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Original scientific paper

SPATIAL DISTRIBUTION OF THALLIUM IN THE SOILS OF NORTH MACEDONIA

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A b s t r a c t: The aim of the study was to determine the spatial distribution and assessment of thallium contamination in the soils of North Macedonia. Topsoil samples (0–30 cm) were collected from 995 locations throughout the country in a grid of 5×5 km between sampling points. The soil samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) using the total digestion method. The distribution of thallium in the soils according to the eight statistical regions of the country is discussed, as well as the distribution based on the 15 most common geological formations and the distribution based on 13 pedological units. The thallium content varied in Macedonian soils from <0.05 to 15.5 mg/kg (median 0.70 mg/kg), which corresponds to the total Tl content for the European soils with a range of 0.01 to 21.3 mg/kg and a median of 0.66 mg/kg. The spatial distribution patterns of Tl in the collected soil samples are mainly determined by the geology (parent material and mineralization). In some areas, the natural anomaly pattern is overlaid by anthropogenic emissions from past and present mining, ore processing and associated metal industries.

Key words: thallium; soil; spatial distribution; North Macedonia

INTRODUCTION

Thallium (atomic number 81) is a rare trace element, a metal, and it is the 61st most abundant element in the upper continental crust with an estimated abundance of 0.55 mg/kg (Hu & Gao, 2008). The average Tl content in European topsoil is 0.66 mg/kg (Salminen et al., 2005), while the average content in arable and pasture soils is 0.12 mg/kg (Reimann et al., 2014). Thallium occurs in two oxidation states (I and III), with Tl^{+} being more stable than Tl^{3+} (Chang & Chiang, 2024). Thallium occurs mainly in sulfide minerals associated with low temperature hydrothermal mineralization. A total of 89 thallium minerals are known (Zhao & Gu, 2021), of which crookesite [$(Cu,Tl,Ag)_2Se$)] and lorandite ($TlAsS_2$) are two of the generally very rare Tl minerals. However, thallium can replace K in several common rock-forming minerals, such as K-feldspar and mica (up to several hundred mg/kg). Thallium is also present in pyrite and is extracted during the roasting of this ore in connection with the production of sulfuric acid. It should be mentioned that one of the largest deposits of thallium mineralization is found in the Allchar mine in North Macedonia, where 13 different thallium minerals occur: lorandite – $TlAsS_2$, bernardite – $Tl(As,Sb)_5S_8$, fangite – Tl_3AsS_4, parapierrotite – $Tl(Sb,As)_5S_8$, picotpaulite – $TlFe_2S_3$, raguinite – $TlFeS_2$, weissbergite – $TlSbS_2$, vrbaite – $Tl_4Hg_3As_8Sb_2S_{20}$, dorallcharite – $(Tl,K)Fe_3(SO_4)_2(OH)_6$, and four thallium minerals found only in this mine: jankovićite – $Tl_5Sb_9(As,Sb)_4S_{22}$, rebulite – $Tl_5Sb_5As_8S_{22}$, simonite – $TlHgAs_3S_6$ and thalliumpharmacosiderite – $TlFe_4(AsO_4)_3(OH)_4{\cdot}4H_2O$ (Boev et al., 2001–2002; Jovanovski et al., 2018).

Thallium is more enriched in felsic rocks (about 1 mg/kg) than in mafic and ultramafic rocks (less than 0.1 mg/kg). The content in sedimentary rock is very low (0.05 mg/kg in limestone). The highest contents are found in shale and schist (about 1 mg/kg) and coal (3 mg/kg). The mobility of thallium is limited as it is precipitated together with Fe and Mn oxyhydroxides and binds strongly to organic material and clay (Reimann et al., 2014). Thallium is present in lead and zinc mineralizations and is usually recovered as a metal during the smelting of lead and zinc ores (Vaněk et al., 2009; Reimann et al., 2014).

Thallium is naturally present in the environment, especially in its terrestrial elements, although usually in low concentrations. The enrichment of certain niches with thallium-containing compounds is a direct consequence of a specific transport pattern. Emissions leading to increased thallium concentrations in the environment can be natural or related to anthropogenic activities (Pavlíčková et al., 2006; Karbowska, 2016; Belzile & Chen, 2017).

Thallium was once frequently used as a rat poison and ant killer. Today, it is mainly used in the electronics industry (60–70% of global production is used in this way), in glass production, for a variety of alloys and in the pharmaceutical industry. The electrical conductivity of thallium sulfide changes when irradiated with infrared light and this compound is used in photocells. Thallium bromide-iodide crystals are used as optical infrared materials. Thallium is used together with sulfur or selenium and arsenic to produce glasses with a low melting point. Thallium oxide is used to produce glasses with a high refractive index. A mercury-thallium alloy that forms a eutectic at 8.5% thallium is reported to freeze at –60ºC, about 20 degrees below the freezing point of mercury.

Thallium can enter the environment through coal combustion, waste incineration, oil refining and Pb, Zn and Cu smelters. In the past, cement factories were a major emitter of thallium. Thallium is not considered essential to life and is highly toxic. It is probably the least studied highly toxic element. It has also been found that some plants are good hyperaccumulators of thallium (Bačeva et al., 2014a, 2015, 2024).

