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Moss biomonitoring of the distribution of chemical elements in the air in the Prespa region, North Macedonia

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Abstract

A study was conducted to investigate atmospheric deposition and to explore the natural distribution and possible contamination with potentially toxic elements (PTEs) in the Prespa region, North Macedonia, using moss samples as biomonitors for air pollution. The distribution of 19 chemical elements (Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V, and Zn) was detected in 11 moss samples from this area. The moss samples were analysed after microwave digestion using inductively coupled plasma – atomic emission spectrometry (ICP-AES). R-mode factor analysis was used to identify and characterise the elemental associations, and four associations of elements were identified. Four factors were separated from the group of elements: Factor 1 (Fe-Al-Cr-V-Ni), Factor 2 (Sr-Ba-Mg), Factor 3 (K-P-Zn) and Factor 4 (Pb-Cu). All element factors were found to be typical geochemical associations, with the exception of the distribution of K and P in the agricultural areas of the study area where fertilisers are used over a long period of time.

Keywords: Moss biomonitoring, air pollution, potentially toxic elements, Prespa region, North Macedonia

Introduction

The monitoring of potentially toxic elements (PTEs) in the air plays an important role in understanding the spatial and temporal distribution of these pollutants. In addition to direct physical and chemical methods for monitoring air pollution, bioindicators have also been used in recent years to assess the risk of air pollution. Biomonitoring is a method of obtaining quantitative information on certain characteristics of the biosphere. Organisms that provide quantitative data on the presence of pollutants in the environment are biomonitors (Wolterbeek, 2002; Szczepaniak & Biziuk, 2003; Škrbić et al., 2012; Kłos et al., 2018; Stafilov et al., 2018; Lazo et al., 2019).

Mosses are considered the most suitable biomonitors due to their widespread distribution around the world (Groet, 1976; Rühling & Steinnes, 1998; Elias et al., 2008; Harmens et al., 2004, 2010, 2015). Mosses are characterized by little change in morphology during the growth period and are widely distributed due to their adaptability under different environmental conditions. They have rhizoids with which they anchor themselves to their substrate and obtain their minerals mainly from moist and dry sediments (Rühling & Steinnes, 1998). Moss samples are not only used to monitor the distribution of potentially toxic metals, but are also suitable as biomonitoring media for analysing the atmospheric deposition of organic pollutants (Vuković et al., 2016).

For the first time, an area-wide study on air pollution by heavy metals was conducted in North Macedonia in 2002, using mosses as biomonitors in the framework of the United Nations Economic Commission for Europe International Co-operative Programme on the Effects of Air Pollution on Natural Vegetation and Crops with Heavy

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Metals in Europe (UNECE ICP Vegetation) (Harmens, H., Norris, D. 2008; Harmens et al., 2004, 2008, 2010, 2015). North Macedonia joined this Programme in 2002 (Barandovski et al., 2008) and subsequently moss samples were collected in 2005, 2010, 2015 and 2020 at the same 72 sites across the country (Barandovski et al., 2008, 2012, 2015, 2020, 2024; Stafilov et al., 2018). It was found that the highest air pollution with potentially toxic elements occurs mainly in the area of mining and metallurgical activities.

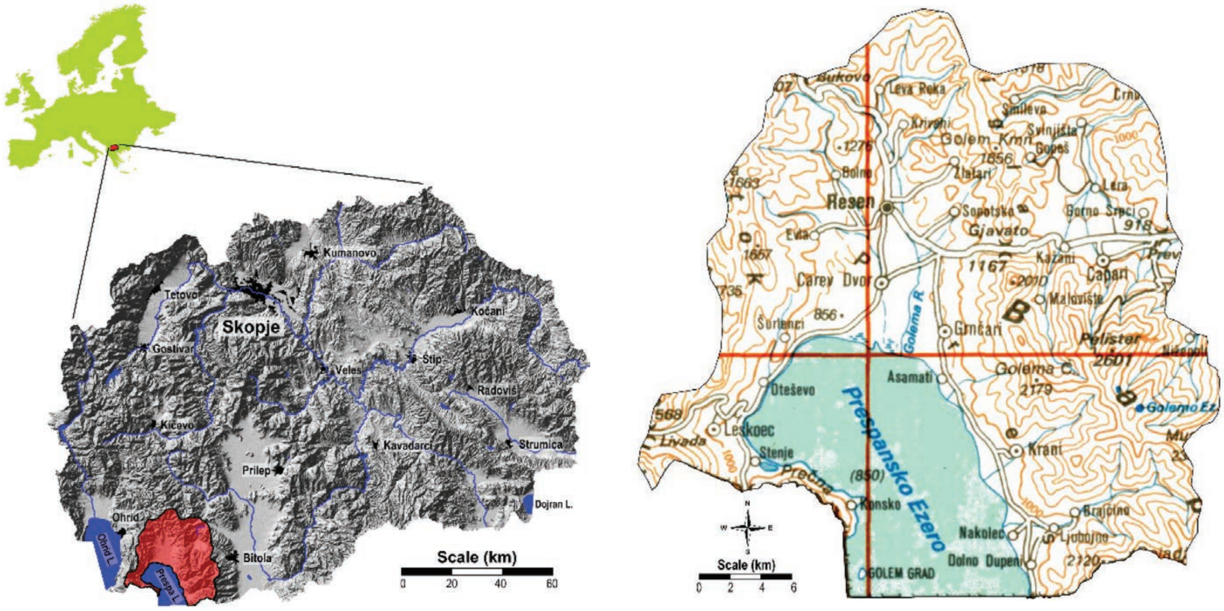
The initial results of air pollution biomonitoring research with PTEs have increased interest in the application of biomonitoring with mosses, focusing on individual regions in Macedonia, such as the Bučim copper mine near the town of Radoviš (Balabanova et al, 2010, 2014), in the area of the ferronickel smelting plant near the town of Kavadarci (Bačeva et al, 2012), the Pb-Zn mines and flotation plants "Toranica" (Angelovska et al., 2016), "Zletovo" and "Sasa" (Balabanova et al., 2016, 2017). The study was also conducted in the vicinity of the abandoned As-Sb-Tl mine "Allchar" on the Kožuf Mountain (Bačeva et al., 2013) and in the vicinity of the thermoelectric coal-fired power plants in Bitola (Dimovska et al., 2014; Stafilov et al., 2023). In addition, the lithological and anthropogenic origin of various chemical elements was monitored in several regions of North Macedonia, such as the Kumanovo region (Stafilov et al., 2022), the Crn Drim river basin (Stafilov et al., 2023) or the Polog region (Stafilov et al., 2024).

