. For the Geochemical Atlas of North Macedonia, the entire country was divided into 20 geographically clustered parts (Figure 3A, Table 1). For this purpose, a sampling grid of 5 × 5 km was chosen, in which a total of 1990 soil samples were taken at 995 locations in two layers, topsoil (0–5 cm) and subsoil (20–30 cm). The sampling campaigns for this purpose were carried out between 2012 and 2015.

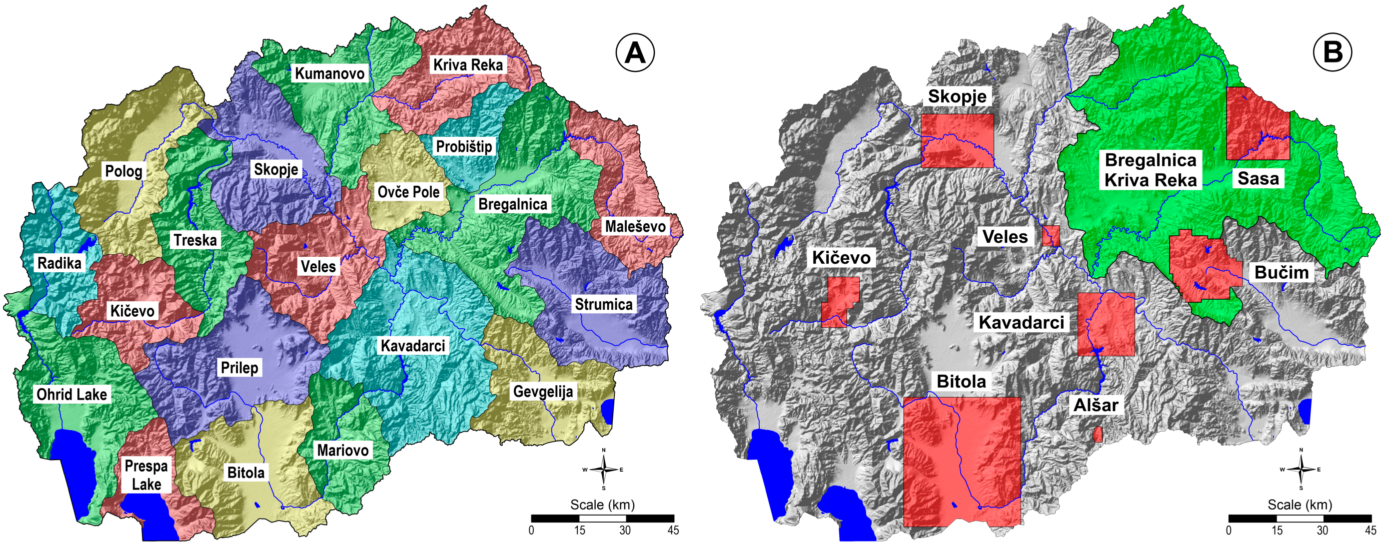

Figure 3. (**A**) Areas investigated within the geochemical map of North Macedonia; (**B**) other investigated areas.

Table 1. Areas investigated within the geochemical atlas of North Macedonia (GA) and other investigated areas.

Area	Samples	Material	Analytics Laboratory (Year)	References
N. Macedonia (Geochemical Atlas)	995	T/S *	ACME (2016)	[28,101]
Bregalnica (GA)	166	T/S	IC (2012), ICIA (2012)	[67,102]
Gevgelija (GA)	86	T/S	IC (2014), ICIA (2015)	[103]
Kavadarci (GA)	204	T/S	IC (2015), ICIA (2015)	–
Kičevo (GA)	70	T/S	IC (2015), ICIA (2015)	–
Kriva Reka (GA)	96	T/S	IC (2012), ICIA (2015)	[67,104]
Kumanovo (GA)	102	T/S	IC (2014), ICIA (2014)	[105]
Maleševo (GA)	82	T/S	IC (2012), ICIA (2012)	[67,102]
Mariovo (GA)	72	T/S	IC (2014), ICIA (2014)	[106]
Ohrid Lake (GA)	128	T/S	IC (2014), ICIA (2014)	[107]
Ovče Pole (GA)	50	T/S	IC (2012), ICIA (2015)	[67,102]
Bitola (GA)	100	T/S	IC (2012), ICIA (2015)	[108]
Prilep (GA)	146	T/S	IC (2014), ICIA (2015)	[108]

Table 1. *Cont.*

Area	Samples	Material	Analytics Laboratory (Year)	References
Polog (GA)	116	T/S	IC (2012), ICIA (2015)	[109]
Prespa Lake (GA)	50	T/S	IC (2014), ICIA (2015)	[110]
Probištip (GA)	42	T/S	IC (2012), ICIA (2012)	[67,102]
Radika (GA)	62	T/S	IC (2015), ICIA (2015)	[111]
Skopje (GA)	120	T/S	IC (2014), ICIA (2014)	[68]
Strumica (GA)	132	T/S	IC (2014), ICIA (2015)	[112]
Treska (GA)	88	T/S	IC (2015), ICIA (2015)	[113]
Veles (GA)	106	T/S	IC (2014), ICIA (2015)	[78]
Allchar	136	T/S	IC (2012), ICIA (2012)	–
Bitola	116	T/S, TS	IC (2012/2016)	[108]
Bregalnica	185	T/S, TS	IC (2012), ICIA (2012)	[67,102]
Bučim	40	T/S	IC (2009)	[67]
Crna Reka	74	T/S	IC (2012/2017), ICIA (2014)	[65]
Drim	32	T/S	IC (2016)	[66]
Kavadarci	344	T/S	ACME (2007)	[85,114]
Kičevo	52	T	IC (2009)	[115]
Kriva Reka	62	T/S	IC (2009), ICIA (2015)	[104]
N. Macedonia (Soil/Moss)	144	T/S	IC (2011)	[116]
Pčinja	20	T/S	IC (2017)	[88]
Skopje	234	T	IC (2009/2014), ICIA (2014)	[117,118]
Strumica	24	T/S	IC (2015)	–
N. Macedonia (Tobacco fields)	149	TS	IC (2013)	[119]
Vardar	56	T/S	IC (2012), ICIA (2012)	[63]
Veles	325	T	IC (2006/2012/2015), JINR (2006/2012)	[57,120]

GA—Geochemical Atlas, T—topsoil (0–5 cm), S—subsoil (20–30 cm), TS—soil (0–30 cm), T/S *—composite soil (0–5/20–30 cm), ACME—Bureau Veritas Commodities Canada Ltd. (former ACME), IC—Institute of Chemistry, Faculty of Natural Sciences in Skopje at the Ss. Cyril and Methodius University in Skopje, North Macedonia, ICIA—Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania, JINR—Joint Institute for Nuclear Research in Dubna, Moscow Region, Russia.

In addition to sampling the soil as part of the Geochemical Atlas, 16 independent (separate) areas of soil contamination were also sampled (Figure 3B, Table 1). This means that in some specific regions, somewhat denser sampling was carried out. The soil sampling methods used are very comparable, often identical or do not take into account the different soil layers. In Bitola, Bregalnica and Tobacco Fields, composite samples from 0 to 30 cm were taken, while in Kičevo, Skopje and Veles, only the topsoil (0 to 5 cm) was sampled.

The sampling density in the individual areas varied, such as in the areas of Bučim (5 × 5 km), Kičevo (1 × 1 km), Kavadarci, Skopje and Veles (1 × 1 km and 0.5 × 0.5 km), and Allchar (0.5 × 0.5 km). An irregular sampling grid was used when sampling in the areas of Bitola, Bregalnica, Kriva Reka or Tobacco fields, as well as when sampling in the river valleys of Bregalnica, Drim, Crna Reka, Kriva Reka, Pčinja, Strumica and Vardar.

Their total number is 1993 from 1454 different locations. However, the sum of all soil samples ever collected is 3983 from 2449 different locations in North Macedonia in the period from 2006 to 2017.

The soil samples were first freed from plants and stones, homogenized and then dried at room temperature. The dry samples were passed through a 2 mm sieve and pulverized to a fine-grain size (125 μm) in an agate mill.

3.2. Chemical Analyses

Prior to the determination of the elements via atomic absorption spectrometry (AAS), inductively coupled plasma–atomic emission spectrometry (ICP-AES) and inductively coupled plasma–mass spectrometry (ICP-MS), the samples were chemically prepared with an acid mixture according to the international standards (ISO 14869–1:2001) [121].