Thallium is highly toxic, regardless of the route of exposure, and is considered one of the most harmful metals to mammals. Occupational exposure to Tl-containing dust or fumes causes symptoms such as nausea, abdominal pain and loss of appetite, followed by hair loss all over the body, abnormal nail growth, neurotoxicity (hand tremors, foot numbness, depression and behavioral changes), optic nerve damage leading to visual disturbances, tachycardia and cardiac arrhythmias, and respiratory problems often leading to death. Tl poisoning also affects other aspects of health, including fertility in women and men exposed to the substance in the workplace (Kazantzis, 2000; Peter & Viraraghavan, 2005; Rodriguez-Mercado & Altamirano-Lozano, 2013).

In humans, increased thallium intake can lead to adverse effects on kidney health, hypertension, psychological, metabolic and other effects, mitochondrial-mediated oxidative stress, cellular toxicity through induction of endoplasmic reticulum stress, or thallium can induce genetic toxicity or abnormal attenuation of immune cells (Chang, & Chiang, 2024). Thallium-induced systemic toxicity can affect cell metabolism, including redox changes, mitochondrial dysfunction, and activation of apoptotic signaling pathways. Recent studies also show that Tl toxicity may be responsible for cytogenetic damage, mutations and epigenetic changes, i.e., negative effects on DNA (Sánchez-Chapul et al., 2023).

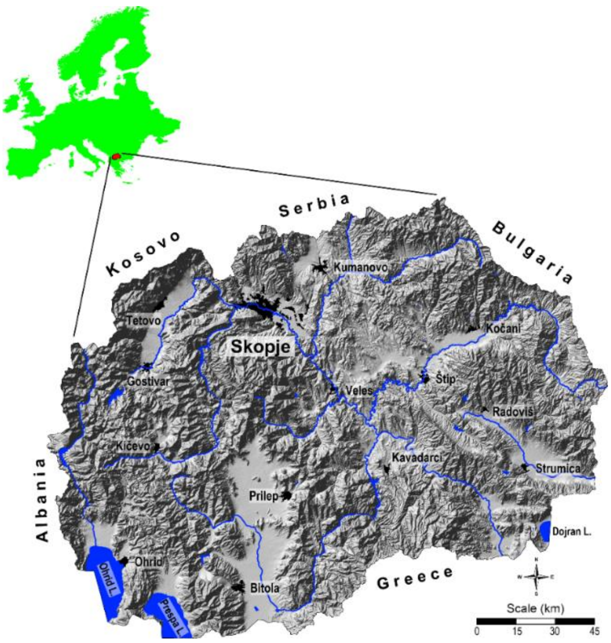
Several mechanisms and modes of action have been proposed to explain the high toxicity of Tl. Tl3+ has a strong oxidizing ability and is slowly converted to Tl+, which is more stable. Both ionic species of Tl enhance the production of reactive oxygen species in cells. The toxicity of Tl may also be due to its chemical properties, which are similar to those of potassium. TI+ can compete with and replace potassium, thereby altering the enzymatic activation of Na+/K+ ATPases, pyruvate kinase, fructose 1-6-bisphosphatase and other proteins that are dependent on metal ions (Rodriguez-Mercado & Altamirano-Lozano, 2013).

The aim of this work is to monitor and determine the distribution of thallium in soils from the entire area of North Macedonia. Topsoil samples (0–30 cm) were collected from 995 sites in the studied region. The thallium content was analyzed using inductively coupled plasma mass spectrometry (ICP-MS). All data on thallium content were statistically analyzed and a distribution map was created from the results. The spatial distribution of thallium in surface soils from the area of North Macedonia and the distribution according to statistical regions, geological formations and pedological units are discussed.

MATERIAL AND METHODS

Study area

North Macedonia is a landlocked country in the central part of the Balkan Peninsula and lies between 40º50´ and 42º20´ north latitude and between 20º28´ and 23º05´ east longitude (Figure 1). North Macedonia covers an area of 25,436 km^2. It has a total population of 1,837,000 inhabitants (2021 census). Macedonia is geographically defined by a central valley formed by the Vardar river and framed by mountain ranges. Macedonia is rich in minerals, with significant deposits of chromium and other non-ferrous metals (Cu, Pb, Zn, Ni, and Mn). The country also has gypsum, marble and granite mines, while lignite provides 80% of Macedonia's electricity (Stafilov & Šajn, 2016). Macedonia is divided into eight statistical regions: Skopje, Pelagonia, Polog, Vardar, Eastern, Southeastern, Northeastern, and Southwestern.



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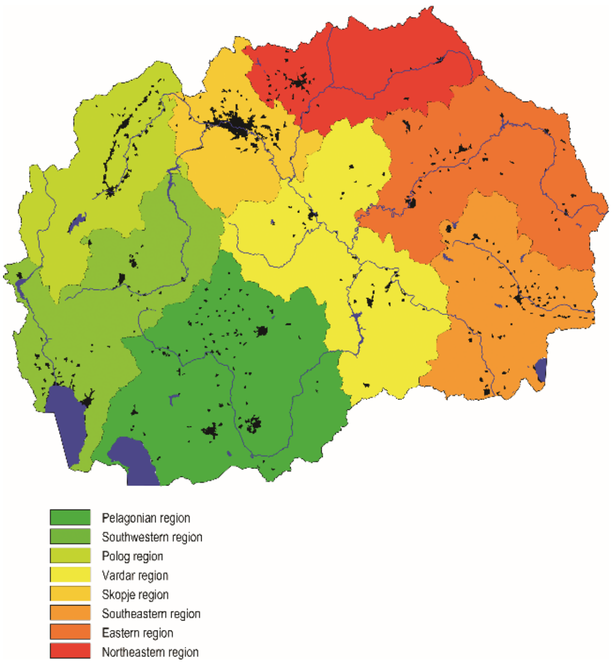