The aim of this study is to track the potential impact of air pollution from industrial and urban activities in the Prespa region, North Macedonia, using moss biomonitoring. For this purpose, moss samples were collected at 11 sites and after microwave digestion of the samples, 19 elements were analysed by inductively coupled plasma - atomic emission spectrometry (ICP-AES). Factor analysis was applied to reveal the possible association of the analysed elements in terms of geochemical similarities as well as the separation of anthropogenic associations of the elements (Škrbić et al., 2022). Based on the results obtained, distribution maps for the isolated factor groups and the analysed elements are generated, paying special attention to the elements of lithological and anthropogenic origin.

Materials and methods

Study area

The study area is located in the southwestern part of North Macedonia with an area of 34 km (W-E) x 35 km (S-N), in a total of 1190 km^2 (Figure 1). The Prespa Valley (Fig. 1) is surrounded by high mountains: to the east is the Baba mountain with the highest peak Pelister (2601 m), to the north Bigla (1933 m), to the west Galicica (2255 m), to the south Korbec (1750 m) (Figure 1b). The valley itself is divided by three countries, of which the largest part belongs to North Macedonia (65%) and the rest to Albania (18%) and Greece (17%). There are two lakes in the valley: the Great Prespa lake and the Small Prespa Lake. The hydrography of the valley is made up of groundwater, springs, natural watercourses, man-made waters, and the natural accumulation of the lakes. The Great Prespa Lake has an area of 284 km^2 with an height of 853 m and a maximum depth of 54 m (Kolčakovski, 2004; Stafilov et al., 2022).



a) b)

Figure 1. Location of the study area in North Macedonia (a) and its topographic map (b)

The specific orographic conditions have an influence on the climate of the study area. Together with the effects of geographical and local factors, three different climate types are created in the entire watershed: a warm and cold sub-Mediterranean climate, a submontane and mountainous sub-Mediterranean climate and a subalpine and alpine climate. The average annual temperature is relatively low, but is very suitable for orchards and especially for apple trees (Lazarevski, 1993).

The most important mineral resources are limestone and dolomite in the western part. Sand and gravel are mined around the mouth of the river Golema Reka into Lake Prespa (Petrovska et al., 2012). In terms of land use, about 32% of the Macedonian part of the basin is covered by forests, while 27% of the area is used for agriculture, of which 16% is arable land. Agriculture plays an important role in employment and economic sustainability. Industry, including the food, textile, metal, paper, chemical and construction industries is mainly represented by medium-sized companies. There is currently no significant tourism industry (Petrovska et al., 2012; Stafilov et al., 2022).

The Prespa valley is part of the Western Macedonian tectonic zone. The most important morphological structures are the block of the Baba Mountains in the east, separated from the block of the Bigla, Ilinska and Placenska Mountains in the north by the Gjavato Fault, and the block of the Galičica Mountains in the west (Arsovski, 1997; Blažev and Arsovski 2001; Stafilov and Šajn, 2016; Petrušev et al., 2021; Stafilov et al., 2022). Paleozoic schists and felsic plutonites (mostly granite, water-resistant rock masses) predominate on the eastern border with the Baba, Bigla and Placenska Mountains (Blažev and Arsovski, 2001). The western frame (Galičica, Stara, Ivan and Korbec Mountains) consists mostly of porous Mesozoic and Paleozoic carbonates (mainly limestone). The valley floor consists of Quaternary alluvial sediments (mostly gravelly-sandy and clayey). The northern part of the study area is similar to the western part and consists of Palaeozoic shales and felsic plutonites and a small part of Palaeozoic sandstones (Fig. 2).