In some studies, AAS was used for the analysis of As, Cd, Cr, Cu, Fe, Hg, Mn, Pb, Sb and Zn by flame AAS (Varian SpectrAA 55B) or by Zeeman electrothermal AAS (Varian SpectrAA 640Z), while mercury was analysed by cold vapour AAS (Varian VGA–76). All these analyses were performed at the Institute of Chemistry of the Faculty of Natural Sciences in Skopje at the Ss. Cyril and Methodius University in Skopje, North Macedonia. This method was applied to 201 samples in 2006 (Table 1) [120]. For quality control, the certified reference standard materials JSAC 0401 (soil) and SARM 3 (rock) were used, yielding values very close to the certified values.

When using ICP-AES (Varian, model 715), the instrumental conditions were previously optimised for each of the 23 elements analysed (Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Ga, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, V and Zn). The quality control of the analyses was checked considering the recovery rate, which was between 98.2% and 100.8%. Quality control was also performed by analysing certified reference samples: soil sample JSAC 0401 (The Japan Society for Analytical Chemistry), rock CRM samples unsaturated igneous rock SARM 3 NIM–L Lujaurite (SA Bureau of Standards, Pretoria, S. Africa) and rock NCS DC71306 (GBW07114) (China National Analysis Centre) [122]. From 2009 to 2017, a total of 3464 samples were analysed using this method (Table 1).

Most of the elements (Ag, As, Au, B, Ba, Be, Bi, Br, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, V, W, Y, Yb, Zn and Zr) were analysed using ICP-MS. These measurements were performed with the SCIEX Perkin Elmer Elan DRC II (Canada) ICP-MS (quadrupole as single detector) at INCDO-INOE2000 at the Research Institute for Analytical Instrumentation (ICIA), Cluj-Napoca, Romania. All measurements were performed using the semi-quantitative method (TotalQuant) in Elan 3.4 software. A multi-element standard solution Merck VI was used, which was diluted to simulate real sample consumption [63]. In the period from 2012 to 2015, this method was applied to 2672 soil samples (Table 1).

For some case studies [57], non-destructive epithermal neutron activation analysis (ENAA) was used for analysis in the IBR-2 reactor, FLNP Joint Institute for Nuclear Research in Dubna, Moscow Region, Russia [123]. Thirty-nine elements (Al, Ca, Fe, K, Mg, Na, Ti, As, Au, Ba, Br, Ce, Co, Cr, Cs, Cu, Dy, Hf, In, La, Mn, Mo, Nd, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Tm, U, V, W, Yb and Zn) were analysed using this method. The quality control of the ENAA results was ensured by the simultaneous analysis of the analysed samples and the reference materials, SDM (soil) and Sl-1 (bottom sediments) of the IAEA (International Atomic Energy Agency). The total number of samples analysed using this method amounts to 267 in the period from 2006 to 2012.

The element concentrations were also analysed in 2007 at Acme Labs, Vancouver, Canada (accredited according to ISO 9001:2008) [124]. The concentration of 37 chemical elements (Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Te, Th, Ti, Tl, U, V, W and Zn) was analysed after digestion with aqua regia (1:1:1 $HCl:HNO_3:H_2O$) for 3 h at 95 °C using ICP-MS. In 2016, the concentrations of 45 elements (Ag, Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hf, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn and Zr) were analysed by inductively coupled plasma emission spectroscopy (ICP-ES) after four acid digestions ($HClO_4$, HNO_3, HCl and HF) [124]. The total number of soil samples analysed in the ACME laboratory was 1387.

The sum of all soil samples analysed in all four laboratories mentioned is 7991 in the period from 2006 to 2017.

3.3. Data Processing

All data processing and calculations, geostatistical data interpretation and visualisation (mapping) were performed with the following software: Statistica [125], QGIS [126] and Surfer [127].

The data were evaluated using a series of data analysis and statistical methods. Individual elements were assessed using univariate, bivariate and multivariate data analysis techniques and spatial mapping of the content of individual elements. The Box–Cox transformation method [128] was frequently used to normalise the data. Multivariate cluster analysis (HCA) and factor analysis (FA) [129–131] were used to reveal the relationships between the chemical elements.

Cluster analysis was applied to partition multivariate observations into several meaningful multivariate homogeneous groups or centres called centroids [132,133]. Due to the complex nature of regional geochemical data [134,135], appropriate data transformations must be performed before performing a cluster analysis. The results of the analysis also depend on the chosen clustering algorithm [132,136,137].

The method of factor analysis was introduced by Sperman [138]. It represents a complicated system of procedures that can be used to identify the relationships between a large number of observed variables [28]. Factor analysis is known as a dimension reduction method, which means that the data are presented in a more concentrated form [139]. The main objective of factor analysis is to explain the variation in a multivariate data set by some representative factors that represent certain characteristics inherent in the data [129,140].

The method of factor analysis is also useful in the presentation of geochemical maps in geochemical studies. One advantage is that instead of maps for 40–50 (or more) elements, only maps for a few representative factors need to be presented.

4. Studies on the Distribution of Chemical Elements in Soil from North Macedonia

Table 2 contains the European median values as well as the median values for North Macedonia (sampling grid 5 × 5 km) and selected case studies, where the sampling grid was denser. The basic information on the total number of samples collected and the analytical treatment with the corresponding references is included in Table 1.

Table 2. Estimated European and North Macedonian medians of selected chemical elements.

	Unit	$EU_{(MA)}$ *	$EU_{(AR)}$ *	North Macedonia	Allchar	Bitola	Bučim	Kavadarci	Kičevo	Skopje	Veles
Al	%	5.8	1.1	6.6	3.8	2.2	1.8	1.5	1.4	3.8	6.2
As	mg/kg	7.0	5.6	10	73	18	12	8.8	7.8	12	9.2
Ba	mg/kg	380	63	430	380	320	250	110	380	300	460
Be	mg/kg	<2.0	0.51	2.0	2.2	-	-	-	-	5.1	-
Bi	mg/kg	<0.50	0.18	0.30	0.14	-	-	0.20	-	-	-
Ca	%	0.66	0.31	1.3	1.5	0.52	0.41	3.6	0.24	4.8	4.1
Cd	mg/kg	0.15	0.20	0.30	0.27	0.26	-	0.30	0.42	0.54	6.4
Ce	mg/kg	48	27	56	22	-	-	-	-	52	65
Co	mg/kg	7.8	7.2	17	11	8.7	-	15	11	38	13

Table 2. *Cont.*

	Unit	$EU_{(MA)}$ *	$EU_{(AR)}$ *	North Macedonia	Allchar	Bitola	Bučim	Kavadarci	Kičevo	Skopje	Veles
Cr	mg/kg	60	20	88	61	57	55	50	43	100	160
Cs	mg/kg	3.7	1.1	-	4.1	-	-	-	-	4.0	3.7
Cu	mg/kg	13	15	28	19	20	23	30	14	33	41
Fe	%	3.2	1.7	3.5	1.9	2.0	2.6	2.3	2.8	3.1	2.8
Ga	mg/kg	14	3.4	-	9.3	-	13	4.0	-	26	-
Ge	mg/kg	0.037	-	-	0.17	-	-	-	-	0.84	-
Hf	mg/kg	5.6	<0.020	1.0	0.78	-	-	-	-	0.88	4.4
Hg	mg/kg	-	0.035	-	0.11	-	-	0.020	-	0.13	0.28
In	mg/kg	0.050	<0.020	-	0.020	-	-	-	-	0.025	0.24
K	%	1.6	0.11	1.9	1.9	1.8	0.88	0.26	1.4	1.2	2.2
La	mg/kg	24	14	25	13	-	-	15	-	26	29
Li	mg/kg	-	11	26	18	14	12	-	11	28	-
Mg	%	0.46	0.28	0.94	1.0	0.41	0.71	0.92	0.59	1.2	0.36
Mn	mg/kg	500	440	900	480	550	440	780	690	720	830
Mo	mg/kg	0.62	0.42	0.90	0.35	-	-	0.30	-	1.5	0.54
Na	%	0.59	0.005	1.2	0.49	1.1	1.3	0.008	0.50	0.53	1.0
Nb	mg/kg	9.7	0.52	11	6.3	-	-	-	-	22	-
Ni	mg/kg	18	14	46	39	25	27	72	18	86	54
P	%	0.056	0.065	0.062	0.072	0.048	-	0.049	-	-	-
Pb	mg/kg	23	18	32	87	10	23	21	71	51	210
Rb	mg/kg	80	14	86	47	-	-	-	-	110	93
Sb	mg/kg	0.60	0.28	0.80	3.4	-	-	0.20	-	1.2	1.9
Sc	mg/kg	8.2	2.0	12	6.6	-	-	3.7	-	24	9.6
Sn	mg/kg	3.0	0.81	2.6	1.2	-	-	-	-	4.8	-
Sr	mg/kg	89	18	140	93	68	39	62	15	91	230
Ta	mg/kg	0.68	<0.005	0.70	0.43	-	-	-	-	0.70	1.3
Th	mg/kg	7.2	2.5	9.5	0.83	-	-	4.7	-	-	10
Ti	%	0.34	0.007	0.34	-	-	-	0.015	-	0.88	0.36
Tl	mg/kg	0.66	0.12	0.70	5.2	-	-	0.20	-	0.19	-
U	mg/kg	2.0	0.74	2.0	-	-	-	0.50	-	-	2.4
V	mg/kg	60	26	89	69	67	59	37	-	-	78
W	mg/kg	<5.0	0.09	1.3	2.7	-	-	0.10	-	1.3	9.7
Y	mg/kg	21	6.5	18	5.8	-	-	-	-	24	-
Zn	mg/kg	52	46	83	55	59	71	57	97	100	210
Zr	mg/kg	230	1.6	35	32	-	-	-	-	75	-

* EU—European medians [13–16]; (MA)—four-acid digestion; (AR)—aqua regia digestion; data rounded to two digits.