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Fig. 1. Topographic map
(a) Map of statistical regions. (b) North Macedonia

Geological characteristics

The main geological and tectonic features of North Macedonia are described in detail by Stafilov & Šajn (2016, 2019) and Petrušev et al. (2021) based on the earlier studies by Pendžerkovski (1976), Pendžerkovski and Hadži-Mitrova (1977), Dumurdžanov et al. (2004, 2005) and Arsovski (1997). From a tectonic point of view, Macedonia comprises six major tectonic units: the Vardar zone (VZ) in the central region, the Pelagonian massif (PM), the West-Macedonian zone (WMZ), and a small part of the Čukali-Krasta zone (CKZ) in the west, and the Serbo-Macedonian massif (SMM) and the Kraishtide zone (KZ) in the east of the country (Figure 2).

The Čukali-Krasta zone consists of Upper Cretaceous conglomerates – sandstones, claystones, and limestones with olistostromes and rudist limestones. Evaporites and smaller Paleogene sediments are present in this zone. Very important in this zone is the diapiric structure of Mount Dešat, which consists of anhydrite and gypsum. The West-Macedonian zone consists of low-grade metamorphic rocks and anchi-metamorphic Paleozoic rocks and magmatites, Triassic and Jurassic sediments and magmatites, and Tertiary sediments. The Pelagonian massif consists of Proterozoic crystalline mass, with pronounced domes, brachy and open folds. Lithologically, it consists of highly metamorphic rocks and granitoids. The marble formation represents the upper part of the Proterozoic metamorphic complex. The Vardar zone is characterized by the presence of crystal blocks of the Kozjak and Kožuf mountains, the Serta Gradeški Mt. and the Bučim block, as well as Paleozoic low-metamorphic rocks, Triassic continental sediments, Jurassic ophiolites and ultrabasites, and Cretaceous sediments, all of which are divided into many shells that intrude SW and W into Eocene-Oligocene sediments and volcanites.

The main mass of the Serbo-Macedonian massif (SMM) consists of Lower or overthrusting Proterozoic and Upper Riphean-Cambrian complexes, as well as a relicts of Lower Paleozoic schists and intrusions of Hercynian granitoids. In the northeast there are numerous cliffs of Triassic sediments as well as small masses of Eocene-Oligocene sediments and Oligo-Miocene volcanic rocks. The Kraishtide zone (KZ) represents the increased occurrence of metagabbros, metadiabases, and green metasandstones floating in Hercynian aplitic granitoids.

The territory of Macedonia is covered by the following 15 main geological units listed in Figure

2: Quaternary alluvium (10.1%), Quaternary deluvium/proluvium (8.3%), Neogene clastites (9.7%), Paleogene clastites (5.0%), Mesozoic clastites (4.1%), Mesozoic carbonates (5.2%), Paleozoic carbonates (3.0%), Proterozoic carbonates (3.6%), Paleozoic metamorphic rocks (14.1%), metamorphic rocks of the Pelagonian massif (8.5%), metamorphic rocks of the Serbo-Macedonian massif (11.6%), Neogene magmatic rocks (5.6%), Paleogene magmatic rocks (0.4%), Mesozoic magmatic rocks (4.8%) and Paleozoic magmatic rocks (5.3%).