Moss sampling

Moss sampling was conducted out according to the instructions of the monitoring manual provided by the United Nations Economic Commission for Europe under the Convention on Long-range Transboundary Air Pollution (ICP Vegetation, 2015). Each sample was placed on a separate laboratory paper and turned several times until the moss had dried at room temperature and reached a constant weight.

In summer of 2014, a total of 18 moss samples were collected in the study area (corresponding to a grid of 5 × 5 km), including 6 samples of *Hypnum cupressiforme* and 5 samples of *Camptothecium lutescens*. A map showing the locations of the moss samples can be found in Figure 3.

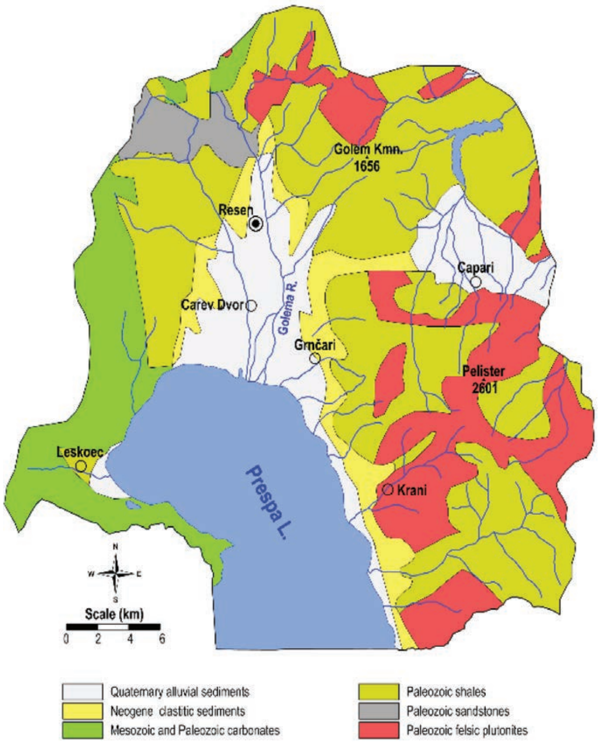


Figure 2. Geological map of the study area

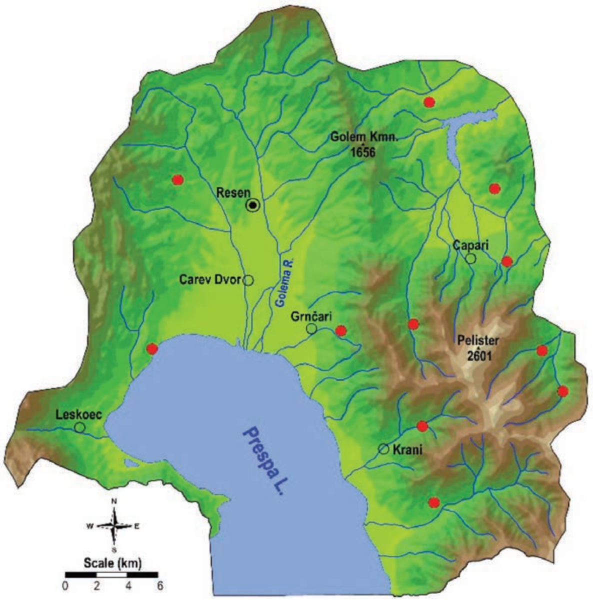


Figure 3. Study area with sampling locations

Table 1. Descriptive statistic of measurements for moss samples (*n*=11)