There is a significant difference between the geochemical map of North Macedonia and individual local areas. The sampling grid of the geochemical map (5 × 5 km) is quite sparse, so that the geochemical groups mainly represent natural distributions. On the other hand, in individual local areas, we targeted sampling in areas where we expected strong impacts from mining and smelting (Allchar, Bregalnica, Bučim, Kavadarci, Kriva Reka, Veles), operation of thermal power plants (Bitola, Kičevo), anthropogenic impacts (Skopje) and impacts from agriculture (Tobacco Fields). Much denser grids were used, e.g., regular or irregular sampling grids adapted to each case study. The local research, therefore, mainly reflects anthropogenic influences.

4.1. Geochemical Atlas of North Macedonia [28]

The Geochemical Atlas of North Macedonia is the result of the voluntary and enthusiastic work of Prof. Trajče Stafilov's group and his PhD and Master's students, as well as individual experts from North Macedonia and Slovenia, Romania and Russia. The Atlas provides a comprehensive picture of the fundamental chemistry that supports life on land, which has evolved from the complex interactions of air, water, soil and human activities. It could fulfil the future requirements of the European Soil Framework Directive while ensuring high quality and scientifically sound information on the state of the soil at a national level. The monograph "Geochemical Atlas of the Republic of Macedonia" was awarded the state prize "Goce Delčev" for the best scientific achievements in 2016.

The study focussed on assessing the levels of 39 of the 45 chemicals (Ag, Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hf, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn and Zr) in mixed composite samples in which both soil horizons (topsoil and subsoil) were included. This study includes samples collected in 2012–2015 at 995 sites in a sampling grid of 5 × 5 km. After the application of multivariate statistical methods, the following geochemical associations were isolated: Ba-Be-Ce-K-La-Rb-Th-Tl-U (Figure 4A), Co-Cu-Fe-Mn-Sc-Ti-V (Figure 4B), Hf-Zr, Nb-Ta, Cr-Ni (Figure 5A), Ca-Mg, Bi-Pb-Sn (Figure 5B), Cd-P-Zn (Figure 6A) and Sb-As (Figure 6B).

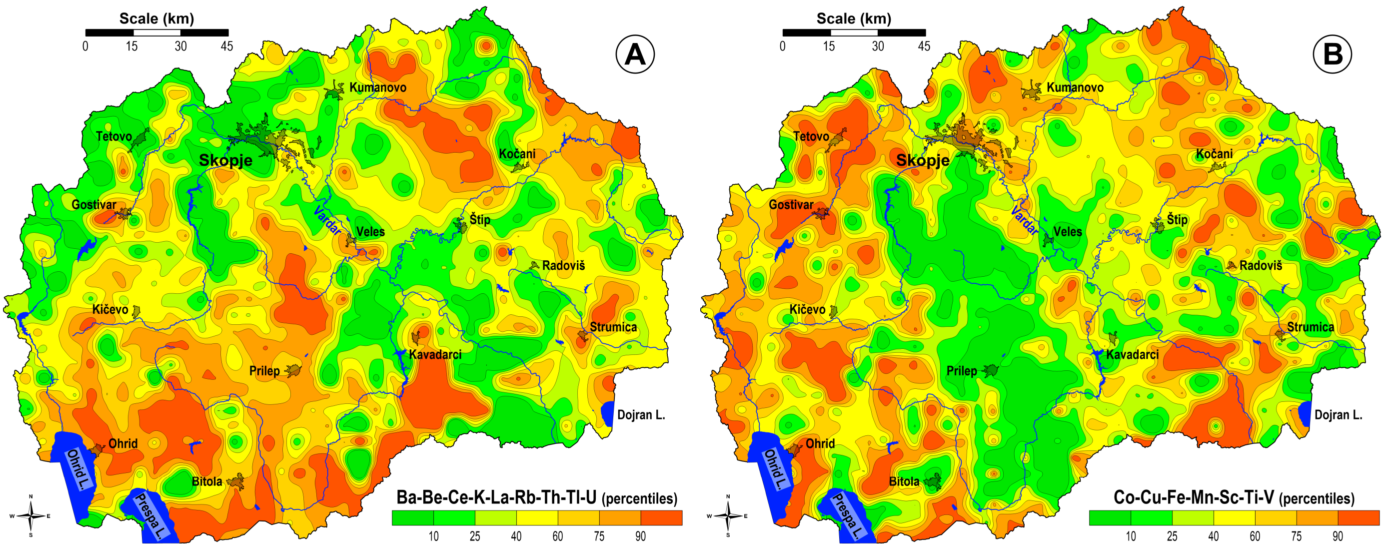

Figure 4. Spatial distribution of the geochemical associations, North Macedonia: (**A**) Ba-Be-Ce-K-La-Rb-Th, Ti-U; (**B**) Co-Cu-Fe-Mn-Sc-Ti-V) [28].

Based on the results of the factor analyses, the chemical levels can be associated with the lithological units. Shown in Figure 4A, this is mainly associated with Neogene and Quaternary volcanism, but some subclusters within the association could be distinguished: Ce-La, Th-U, Hf-Zr and Sr. In general, Ce and La reflect the characteristics of all REEs. Their highest values are associated with lithological units in the south of the country that belong to the young volcanism of the Neogene–Quaternary. The Th-U subcluster could be representative of the radioactive elements in the soil, whose highest values, in addition to the previous subcluster, occur in the metamorphic rocks of the Pelagonian Massif associated with the Kratovo-Zletovo Massif.

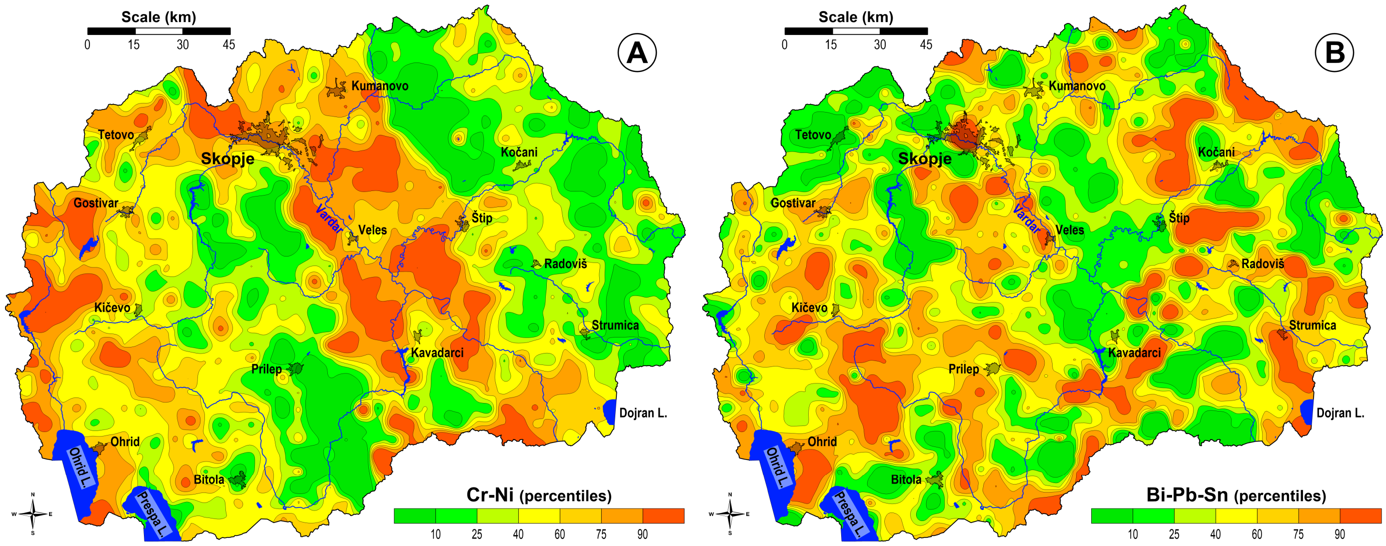

Figure 5. Spatial distribution of the geochemical associations North Macedonia: (**A**) Cr-Ni; (**B**) Bi-Pb-Sn [28].