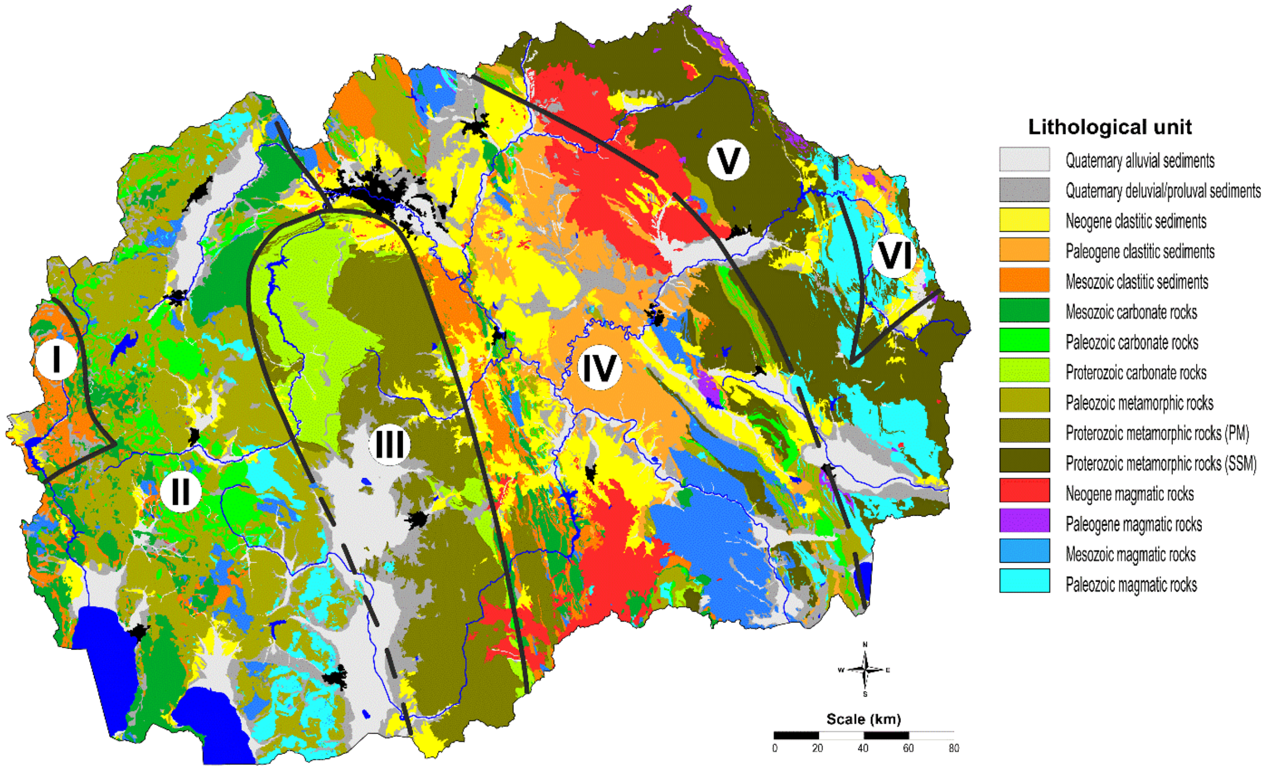

Fig. 2. Simplified geological map of North Macedonia.
Tectonic units: I – Čukali-Krasta zone (CKZ), II – West-Macedonian zone (WMZ), III – Pelagonian massif (PM), IV – Vardar zone (VZ), V – Serbo-Macedonian massif (SMM), VI – Kraishtide zone (KZ).

Pedology

In 2015, the development of the Pedological map of North Macedonia was completed (Filipovski et al., 2015), which was produced in digital (www.msksoil.ukim/mk/masis) and printed form (1:50,000) with appropriate interpretation, and a general pedological map of North Macedonia was produced at a scale of 1 : 200,000, which also contains an interpretation. The soils in North Macedonia are very heterogeneous and vary greatly over small distances. The following soil types were defined: lithosols, regosols, arenosols, colluvial soils, rendzinas on hard limestones and dolomites, rendzinas, rankers, vertisols, chernozems, chromic cambisols, red soils (terra rossa), brown soils on limestones and dolomites, brown forest soils, illimerised soils, brown podzolic soils, alluvial soils, fluviatile meadow soils, hydromorphic black soils, gleyic soils, peat soils (histosols), pseudogleys, solonchaks and solonetz (Mitkova & Mitrikeski, 2005).

Soil sampling and analysis

The study includes the determination of the thallium content in the topsoil (0–30 cm). The soil samples were collected between 2012 and 2014 at 995 locations (Figure 3) within networks with a density of 5×5 km (Stafilov & Šajn, 2016; Stafilov et al., 2024). The soil samples were collected according to the relevant standards (Reimann et al., 2012). The soil samples brought to the laboratory were cleaned of plant material and stones, homogenized and dried at room temperature. They were then passed through a 2 mm sieve and ground in a porcelain mortar until they reached a final particle size of 125 µm.