Element	Unit	X	$X_{(BC)}$	Md	Min	Max	P_{25}	P_{75}	P_{10}	P_{90}	S	S_x	CV	A	E	$A_{(BC)}$	$E_{(BC)}$
Ag	µg/kg	120	97	85	38	250	54	170	50	200	69	21	60	0.80	-0.37	0.01	-1.24
Al	%	0.14	0.12	0.12	0.080	0.24	0.092	0.17	0.085	0.20	0.051	0.015	38	1.11	0.72	0.09	-0.81
Ba	mg/kg	35	23	23	7.2	110	12	43	10	90	33	10	94	1.61	1.56	0.06	-0.42
Ca	%	0.53	0.50	0.49	0.37	0.90	0.39	0.62	0.38	0.70	0.16	0.048	30	1.30	1.71	0.12	-0.81
Cr	mg/kg	2.0	1.5	1.6	0.98	6.3	1.1	1.9	1.1	3.5	1.6	0.47	77	2.37	5.84	0.31	-0.86
Cu	mg/kg	4.6	4.7	4.4	2.6	6.0	4.0	5.5	3.8	6.0	1.0	0.31	22	-0.29	-0.12	-0.09	-0.48
Fe	%	0.16	0.14	0.14	0.095	0.34	0.11	0.19	0.11	0.25	0.075	0.023	46	1.65	2.65	0.22	-1.03
K	%	0.19	0.20	0.21	0.090	0.24	0.16	0.22	0.14	0.23	0.045	0.014	24	-1.24	1.11	-0.47	-0.99
Li	mg/kg	0.63	0.61	0.63	0.38	0.99	0.45	0.81	0.43	0.83	0.19	0.058	30	0.37	-0.76	-0.02	-1.17
Mg	%	0.13	0.12	0.13	0.069	0.20	0.092	0.16	0.080	0.19	0.044	0.013	35	0.51	-0.83	0.01	-1.14
Mn	mg/kg	74	65	70	21	150	29	120	22	130	46	14	62	0.29	-1.47	-0.13	-1.60
Mo	mg/kg	0.20	0.18	0.19	0.053	0.41	0.15	0.21	0.097	0.37	0.11	0.032	54	1.05	0.86	-0.01	0.65
Na	mg/kg	50	47	48	20	91	36	55	34	73	19	5.8	39	0.88	1.27	0.00	0.95
Ni	mg/kg	2.8	2.5	2.4	1.4	5.5	2.0	2.9	1.7	4.3	1.2	0.36	43	1.37	1.77	0.05	-0.16
P	mg/kg	770	800	860	250	1100	650	880	580	910	220	66	28	-1.40	2.58	-0.31	0.42
Pb	mg/kg	2.6	2.5	2.5	1.0	4.1	1.0	3.9	1.0	4.0	1.2	0.37	48	-0.11	-1.50	-0.24	-1.45
Sr	mg/kg	16	15	15	6.1	34	8.9	21	8.8	21	7.8	2.3	49	1.22	2.36	-0.01	0.20
V	mg/kg	2.5	2.3	2.5	1.2	5.0	1.7	3.2	1.5	3.2	1.1	0.32	42	1.26	2.32	0.01	-0.05
Zn	mg/kg	4.8	3.6	2.7	0.17	14	2.1	7.2	0.85	10	4.2	1.3	89	1.11	0.47	-0.10	-0.21

X - mean, $X_{(BC)}$ - mean (Box-Cox transformed data), Md - median, Min - minimum, Max - maximum, P_{10} - 10 percentile, P_{25} - 25 percentile, P_{75} - 75 percentile, P_{90} - 90 percentile, S - standard deviation, S_X - standard deviation (standard error), CV - coefficient of variation, A - skewness, E - kurtosis, $A_{(BC)}$ - skewness (Box-Cox transformed data), $E_{(BC)}$ - kurtosis (Box-Cox transformed data)

Digestion and analysis of the moss samples

The moss samples (0.5 g) were placed in Teflon digestion vials, 5 mL of concentrated nitric acid (HNO_3, 69%, trace level for trace analysis) and 2 mL of H_2O_2 (30%, m/V trace level for trace analysis) were added and the vessels were capped, tightened and placed in the rotor of the Mars Microwave Digestion System (Mars, CEM, USA). The digestion was carried out with the following programme: Step (1) temperature 180 °C, 20 minutes ramp time, with a power of 800 W and Step (2) temperature 180 °C, 25 minutes hold time, with a power of 800 W. After cooling, the digested samples were quantitatively transferred to calibrated 25 mL flasks.

A total of 19 chemical elements (Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V and Zn) were analysed in all digested moss samples by inductively coupled plasma – atomic emission spectrometry - ICP-AES (Varian, 715-ES) using the previously optimised instrument and operating conditions (Balabanova et al., 2010). Quality control was also ensured by standard moss reference materials M2 and M3 prepared for the European moss survey (Steinnes et al., 1997). The measured concentrations were within the recommended values. The difference between the measured and certified values was within 15%.

Data processing and statistical analysis

The interpretation of the geostatistical data and the visualisation (mapping) were carried out with the following software packages: Statistica (Stat Soft, Inc.), Autodesk MAP 3D (Autodesk, Inc.), ArcInfo (ESRI, Inc.) and Surfer (Golden Software, Inc.). Parametric and non-parametric statistical methods were used (Zhang et al., 1998), and normality tests of the data distributions were performed.

Data transformation was performed because we wanted to reduce the difference between the extreme values. Based on the results and our experience, we applied a Box-Cox transformation, which is one of the most commonly used transformations in environmental and earth sciences (Box & Cox, 1964). Multivariate cluster and R-mode factor analyses (FA) were used to reveal associations of chemical elements (Reimann et al., 2002). Factor analysis (FA) was performed with variables standardised to a mean of zero and a standard deviation of one unit. The varimax method was used for orthogonal rotation. The universal kriging method with linear variogram interpolation was used to create maps of the spatial distribution of factor values and maps showing the distribution of trace elements (Davis, 1986). The base size of the grid cells for interpolation was 25×25 m. Seven classes of percentile values of the distribution of interpolated values were chosen for the class boundaries (0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100).