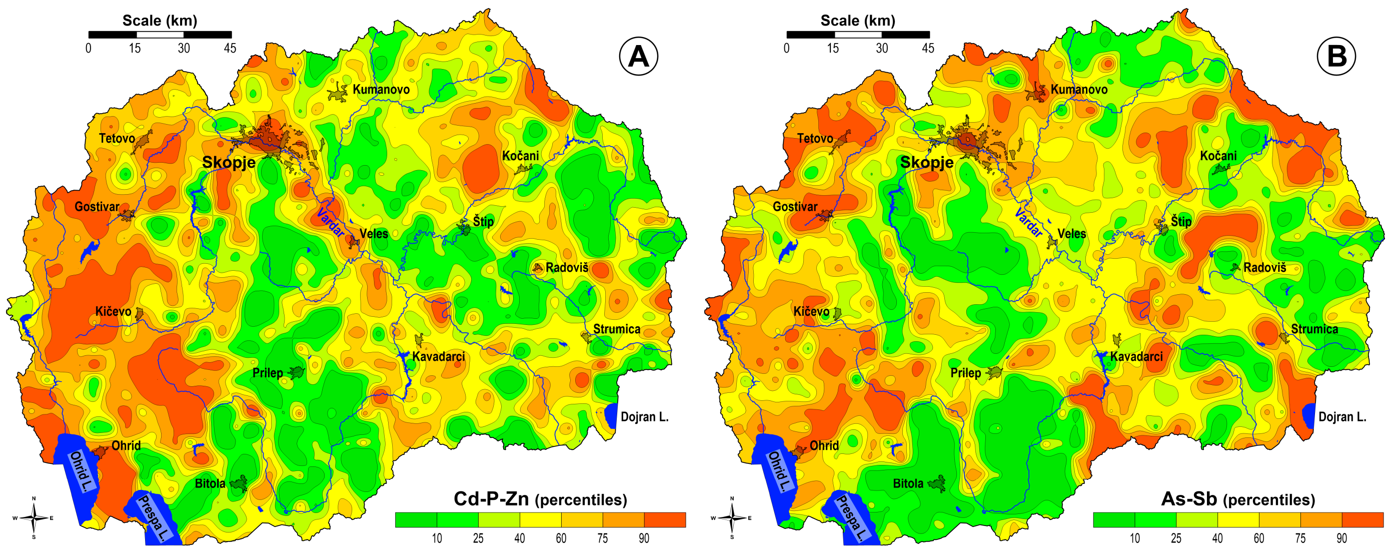

Figure 6. Spatial distribution of the geochemical associations North Macedonia: (**A**) Cd-Pb-Zn; (**B**) As-Sb [28].

The next association, the so-called siderophile group, comprises the elements shown in Figure 4B. The highest values are found in soils formed on Mesozoic and Palaeozoic igneous rocks of the Pelagonian Massif, followed by areas where metamorphic rocks of the SMM and in the Palaeozoic metamorphic rocks of the WMZ occur. Insignificant concentrations are found in the Precambrian metamorphic and carbonate rocks of the PM. Chromium and nickel are associated with ophiolites and Mesozoic ultrabasic magmatic rocks of the Vardar Zone (Figure 5A). Their increased levels are found in soil formed over Neogene, Paleogene and Mesozoic clastites, but their main source is due to the weathering of Mesozoic ophiolites and ultrabasic magmatic rocks. Significant levels have been found in sediments along the Vardar River in the Vardar Zone.

Three subclusters of sulphide elements are isolated in Figures 5B and 6A,B. The spatial distribution maps show that all three groups have both natural and anthropogenic influences. Notable levels of Bi-Pb-Sn are found in the southeast of North Macedonia, where Palaeogene and Neogene volcanism of the Pelagonian Massif predominates, but also in Quaternary deposits, especially in the Vardar River valley. The anthropogenic effects of the Pb-Zn smelter in Veles and the urban area of the capital Skopje are primary sources of their increased levels in soil, but their natural increase is mainly due to volcanic activity. The distribution of As and Sb is similar to the previous group. High contents of Bi, Pb and Sn are found mainly in the mining areas in the east of the country (Sasa, Toranica and Zletovo mines) and in the town of Veles (Pb-Zn smelter).

4.2. Investigations of Selected Certain Areas

4.2.1. Soil Pollution in the Town of Veles and Its Environ [57,120]

The city of Veles is located in the valley of the Vardar River (in the central part of North Macedonia) (Figure 1). Veles is a special urban and industrial area in many respects. Situated in the middle region of North Macedonia, in the valley of the Vardar River, lies the city of Veles (Figure 1). In many ways, Veles is a unique urban and industrial district. Situated in the basin of the Vardar River, the city is surrounded by hills and mountains.

In 2002, 44,000 inhabitants were registered in the city. Veles is one of the most polluted cities in North Macedonia, due to pollution from the Pb-Zn smelter located in the city (which was closed in 2002). The capacity of the smelter was about 100,000 tons of zinc and lead and 120,000 tons of sulphuric acid per year [78] and was the source of emissions of dust containing lead and other PTEs [141].

To determine the possible contamination of the soil in the city and its immediate surroundings with Cd, Pb and Zn (as well as other PTEs), a total of 201 soil samples were taken from an area of 26 km^2. For this purpose, 44 chemical elements were analysed, of which Cu, Cd, Zn, Hg and Pb were determined via atomic absorption spectrometry (AAS) and 39 elements (Al, As, Au, Ba, Br, Ca, Ce, Co, Cr, Cs, Dy, Eu, Fe, Hf, In, K, La, Mg, Mn, Mo, Na, Nd, Ni, Rb, Sb, Sc, Sm, Sr, Ta, Tb, Th, Ti, Tm, U, V, W, Yb, Zn and Zr) through neutron activation analysis (ENAA).

The findings show that the soils in the urban zone and industrial zone have much higher levels of the most common group of PTEs, with an elemental enrichment ranging from 2.2-times for Sb to 27-times for Cd compared to Europe averages [14]. The very high Cd content of in the polluted area reaches 600 mg/kg (Figure 7A), 1.5% for Pb (Figure 7B) and 2.7% for Zn. The contamination with As, Cu and Hg was also classified as insignificant. According to Dutch standards, an area of 6.8 km^2 was determined to be critically contaminated with all six PTEs mentioned (As, Cd, Cu, Hg, Pb and Zn). Due to rising winds, the critically contaminated area is shaped like an ellipse [93].

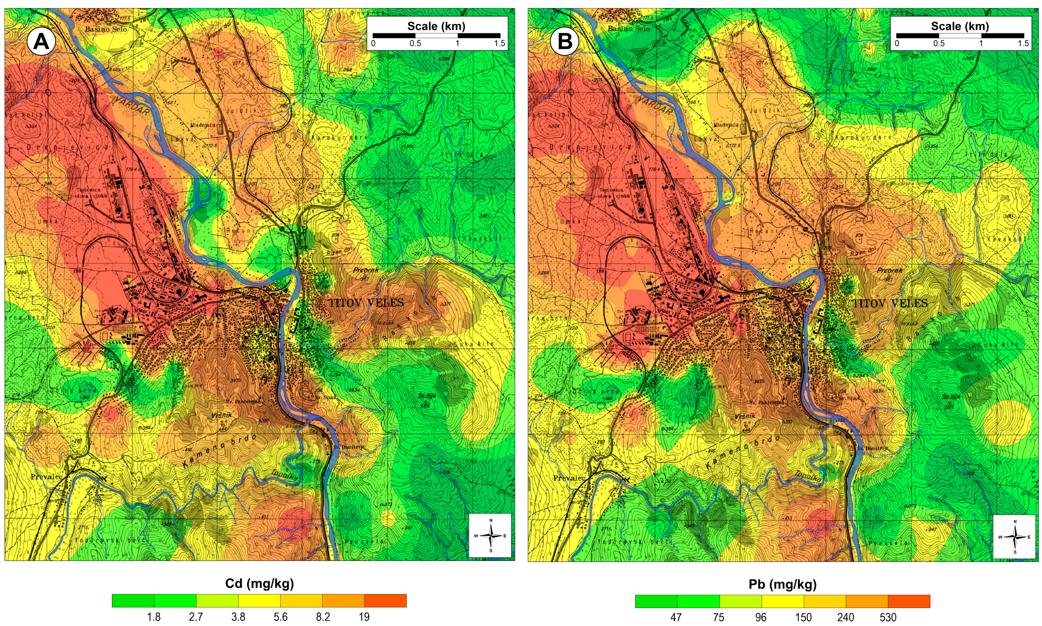

Figure 7. Spatial distribution in Veles area: (**A**) cadmium; (**B**) lead [120].