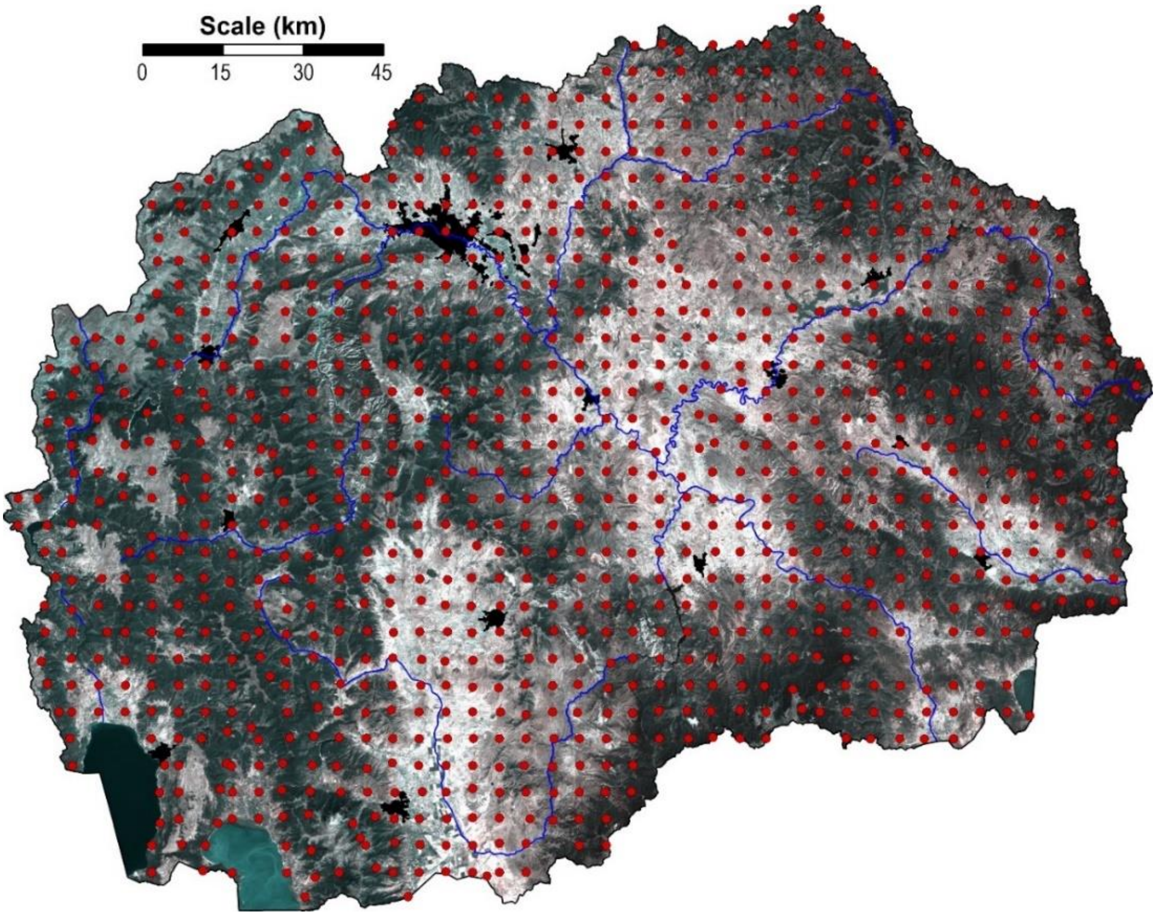

Fig. 3. Locations for soil sampling in the territory of North Macedonia

All soil samples collected were sent to the accredited laboratory ACME Ltd. in Vancouver, Canada. After a complete digestion of the samples (Multi Acid – ICP-ES/MS, Method MA200), the thallium was analyzed using the ICP-MS method. The detection limit for the thallium content of the method was 0.05 mg/kg. Precision was tested using the relative differences between pairs of analytical determinations of the same sample. Thirteen selected samples were replicated for estimation of precision of 9.65%. Estimation of the trueness and precision of two analyzed data sets was performed using the *t*-test. The value of 0.12 at $p < 0.05$ indicates that the difference between the means of the two groups is not statistically significant.

All data processing and calculations, geostatistical data interpretation and visualization (mapping) were performed using the following software programs: Statistica (Stat Soft Inc.), Autodesk MAP 3D (Autodesk Inc.), QGIS (Open Source Geographic Information System), and Surfer (Golden Software Inc.).

RESULTS AND DISCUSSION

The basic statistical data on the thallium content in the topsoil of North Macedonia are presented in Table 1. The mean thallium content in the topsoil of North Macedonia is 0.61 mg/kg, which is below the European mean of 0.82 mg/kg in topsoil. The median thallium content in North Macedonia is 0.70 mg/kg. In some areas of the country, the thallium content was very low (<0.05 mg/kg), while in other areas it was 26 times higher than the mean value (15.5 mg/kg). The mean and median values are below the target value of 1.0 mg/kg according to The Netherlands Environmental Protection Agency's target values, indicative levels for serious soil contamination and background concentrations soil/ sediment (VROM, 2010). In certain areas of the country, however, the content is well above the target value and in some smaller areas even above the guideline value for serious contamination of 15 mg/kg.

T a b l e 1

Descriptive statistics of the analysis of thallium in the topsoil of North Macedonia

Parameter	Value (mg/kg)
Detection limit	0.05
Number of sampling locations	995
Arithmetic average (mean)	**0.77**
Geometrical mean	0.62
Box-Cox transformed average	0.61
Arithmetic standard deviation	0.86
Geometric standard deviation	0.027
Coefficient of variation	112
Minimum	**<0.05**
P_{10} – 10th percentile	0.25
P_{25} – 25th percentile	0.5
Median	**0.7**
P_{75} – 75th percentile	0.9
P_{90} – 90th percentile	1.2
Maximum	**15.5**
Skewness	11.63
Kurtosis	181.84
Box-Cox transformed skewness	–0.01
Box-Cox transformed kurtosis	0.39

The comparison of the obtained basic statistical data (0.77 mg/kg mean, 0.70 mg/kg median, 0.05 mg/kg minimum and 15.5 mg/kg maximum) for the abundance of thallium in soils from North Macedonia (Table 2) shows that they are very similar to those for surface soils in Europe (0.828 mg/kg mean, 0.66 mg/kg median, 0.01 mg/kg minimum and 21.3 mg/kg maximum), and the mean value for the upper continental crust (0.9 mg/kg).

The basic statistical data (mean, median, minimum and maximum) of thallium content in soils by country regions (Table 3, Figure 4) showed higher median values (0.80 mg/kg) in the western part of the country (Pelagonian and Southwestern regions), while in the other regions the median content of 0.60 mg/kg was lower than the median value for the whole territory of Macedonia. The only exception is the Northeastern region, where the median value corresponds to the median value for soils at national level (0.70 mg/kg). The elevated thallium contents in these three regions are mainly due to the presence of Neogene magmatic rocks and Mesozoic carbonates, which have relatively high Tl contents compared to other geological formations.

T a b l e 2

Comparison of data on thallium content in soils of North Macedonia, Europe and the world

Thallium	North Macedonia (This work)	Europe, topsoil (Salminen et al., 2005)	World (upper continental crust) (Rudnick & Gao 2014)
Average	0.77	0.828	0.9
Median	0.70	0.66	
Minimum	< 0.05	0.01	
Maximum	15.50	21.3	

T a b l e 3

Mean, median, minimum, and maximum Tl content by statistical regions in North Macedonia

Region	Number of samples	Mean	Median	Minimum	Maximum
Pelagonian	192	0.74	0.80	<0.50	2.2
Southwestern	135	0.72	0.80	<0.50	3.0
Polog	96	0.57	0.60	<0.50	15
Vardar	162	0.56	0.60	<0.50	15
Skopje	72	0.54	0.60	<0.50	2.7
Southeastern	105	0.50	0.60	<0.50	1.5
Eastern	141	0.59	0.60	<0.50	10
Northeastern	92	0.59	0.70	<0.50	3.4

According to the geological formations (Table 4, Figure 4), the highest median thallium contents (1.0 mg/kg) were found in the soils in the area where Neogene magmatic rocks occur mainly in the southern and northeastern parts of the Vardar geotectonic zone and in the part of the Serbo-Macedonian massif zone, as well as in the small areas with Paleogene magmatic rocks in the West-Macedonian zone and in the Serbo-Macedonian massif.