Results and discussion

The statistics with all data of the 19 analyzed elements (Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V and Zn) in the moss samples from the investigated region (n=18) are shown in Table 1. The values for the content of Al, Ca, Fe, K and Mg are given in percent, for Ag and Mo in µg/kg and for the other elements in mg/kg. The median values result in the following order for the content of macroelements: Ca (0.48%), K (0.26%), Al (0.16%), Fe (0.12%, Mg (0.12%) and P (0.057%). The elements

Table 2. Comparison of the results obtained in the present study (Veles region) with those from the whole territory of North Macedonia in 2015 (in mg/kg)

Element	Veles region (present work); *n*=11		North Macedonia, 2015 (Stafilov et al., 2018); *n*=72	
	Median	Range	Median	Range
Ag	0.097	0.038-0.25	-	-
Al	1200	800-2400	2100	750-7400
Ba	23	7.2-110	42	9.7-180
Ca	49000	3700-9000	6900	3500-13000
Cr	1.6	0.98-6.3	5.7	1.8-31
Cu	4.4	2.6-6.0	4.6	3.0-8.3
Fe	1400	950-3700	1700	510-4600
K	2100	900-2400	6000	3100-14000
Li	0.63	0.38-0.99	0.79	0.32-3.5
Mg	1300	690-2000	1900	1200-1200
Mn	70	21-150	160	33-510
Mo	0.19	0.053-0.41	0.17	0.085–0.51
Na	48	20-91	190	140-380
Ni	2.4	1.4-5.5	3.5	0.68-63
P	860	250-1100	1100	420-2000
Pb	2.5	1.0-4.1	4.9	2.2-14
Sr	15	6.1-34	25	6.5-220
V	2.5	1.2-5.0	3.3	0.47-11
Zn	2.7	0.17-14	30	12-66

in the traces have the following order according to the value of the median of their content: Na (90 mg/kg), Mn (60 mg/kg), Zn (27 mg/kg), Ba (21 mg/kg), Sr (16 mg/kg), Cu (4.9 mg/kg), Ni (4.8 mg/kg), Cr (2.7 mg/kg), V (2.2 mg/kg), Pb (2.1 mg/kg), Li (1.3 mg/kg), As (0.66 mg/kg), Cd (0.30 mg/kg), Mo (0.10 mg/kg) and Ag (0.073 mg/kg).

Table 2 shows the comparison of the median, minimum and maximum values for the content of the analyzed elements in the moss from the Polog region with the values for North Macedonia from 2015 (Stafilov et al., 2018). It was found that the median values for the content of almost all analyzed elements in the moss samples from the Prespa region are lower than the values for North Macedonia, which indicates that in this region there is no anthropogenic influence on the values of PTEs in particular in the moss samples from the entire territory of the country. The results regarding the content of the analyzed elements in the moss samples and the soil samples taken from the same locations (Table 3) also lead to this conclusion (Stafilov et al., 2024). The only elements for which this relationship shows a significant difference are Cr and Fe, but this is still a consequence of the lithological peculiarities of this region compared to the country as a whole.

Table 3. Ratio (R) of the content of the analysed elements in moss (M) and topsoil (T) samples in the Prespa region

Element	R(M/T)	Significance
Ag	-0.04	NS
Al	0.55	NS
Ba	-0.11	NS
Ca	-0.18	NS
Cr	0.65	*
Cu	0.29	NS
Fe	0.68	*
K	0.57	NS
Li	-0.04	NS
Mg	-0.12	NS
Mn	-0.41	NS
Na	0.01	NS
Ni	0.44	NS
P	0.53	NS
Pb	-0.53	NS
Sr	0.01	NS
V	0.35	NS
Zn	0.02	NS

NS – Not significant; * - Significant

The degree of correlation between the contents of chemical elements in the moss samples was assessed using the Pearson correlation coefficient (r). It was qualitatively assumed that the absolute values of r between 0.5 and 0.7 indicate a good association, which means that the coefficient of determination is in the range between 25% and 50%, and when r>0.70 provides a strong association between the elements due to the very similar distribution of the elements. The values for the content of the individual elements were correlated with the values for the content of the other elements (Reimann et al., 2002). All correlation coefficients between all elements for the elements are shown in the matrix of correlation coefficients (Table 3). The correlation coefficients of the contents of the analysed elements (Table 4) show that there are strong correlations between several elements, e.g. between Al and Cr, Fe, and Ni; Ba and Sr, Cr and Fe, Ni and V; Cu and Mo and V; Ni and V, Li and Sr Mg and Sr; Mo and Pb; Ni and V.

Factor analysis of a large number of variables yields a small number of synthetic variables called factors. These factors contain important information about the original variables and have a clearly defined meaning. Factor analysis is performed with variables that are standardized to the value zero and the unit of standard deviation (Reimann et al., 2002). In factor analysis, the distribution is reduced to four synthetic variables. The values of the factor loadings for the moss samples from the Prespa region are shown in Table 5. Four factors were identified: Factor 1 (F1), containing Fe, Al, Cr, V and Ni; Factor 2 (F2), containing Sr, Ba and Mg; Factor 3, containing K, P and Zn; and Factor 4 (F4), containing Pb and Cu. Silver, calcium, lithium, manganese, molybdenum and sodium were excluded from further analysis as they tend to form their own factors that are not associated with other elements.