As a result of the high soil contamination in the region of the city of Veles, vegetables produced in the gardens of this region were found to be significantly contaminated with Cd and Pb, with concentrations exceeding the maximum permissible concentration in a large number of different vegetables [142]. Furthermore, it was also established that dust from the slag deposits and contaminated soils is being blown into the city. The levels of Ag, As, Cd, Cu, In, Pb, Sb, Se and Zn in house dust samples reflect an anthropogenic association of the elements [143].

4.2.2. The Area of the Town of Kavadarci [85,144]

The town of Kavadarci is located in the Tikveš Valley, about 100 km south of the capital, Skopje (Figure 1). The Kavadarci region is known for its ferronickel industry, which is considered a potential source of heavy metal pollution. The soil survey was conducted to determine the content of 36 major and trace elements in the soils in the town of Kavadarci and its surroundings in order to assess the potential impact of the ferronickel smelter located near the town. In the past, this smelter used nickel ore, with a Ni content of about 1% from its own mine, which is located about 30 km south of the plant [85]. In recent decades, nickel-bearing ores have been imported from Asia, Central America and Africa (2%–2.5%).

The studied area (360 km^2) is covered by a sampling grid of 2 $\times$ 2 km, while in the urban zone and the ferronickel smelter (117 km^2), the sampling grid is 1 $\times$ 1 km. A total of 344 soil samples were collected at 172 locations from two layers (0–5 cm and 20–30 cm). The determination of 36 elements was carried out by ICP-MS [85].

Four geochemical relationships were identified based on the findings of the multivariate statistical analyses and the created distribution maps. The spatial distributions of both associations between Al, Fe, Ga, Sc and V (Figure 8A) and Co, Cr, Mg and Ni show natural occurrence, depending on lithogenesis, since their increased levels are found in both soil horizons. The highest contents were found in the areas of the Paleozoic and Mesozoic rocks and the upper flysch zone of the Eocene, with the lowest values in the area of the Pleistocene tuff, the Holocene diluvium and the Holocene alluvium.

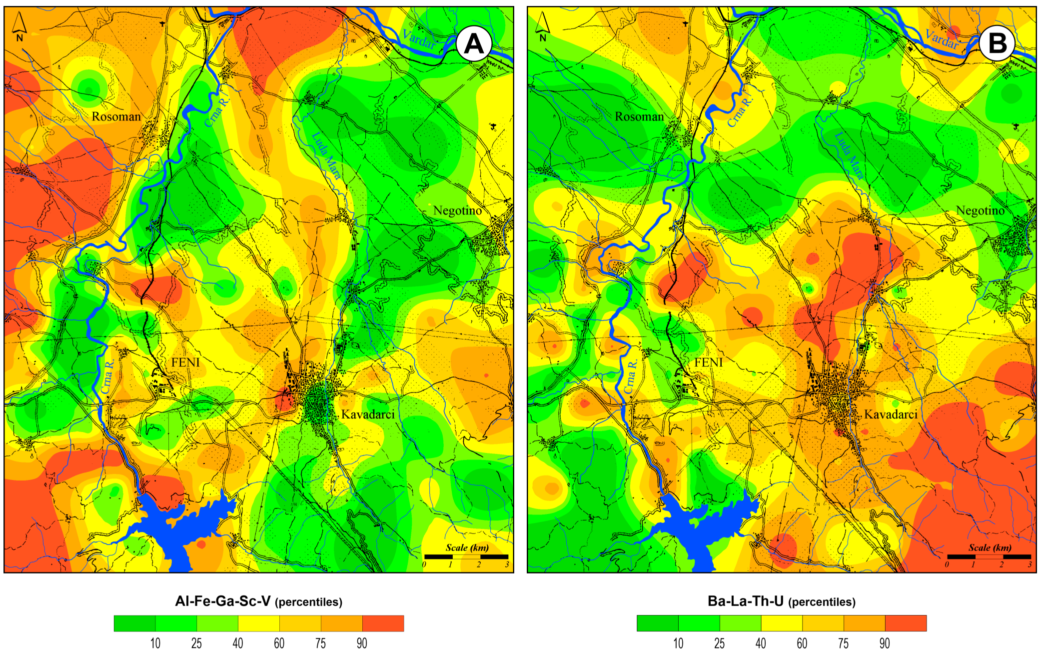

Figure 8. Spatial distribution of geochemical associations in Kavadarci area: (**A**) of Al-Fe-Ga-Sc-V; (**B**) Ba-La-Th-U.

The third association (Figure 8B) is mainly affected by human activities. In some areas, the Pleistocene tuff, Holocene diluvium and Holocene alluvium are predominant, and their concentrations in both soil horizons are increased. The association of Ca and Sr occurs in the upper flysch zone of the Eocene and in the sandy area of the Pliocene.

The map of the spatial distribution of Cd, Hg, Pb and Zn (Figure 9A) shows their enrichment in upper soil horizons, which indicates their anthropogenic origin. The increase in the elements is determined in the Palaeozoic and Mesozoic.

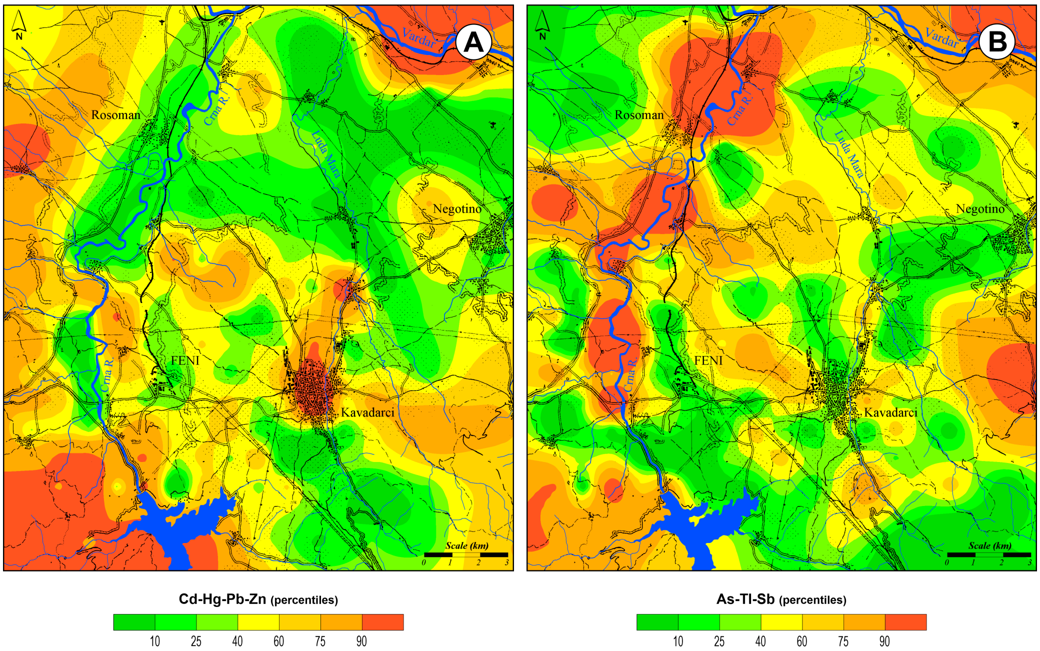

Figure 9. Spatial distribution of geochemical associations in Kavadarci area: (**A**) Cd-Hg-Pb-Zn; (**B**) As-Tl-Sb.

The spatial distribution patterns of the individual elements do not differ significantly. There is a clear anomaly in the topsoil around the Palaeozoic and Mesozoic rocks, in the wider urban area of Kavadarci and in the Holocene alluvium of the Vardar River.

The specific characteristics show the following distinctive group of elements, As, Sb, and Tl, in Figure 9B. The high levels of these elements were identified in samples from the Holocene alluvium of the Crna Reka River, with enrichment exceeding the average of the entire study area by 4 to 4.5. it was concluded that both previous mining operations and natural erosion of the Allchar mine on Kožuf Mountain caused enrichment in the Holocene alluvium. High levels were also found in the river sediments of the Vardar River, which can be attributed to the spread of polluted soils and sediments due to Pb-Zn smelting in the city of Veles [63].

4.2.3. Copper Mine "Bučim" [144]

The Bučim copper mine is located close to the city Radoviš in eastern North Macedonia. The study area covers 400 km^2. The copper ore is processed by flotation into Cu concentrate, with an annual capacity of 4 million tonnes. Over 150 million tonnes of flotation waste is exposed to continuous wind and water particulate matter mobility [122].