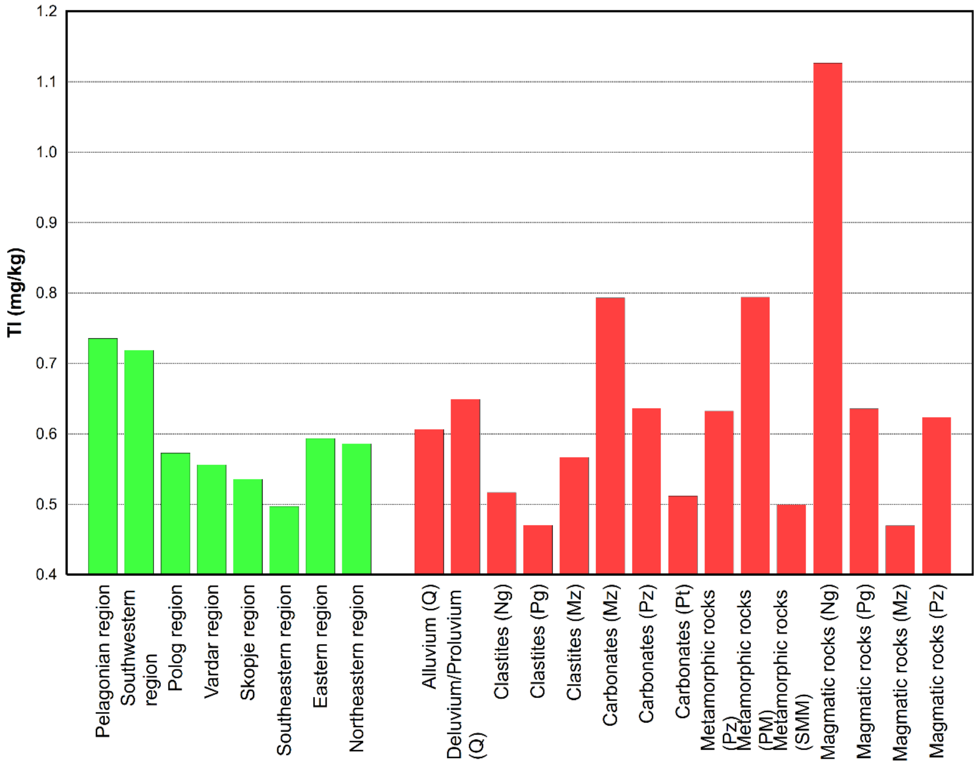

Fig. 4. Mean values of thallium content according to statistical regions and geological formations

T a b l e 4

Mean, median, minimum and maximum thallium content according to main geological formation

Geology	Number of samples	Mean	Median	Minimum	Maximum
Alluvium (Q)	114	0.61	0.70	<0.50	2.8
Deluvium (Q)	80	0.65	0.70	<0.50	3.5
Clastites (Ng)	95	0.52	0.60	<0.50	15
Clastites (Pg)	60	0.47	0.60	<0.50	1.3
Clastites (Mz)	40	0.57	0.65	<0.50	1.3
Carbonates (Mz)	43	0.79	0.90	<0.50	3.8
Carbonates (Pz)	52	0.64	0.70	<0.50	2.2
Carbonates (Pt)	32	0.51	0.60	<0.50	1.9
Metamorphic rocks (Pz)	120	0.63	0.80	<0.50	1.6
Metamorphic rocks (PM)	84	0.79	0.80	<0.50	3.0
Metamorphic rocks (SMM)	115	0.50	0.60	<0.50	2.5
Magmatic rocks (Ng)	50	1.1	1.0	<0.50	15
Magmatic rocks (Pg)	7	0.64	1.0	<0.50	1.4
Magmatic rocks (Mz)	51	0.47	0.60	<0.50	1.3
Magmatic rocks (Pz)	52	0.62	0.70	<0.50	10

Q – Quaternary, Ng – Neogene, Pg – Paleogene, Mz – Mesozoic, Pt – Proterozoic, PM – Pelagonian massif, SMM – Serbo-Macedonian massif, Pz – Paleozoic

A slightly elevated median Tl content (0.90 mg/kg) was also found in the areas where Mesozoic carbonates and Paleozoic metamorphic rocks of the West-Macedonian zone (0.80 mg/kg) and metamorphic rocks in the Pelagonian massif (0.80 mg/kg) occur. The spatial distribution shows a pattern with lower values (0.60 mg/kg) in regions with clastites (Mesozoic clastites dominate in the Vardar and Kraishtide zones and Neogene and Paleogene clastites dominate in the Vardar zone. The same median value (0.60 mg/kg) is also found in the soils in the areas of the Serbo-Macedonian massif, where metamorphic rocks predominate, as well as in the area where Mesozoic magmatic rocks of the Vardar zone predominate.