The cluster grouping of the elements in the dendrogram is given in Figure 4. The elements are divided into clusters according to the degree of correlation between them. The first cluster consists of the elements Al, V, Cr, Fe and Ni. These are the elements that form Factor 1 of the load matrix of the dominant rotating factors (Table 5). The second cluster consists of the elements Cu and Pb, which otherwise belong to Factor 4 of the loading matrix of the dominant rotating factors (Table 5). The third cluster consists of the elements: Ba, Mg and Sr, which is an identical composition to Factor 2, while the fourth cluster comprises the elements K, P and Zn, which belong to Factor 3 (Table 5).

Factor 1 (Fe, Al, Cr, V and Ni) stands for a lithogenic compound of elements. The spatial distribution of the factor scores of F1 and the spatial distribution of the

Table 4. Pearson correlation coefficient between element content in mosses from Prespa region (*n*=11). Values in range 0.5-0.7 (good association) are underlined and in range 0.7-1.0 (strong association) are bolded; Box-Cox transformed values used.

Element	Ag	Al	Ba	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	Sr	V	Zn
Ag	1.00																		
Al	0.23	1.00																	
Ba	-0.27	0.38	1.00																
Ca	0.29	-0.03	0.36	1.00															
Cr	0.30	**0.92**	0.23	0.01	1.00														
Cu	0.05	0.49	0.07	0.01	0.66	1.00													
Fe	0.08	**0.92**	0.19	-0.16	**0.89**	0.55	1.00												
K	-0.08	0.23	0.25	0.23	0.15	0.28	0.28	1.00											
Li	0.03	0.62	0.62	0.40	0.41	0.05	0.42	-0.03	1.00										
Mg	0.11	0.49	0.63	0.36	0.49	0.22	0.44	-0.10	0.55	1.00									
Mn	0.17	0.09	0.63	0.19	-0.01	-0.23	-0.03	0.12	0.15	0.62	1.00								
Mo	0.22	-0.34	-0.17	0.09	-0.41	**-0.78**	-0.42	-0.58	0.08	-0.16	0.03	1.00							
Na	0.05	0.19	0.46	0.34	0.28	0.31	0.10	0.32	0.11	0.42	0.41	-0.55	1.00						
Ni	0.25	**0.84**	0.18	-0.23	**0.89**	0.66	**0.89**	0.15	0.22	0.54	0.17	-0.49	0.16	1.00					
P	0.16	0.01	0.16	0.52	0.03	-0.08	0.06	**0.73**	-0.12	0.15	0.34	-0.25	0.41	-0.02	1.00				
Pb	0.24	0.51	0.22	-0.04	0.60	**0.80**	0.42	0.32	0.05	0.32	0.15	**-0.80**	0.49	0.66	0.07	1.00			
Sr	-0.13	0.43	**0.84**	0.47	0.35	0.29	0.30	0.07	**0.70**	**0.85**	0.53	-0.25	0.37	0.34	0.06	0.35	1.00		
V	0.24	**0.93**	0.38	0.20	**0.90**	0.50	**0.86**	0.31	0.61	0.57	0.08	-0.37	0.22	**0.78**	0.24	0.52	0.51	1.00	
Zn	0.32	0.44	-0.07	-0.07	0.44	0.39	0.44	**0.72**	-0.17	-0.12	0.02	-0.52	0.07	0.49	0.51	0.59	-0.12	0.51	1.00

Table 5. Matrix of rotated factor loadings (*n*=11, 13 selected elements). Box-Cox transformation used.

Element	F1	F2	F3	F4	Comm
Fe	0.94	0.09	0.11	0.16	93.5
Al	0.92	0.24	0.09	0.18	93.8
Cr	0.90	0.15	0.03	0.33	94.7
V	0.86	0.32	0.24	0.17	93.3
Ni	0.84	0.14	0.01	0.42	90.5
Sr	0.19	0.95	-0.03	0.18	96.6
Ba	0.08	0.90	0.16	0.03	84.3
Mg	0.41	0.82	-0.10	0.03	85.0
K	0.08	0.03	0.92	0.21	89.9
P	0.00	0.14	0.90	-0.16	86.4
Zn	0.39	-0.27	0.72	0.39	90.0
Pb	0.31	0.17	0.18	0.87	92.0
Cu	0.38	0.06	0.01	0.86	88.4
Prp.Totl	35.5	20.9	17.9	16.3	90.7
EigenVal	6.50	2.38	1.88	1.03	
Expl.Var	4.61	2.72	2.33	2.12	

F1, F2, F3 and F4 – Factor loadings of Factors 1, 2, 3 and 4; Comm – Communality (%), Prp. Totl – Total amount of the explained system variance; Expl. Var – particular component variance; Eigen Val - Eingene value