In order to evaluate the health risk assessment, the distribution and characterisation of 20 elements (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, V and Zn) were investigated [144]. For this purpose, 40 soil samples were collected from two depths (0–5 cm and 20–30 cm) on a sampling grid of 5 × 5 km. The average median Cu content (23 mg/kg) is relatively low, except in the vicinity of the copper mine and the processing plants (9.3–1200 mg/kg). However, the ratio of Cu enrichment in the soil (subsoil/topsoil) is 2.8, whereas it is ~10 in the vicinity of the mine due to dust mobility at the mine site. No significant enrichment ratios were identified for the other common PTEs (Pb, Ni, V and Zn). The content of lithogenic elements (Al, As, Cr, Ga, Fe, Li, Mg, Mn, Na, Ni, Sr) is stable in the vertical direction (subsoil/topsoil) but varies in the transverse direction depending on the local geology.

4.2.4. Coal Mine and Thermoelectric Power Plant "Oslomej" near the Town of Kičevo [115]

The town of Kičevo is located in the Kičevo Valley in the western part of the country. Kičevo is an important industrial centre in this part of North Macedonia, mostly due to the iron mine in Tajmište (currently closed), the coal mine "Oslomej" and the thermoelectric power plant "Oslomej", which began operating in 1980. The research area covers 148 km^2 and includes 52 sampling sites in a sampling grid of 2 $\times$ 2 km and 1 $\times$ 1 km in the urban zone and around the thermoelectric power plant. The surface samples were collected and analysed for 18 elements using the ICP-AES technique.

The spatial distribution of some PTEs (Pb, Zn, and Cd) shows some trends indicating a local anthropogenic origin. The river transport processes from the iron mine "Tajmište" affected the distribution of Pb, while the distribution of Zn was influenced by the operation of the metal industry. Their average levels are 3–4-times higher compared to the European average, which indicates their anthropogenic origin.

Along the Zajaska and Oslomej rivers, the average Cd levels are up to 50% higher than the background levels. The surrounding Palaeozoic rocks are naturally enriched with these chemicals, but the anthropogenic origin is more significant. The average background levels for Pb (64 mg/kg Pb) are about three-times lower compared to those along the Zajaska River (170 mg/kg) or near the coal mine (200 mg/kg Pb), which are above the target values of the New Dutch List [145].

The distribution of Zn is similar to that of Pb. Thus, the average background content of Zn is 94 mg/kg but 320 mg/kg in the urban area of Kičevo, which exceeds the target values and, in some samples, the intervention values of the New Dutch List [145]. This also indicates an anthropogenic influence, mainly due to the processing industry in Kičevo.

4.2.5. Elemental Distribution in Soil from the City of Skopje [117,118]

Skopje is the capital and the largest city of North Macedonia, with a total population of 550,000 people. It is the political, cultural, economic and academic centre of the country. The Skopje region, which includes the city of Skopje and some smaller neighbouring municipalities, accounts for 45.5% of North Macedonia's GDP. The city's industry is dominated by food processing, textiles, printing and metal processing, including steel production.

The surface samples (0–10 cm) from 231 sampling sites were collected in order to assess the origin and distribution of elements in Skopje. All samples were analysed for 18 elements by ICP-AES and for 47 elements by ICP-MS in two different laboratories.

The results show that the distribution of macro-elements is influenced by the geological formations: Quaternary alluvial deposits, Quaternary marsh deposits and younger Quaternary river terraces, Pliocene and Mesozoic sediments, and Paleozoic rocks. A comparative analysis was carried out between the analysed elements in the soils of North Macedonia [28] and Europe [13]. The spatial distributions of most elements correspond to the lithogenic origin of the rocks.

The levels of Al, Ca and Mg are slightly increased compared to the national average values. The increased levels of Cr and Ni are found in the Vardar zone. Based on the results of the multivariate statistical analyses, several geochemical associations were clustered: Al-Ba-K-Na, Cr-Fe-Mg-Ni, Cd-Cu-Zn and Ca-Sr.

Depending on the land use, higher element contents are found in agricultural and urban areas (Figure 10A). The higher levels of Al-Ba-K-Na (Figure 10A) in samples from the southeastern to the northeastern part of the study area are influenced by the swamp sediments and young and old Quaternary terraces. Higher levels of Cr-Fe-Mg-Ni (Figure 10B) occur in the western and northwestern parts of the city, where sediments from the Pliocene, younger and older Quaternary sediments, and Miocene sediments predominate.

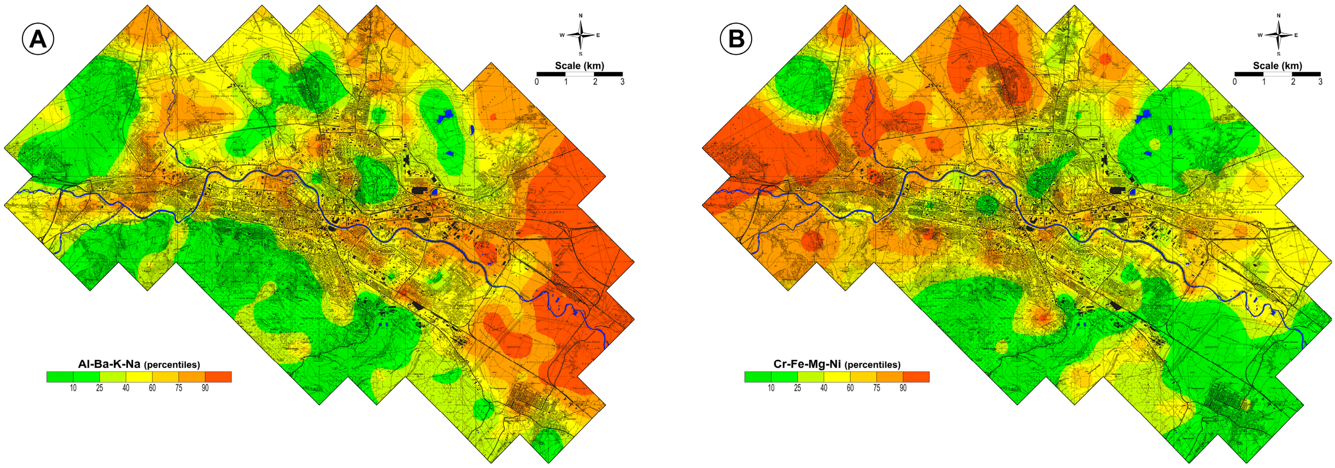

Figure 10. Spatial distribution of geochemical associations in the city of Skopje: (**A**) Al-Ba-K-Na; (**B**) Cr-Fe-Mg-Ni [118].

The soils in the east and north of Skopje, which are mostly covered with Quaternary swamp sediments and young Quaternary sediments, have higher levels of Cd, Cu and Zn, which shows both a lithogenic and anthropogenic origin. The highest levels are found in the industrial area of the city, most likely due to contamination from steel mills (Figure 11A). The last association includes Ca-Sr (Figure 11B), which shows a solely geogenic origin. Its levels are connected to Pliocene sediments, Quaternary young and older river terraces, and Miocene and Quaternary swamp sediments in the south and southeast of the study area.

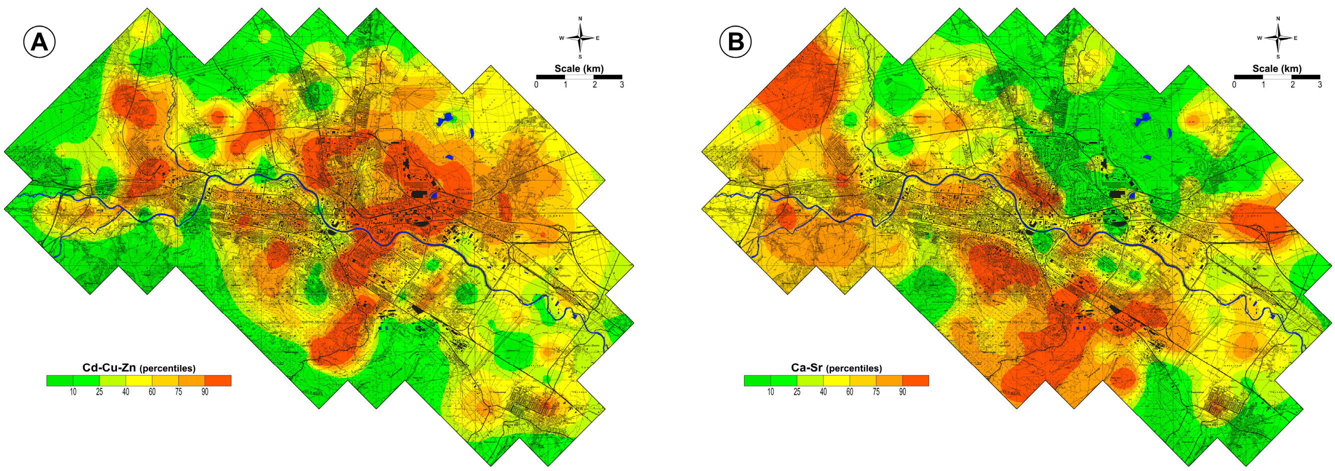

Figure 11. Spatial distribution of geochemical associations in the city of Skopje: (**A**) Cd-Cu-Zn; (**B**) Ca-Sr [118].