According to the pedological units (Table 5), hydromorphic soils (mean content of 0.87 mg/kg), which occur in the valleys of the main rivers of the country, and lithosols on limestone-dolomite-chernozem (0.71 mg/kg), which predominate in the western part of the country, were the richest in thallium. Average thallium levels were very similar regardless of land use, ranging from 0.53 mg/kg in artificial surfaces to 0.65 mg/kg in the soils of forested areas.

Table 5

Mean, median, minimum, and maximum thallium content according to the main pedological units in North Macedonia

Pedological unit	Number of samples	Mean	Median	Minimum	Maximum
Lithosol	57	0.64	0.70	<0.50	1.4
Lithosol (C)	38	0.71	0.80	<0.50	3.8
Regosol	69	0.61	0.70	<0.50	5.5
Colluvial soil	55	0.62	0.70	<0.50	15
Rendzina	72	0.50	0.50	<0.50	1.3
Ranker	72	0.61	0.70	<0.50	10
Vertisol	319	0.60	0.70	<0.50	2.8
Cambisol (H)	99	0.55	0.60	<0.50	2.3
Cambisol (M)	80	0.64	0.70	<0.50	15
Cambisol (C)	15	0.56	0.70	<0.50	3.0
Fluvisol	93	0.61	0.70	<0.50	1.4
Hydromorphic soil	21	0.87	0.90	0.50	1.4
Anthroposol	5	0.50	<0.50	<0.50	0.80

Lithosol (C) – lithosols on limestone-dolomite chernozems; Cambisol (H) – cambisols mostly cinnamomic forest soil; Cambisol (M) – cambisols mostly brown forest soil; Cambisol (C) – cambisols mostly brown soils on limestones and dolomites

The spatial distribution of the thallium content in the soil throughout the country is shown in Figure 5. In general, the spatial distribution patterns of Tl in the collected soil samples are mainly governed by the geology (parent material and mineralization). In some areas, the natural anomaly pattern is overlaid by anthropogenic emissions from past mining, ore processing and associated metal industries.

High thallium levels (4.2–15 mg/kg) were found mainly in soils in the area where Neogene and Paleozoic igneous rocks and Neogene clastites occur in the Polog, Vardar and Eastern regions. The highest thallium content of 15.5 mg/kg was found in a soil sample from Jegunovce in the Polog region, which is located in the area of Neogene clastites. A very similar thallium content was found in a soil sample near the well-known As-Sb-Tl locality „Allchar", where a detailed examination of the surface soils as part of another study revealed a very high Tl content (Janković, 1988; Stafilov et al., 1988, 2013; Balić Žunić et al., 1993; Boev et al., 2001–2002; Bačeva et al., 2014b; Vaněk et al., 2024). On Golak Mountain (Eastern region), another soil sample collected in the southwest of Delčevo showed a high Tl content of 10 mg/kg.

High levels of thallium were also found in soil samples contaminated by anthropogenic emissions from the mining and processing of lead and zinc ores in the northeast of the country. The most specific area is the Zletovo-Probištip area in the Eastern region (northeast of the city of Štip), which is known for its Pb-Zn mineralizsation and more than 70 years of mining activities (Serafimovski & Aleksandrov, 1995; Stafilov, 2014; Stafilov et al., 2014; Balabanova et al., 2015; Serafimovski et al., 2022). For example, two samples from this region, taken in the immediate vicinity of the mine near the village of Zletovo and the flotation processing plants and flotation tailings disposal site near the town of Probištip, show thallium levels of 5.5 mg/kg and 4.2 mg/kg, respectively.

It should also be noted that high levels of thallium have also been detected in the soil around the village of Lojane in the north of the country (near the town of Kumanovo), where the abandoned As-Sb mine with a flotation concentration plant and the production of As and Sb concentrates is located (Deconta, 2007; Serafimovski et al., 2023).