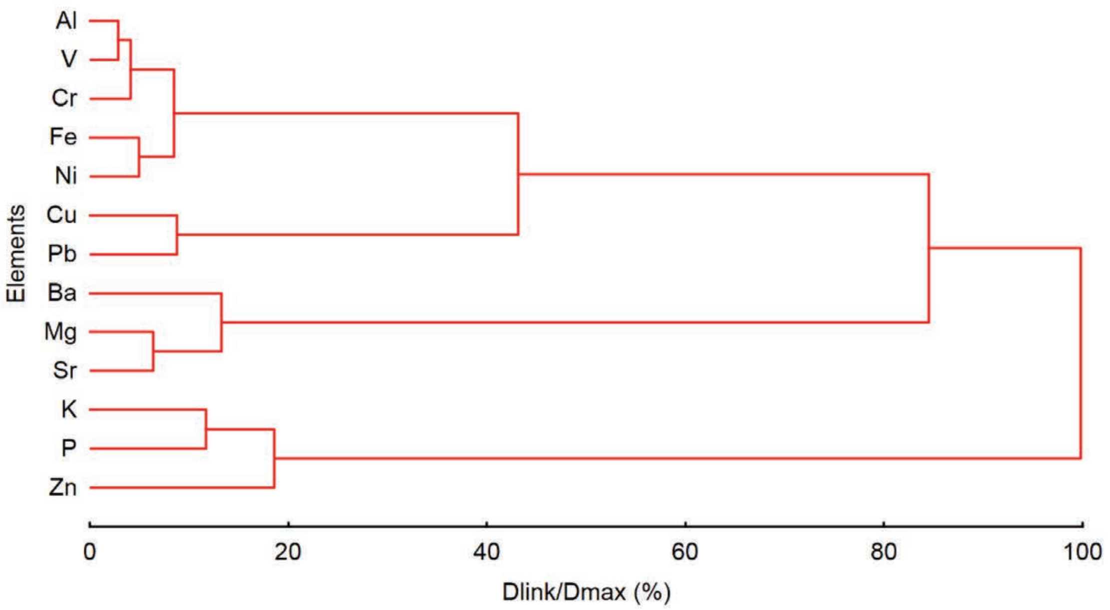


Figure 4. Dendrogram from the cluster analysis of the data from the elemental analysis of moss samples from Prespa region

content of the elements of this Factor are shown in Figure 5. The origin of the elements in this typical lithogenic association is related to the geological composition of the soil in this region. This is also confirmed by the fact that all of these elements, with the exception of Al, are also represented in the association of Factor 1 from the factor analysis (Ni, V, Fe, Cr, Cu, Zn, Mn and Mg) of the content of the elements in the soils of the same area (Stafilov et al., 2022). The distribution maps (Figure 5) show that the high contents of elements from F1 occur in the central part of the study area, where Quaternary alluvium sediments (Carev Dvor and Grnčari villages) and Paleozoic felsic plutonites (Baba Mountain with the Pelister peak area), where their content in the soil is also increased (Stafilov et al., 2022).

Factor 2 consists of Sr, Ba and Mg. The high contents of these elements are found in the moss samples from the central and north-western parts of the area (Figure 6), where Paleozoic felsic plutonites and Paleozoic sandstones predominate.

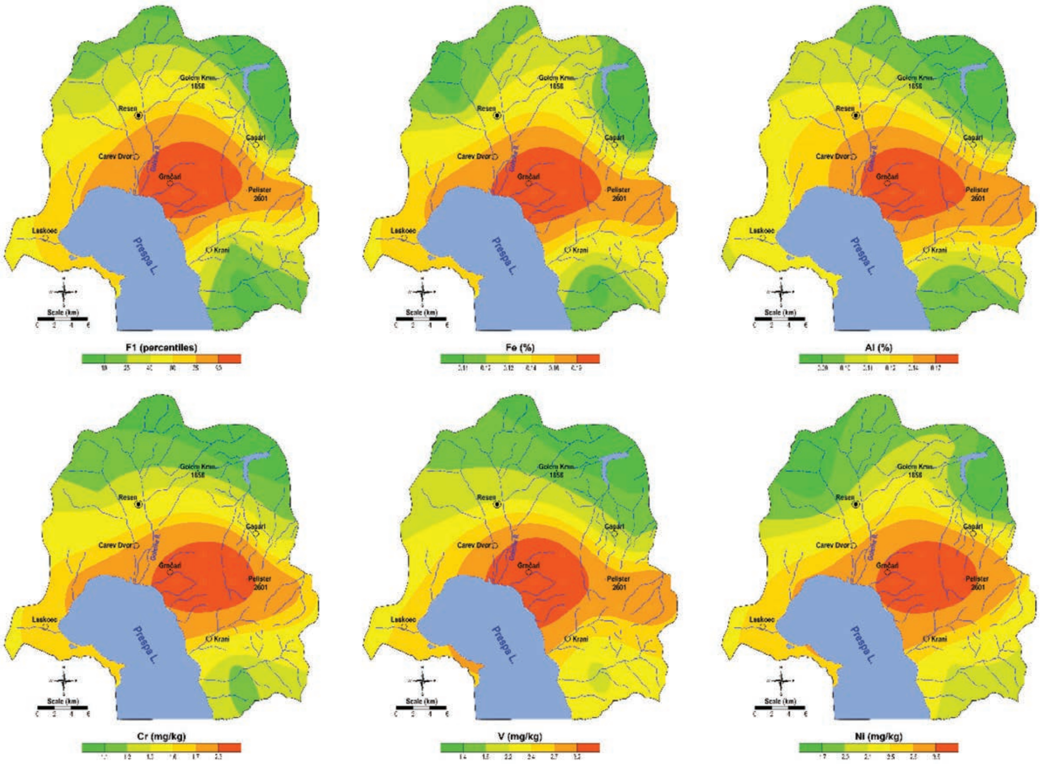


Figure 5. Maps of the spatial distribution of the factor scores of Factor 1 and the content of the elements of Factor 1 (Fe-Al-Cr-V-Ni)