In addition to the elements shown on the distribution maps, the average levels of As (14 mg/kg) and Pb (100 mg/kg) are determined in the study area. The range for As extends from 0.05 mg/kg up to 68 mg/kg. The highest levels are only found at a few isolated sites in the urban zone, but in general, the average values are below the target value according to Dutch standards [115]. The Pb ranges from 5.0 mg/kg to 2900 mg/kg, with the highest levels indicating an anthropogenic origin due to metal processing activities.

4.2.6. Sb-As-Tl Allchar Mine [87]

The Allchar locality is a rare outcrop of As-Sb-Tl mineralisation, on the Kožuf Mountains. The locality of Allchar is unique in its mineral composition, with a total of 45 different minerals [146,147]. In addition to As, Sb and Tl, the other elements of economic interest present are Au, Hg, Ba, as well as traces of Pb, Zn and Cu. It has been confirmed that the Allchar deposit contains economic grades of Tl (0.1%–0.5%), Sb (up to 2.5%), As (1.5%) and Au (>1 g/t) [148]. The mine was active until 1912 and produced arsenic and antimony concentrates.

The entire study area (approx. 13 km^2) was covered by 67 sites, where samples from topsoil (0–5 cm) and subsoil (20–30 cm) were collected and analysed for 67 elements using ICP-MS and ICP-AES.

The main focus was to study the behaviour of As, Sb and Tl (Figure 12) to distinguish between natural enrichment and human impact due to the following: (i) the effects of past volcanism, (ii) mineralisation and (iii) past mining activities.

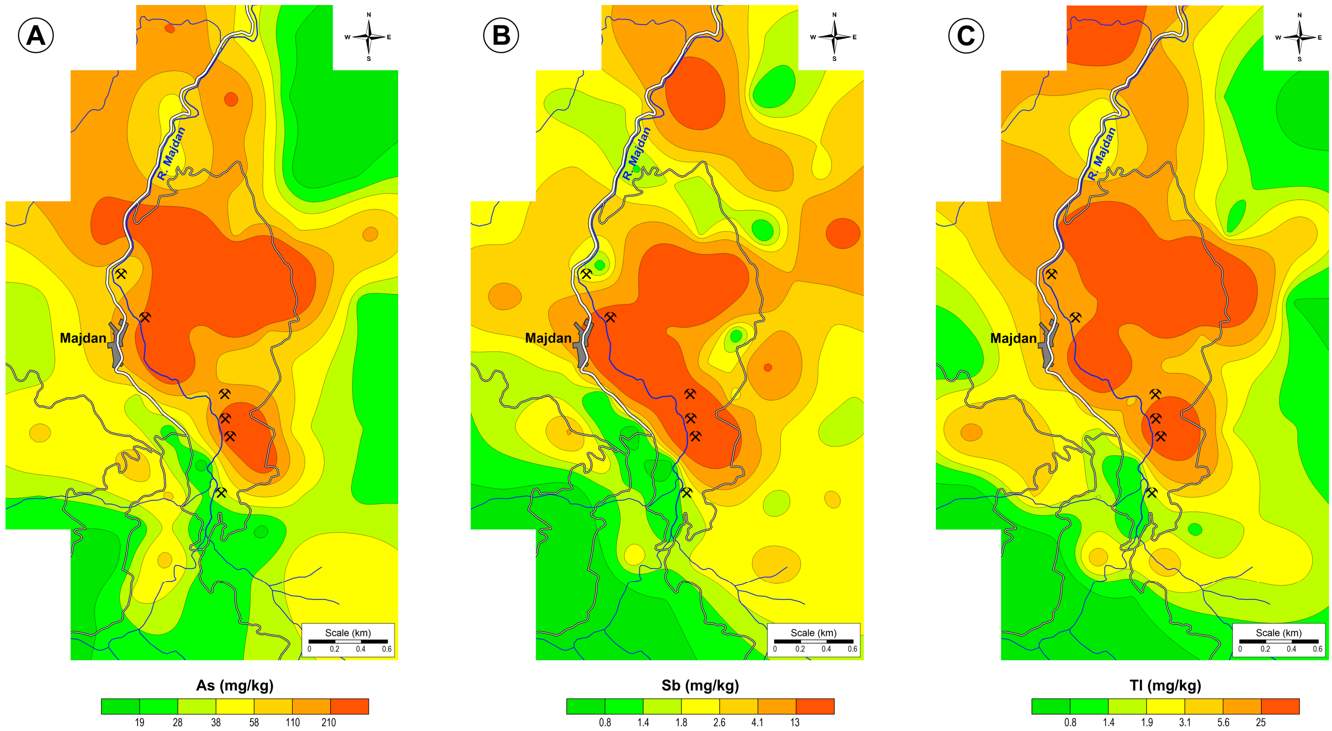

Figure 12. Spatial distribution in Allchar deposit area: (**A**) arsenic; (**B**) antimony; (**C**) thallium.

The As levels in the vicinity of the Allchar mine exceed both the action (55 mg/kg) and the target values (29 mg/kg) according to the New Dutch List and are 90-times higher than the European average. Similar trends with extremely high levels are identified for Sb and Tl. The enrichment ratio of Sb (between 0.24 and 3200 mg/kg) exceeds the European average by 20-times and that for Tl more than 260-times compared to the rest of the Allchar area. All three elements are strongly dependent on the lithology.

4.3. Application of Artificial Neural Networks (ANN-MP) in Geochemical Investigations, North Macedonia [67,149,150]

The Artificial Neural Network–Multilayer Perceptron (ANN-MLP) was used to improve the reconstruction of the main distribution pathways, assess the real size of the affected area and improve the interpretation of the data at two selected sites. This advanced predictive modelling technique combined soil measurements with data from DEM, land cover data and remote sensing developed by Alijagić [149,150].

ANNs represent a method of artificial intelligence based on an analogy of the human brain. Artificial neural networks simulate biological neural networks, whereby the function of a neural network is determined by a model of highly interconnected neurons, a network structure and a learning algorithm. The ANN method can be used to solve specific problems, like pattern recognition and data classification [149,151,152].

The multilayer perceptron (MLP) is the most commonly used ANN, especially in environmental studies. This method can be used for tasks such as feature matching and pattern recognition problems. In addition, MLP can be used to prove the classification of linear, inseparable patterns. MLP represents feedforward neural networks (FNNs), with multiple layers of units between the input and output layers [150]. Compared to other commercial and freely available software packages that allow users to implement neural networks relatively easily by offering only a limited number of training algorithms, the MLP offers an unlimited number of algorithms to achieve better results [153].

The main objective of this section is to compare and improve spatial distribution models for small-scale As-Sb-Tl geochemical associations (Figure 13) and the spatial distribution of Pb at macro-regional-scale (Figure 14) test sites in soil, comparing two methods, universal kriging and artificial intelligence (ANN-MLP). Two river basins in the eastern part of North Macedonia were selected as the main study area, as the anthropogenic impact of long-term mining activities is particularly significant here, and the area is also morphologically and geologically complex.

The comparative data outputs led to the general conclusion that ANN-MPL provides more realistic, reliable and comprehensive results than the universal kriging method. The construction of geochemical maps using the kriging method is much simpler, but the results are not representative, mainly due to errors known as the "Bull's eye" effect, as elongated partitioning occurs in isotropic space. This could possibly be solved by increasing the number of sampling sites or using a denser sampling grid.