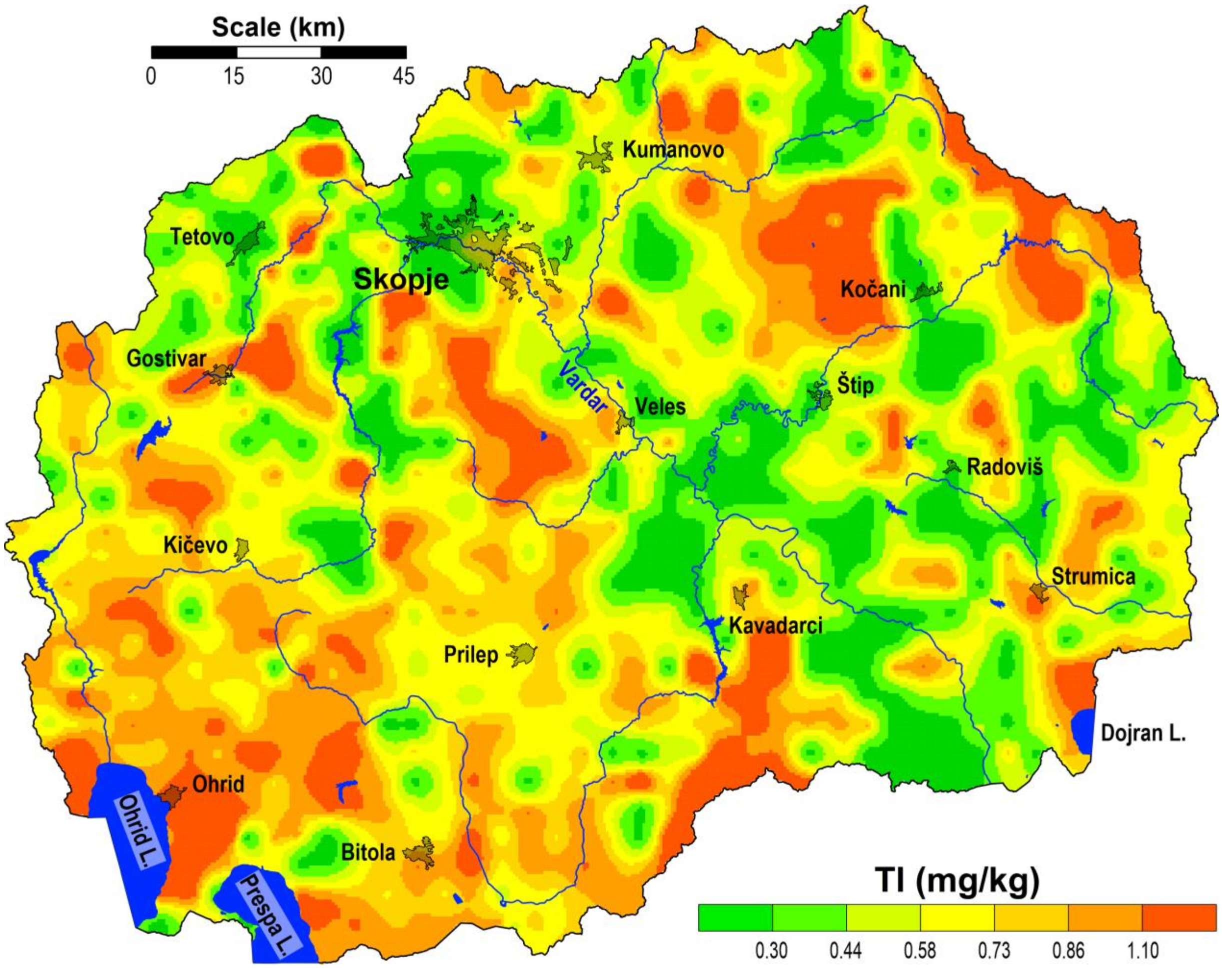

Fig. 5. Spatial distribution of the thallium content

CONCLUSION

The distribution of total thallium content in the surface soil (0–30 cm) collected from 995 sites in a 5×5 km grid in North Macedonia was investigated. Several factors were considered when considering the distribution: regional distribution, lithology, soil properties, anthropogenic influences, and geochemical processes. The average and median values of thallium in soil (0.77 mg/kg and 0.70 mg/kg) are very similar to its content in European soils (0.828 mg/kg) and the value observed in the upper continental crust (0.9 mg/kg).

Regarding the regional distribution of thallium, it was found that the higher values are found in the western part of the country with a median value of 0.80 mg/kg in the Pelagonian and Southwestern regions. According to the geological formations, the highest median thallium contents (1.0 mg/kg) were found in the soils in the area where Neogene igneous rocks occur mainly in the southern and northeastern part of the Vardar geotectonic zone and in the part of the Serbo-Macedonian massif zone. An increased mean Tl content (0.90 mg/kg) was also found in the areas where Mesozoic carbonates and Paleozoic metamorphic rocks of the West-Macedonian zone (0.80 mg/kg) and metamorphic rocks in the Pelagonian massif (0.80 mg/kg) occur. According to the pedological units, these are hydromorphic soils (average content of 0.90 mg/kg) which occur in the valleys of the country's main rivers.

The general spatial distribution of thallium content in soil throughout the country shows that the distribution patterns of thallium are mainly determined by geology (parent material and mineralization). In some areas, the natural anomaly pattern is overlaid by anthropogenic emissions from past mining, ore processing, and associated metal industries. Thus, high thallium levels (4.2–15 mg/kg) were found mainly in soils in the area where Neogene and Paleozoic igneous rocks and Neogene clastites occur in the Polog, Vardar and East regions. A very similar thallium content was found in a soil sample near the well-known As-Sb-Tl locality „Allchar", where a detailed investigation of the surface soils in a previous study revealed a very high Tl content.

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Р е з и м е

ПРОСТОРНА РАСПРЕДЕЛБА НА ТАЛИУМ ВО ПОЧВИТЕ НА СЕВЕРНА МАКЕДОНИЈА

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Клучни зборови: талиум; почви; просторна распределба; Северна Македнија

Целта на истражувањето беше да се утврди просторната дистрибуција и да се изврши процена на контаминацијата со талиум на почвите на Северна Македонија. Примероците од површинскиот слој на почвата (0–30 cm) беа собрани од 995 локации низ целата земја, со мрежа од 5×5 km помеѓу местата за земање примероци. За анализата на примероците е користена масена спектрометрија со индуктивно спрегната плазма (ICP-MS) со примена на целосна дигестија. Дискутирана е дистрибуцијата на талиумот во почвите според осумте статистички региони на државата, како и дистрибуцијата врз основа на 15 најзастапени геолошки формации и врз основа на 13 педолошки единици. Содржината на талиум во македонските почви варира од <0,05 до 15,5 mg/kg (средна вредност 0,70 mg/kg), што е во корелација со вкупната содржина на Tl за европските почви, која се движи од 0,01 до 21,3 mg/kg и има средна вредност од 0,66 mg/kg. На самата просторна дистрибуција на талиумот главно влијание има геологијата (носечкиот материјал и минерализацијата). Во некои области се појавуваат одредени аномалии кои се резултат на антропогени емисии од поранешни и сегашни рударски активности, потоа од преработка на рудата, како и од соодветни металуршки активности.