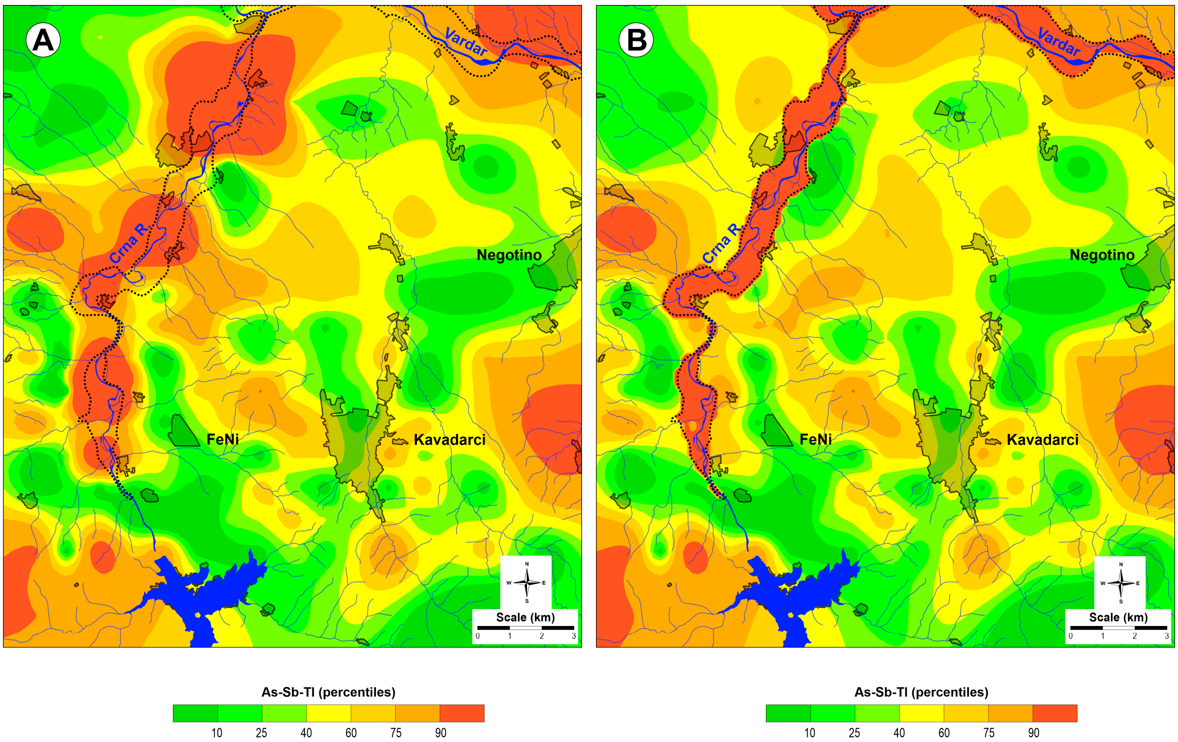

Figure 13. Distribution of geochemical associations: As-Sb-Tl in Kavadarci area (**A**) after application of universal kriging; (**B**) after application of ANN-MLP (The dotted lines means a border of alluvial plains).

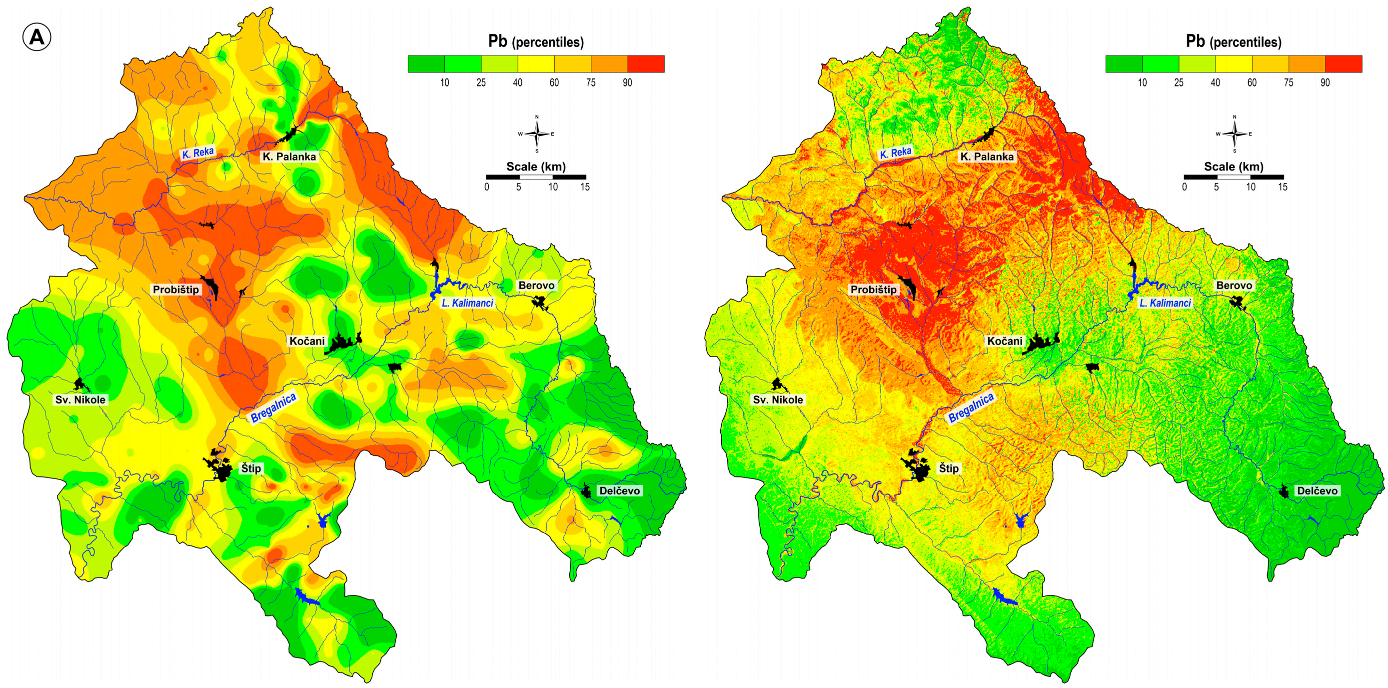

Figure 14. Distribution of Pb in Bregalnica–Kriva Reka area: (**A**) after application of universal kriging; (**B**) after application of ANN-MLP [67].

5. Conclusions

This is a review article about the long-term successful cooperation between the Geological Survey of Slovenia and the Faculty of Natural Sciences in Skopje, Ss. Cyril and Methodius University in Skopje but also some other institutions from Russia, the Joint Institute for Nuclear Research in Dubna, Moscow Region, Russia, and the Romanian Research Institute for Analytical Instrumentation (ICIA). The main contribution comes from the voluntary and enthusiastic work of Prof. Trajče Stafilov's group and his PhD and Master's students.

In less than two decades (2007–2023) of fruitful collaboration, a large number of scientific papers have been published: 8 geochemical atlases (Veles, Kavadarci, Kičevo, Radoviš, Bregalnica River Basin, Pelagonia Valley, Skopje, North Macedonia); 23 chapters in monographs; 188 scientific publications; 12 invited lectures; and 100 conference presentations. This tremendous work was recognised with two state awards from the Government of the Republic of Macedonia "Goce Delčev" for scientific achievements in 2009 and 2016.

In all considered case studies, the obtained data were processed with multivariate statistical methods (such as HCA, FA and PCA), but for the creation of predictive maps, universal kriging methods were applied. To improve the reconstruction of the main distribution pathways, estimate the real size of the affected area and improve data interpretation at the two selected sites, the artificial neural network–multilayer perceptron (ANN-MLP) was successfully applied. This advanced predictive modelling technique combined soil measurements with data obtained from DEM, land cover data and remote sensing.

For the creation of the Geochemical Atlas, the territory of North Macedonia was covered, with a sampling grid of 5 × 5 km, but a much denser sampling grid was used in all other 16 selected studies. However, the total sum of all collected soil samples amounts to 3983 from 2449 different sampling sites in the period from 2006 to 2017. The soil samples were mainly collected from two depths (0–5 cm and 20–30 cm). The methods of soil sampling are very comparable according to the European guidelines, often the same or do not consider different soil layers. In Bitola, Bregalnica, Tobacco Fields, composite samples from 0 to 30 cm were taken, and in Kičevo, Skopje and Veles, only topsoil (0–5 cm) was taken.

The analyses were performed at the Institute of Chemistry of the Faculty of Natural Sciences in Skopje, Ss. Cyril and Methodius University in Skopje, North Macedonia, at the Research Institute for Analytical Instrumentation (ICIA), Cluj-Napoca, Romania, at the Joint Institute for Nuclear Research in Dubna, Moscow Region, Russia, and at Acme Labs, Vancouver, Canada. The sum of all analysed soil samples in all four mentioned laboratories is 7991 in the period from 2006 to 2017.

It is important to emphasise that the aforementioned scientific work has been financially supported by government agencies but is the result of personal keenness, enthusiasm and volunteer work.

Author Contributions: Conceptualization, T.S. and R.Š.; methodology, T.S. and R.Š.; software, R.Š.; validation, R.Š.; resources, T.S. and R.Š.; writing—original draft preparation, T.S., R.Š. and J.A.; writing—review and editing, T.S., R.Š. and J.A. All authors have read and agreed to the published version of the manuscript.

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