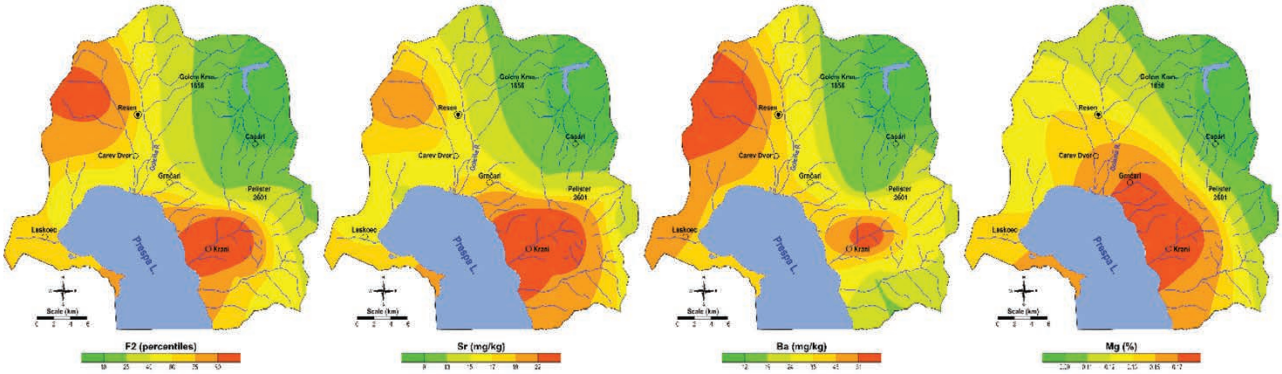


Figure 6. Maps of the spatial distribution of the factor scores of Factor 2 and the content of the elements of Factor 2 (Sr-Ba-Mg)

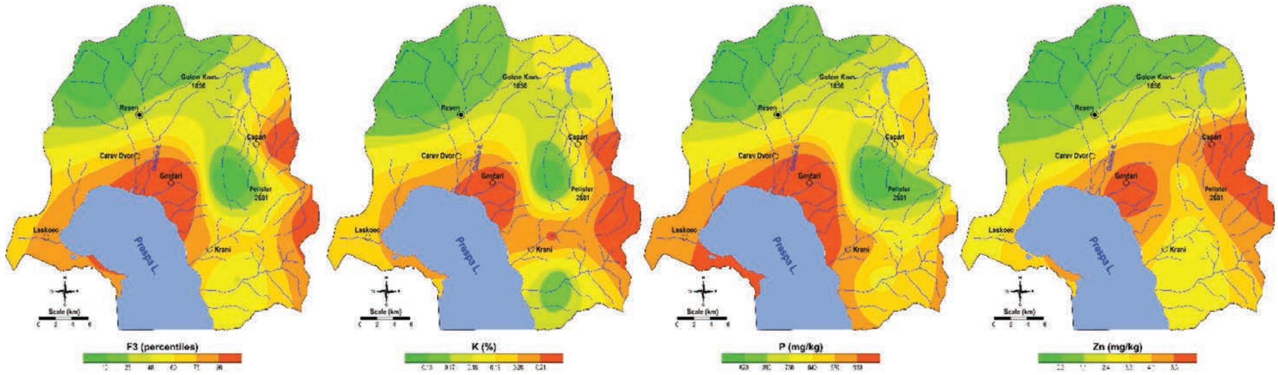


Figure 7. Maps of the spatial distribution of the factor scores of Factor 3 and the content of the elements of Factor 3 (K-P-Zn)

Factor 3 consists of K, P and Zn. The high contents of these elements are found in the moss samples from the central part of the area (Figure 7), where agricultural activities predominate, which leading to the conclusion that in this area there is an increase in the content, especially of K and P, in the soils due to the use of artificial fertilizers with these combinations of these elements. High content of K and Zn are also found in the moss samples from the Baba Mountain, where Paleozoic felsic plutonites are predominate.

According to the spatial distribution of factor scores of Factor 4 (Factor 4 (Pb and Cu) shown in Figure 8, which is also a lithogenic association with the highest content in the moss samples from the areas around the town of Veles, Baba, mountain where Paleozoic felsic plutonites and Paleozoic shales predominate.

Of the total of 19 elements analysed, the factor analysis is reduced to 13, which have a total share of 90.7% of the utility (Table 5). The other elements (Ag, Ca, li, Mn, Mo and Na) are eliminated as they do not contribute to the communality. The spatial distribution maps of the content of these elements in the moss samples are presented in Figure 9.

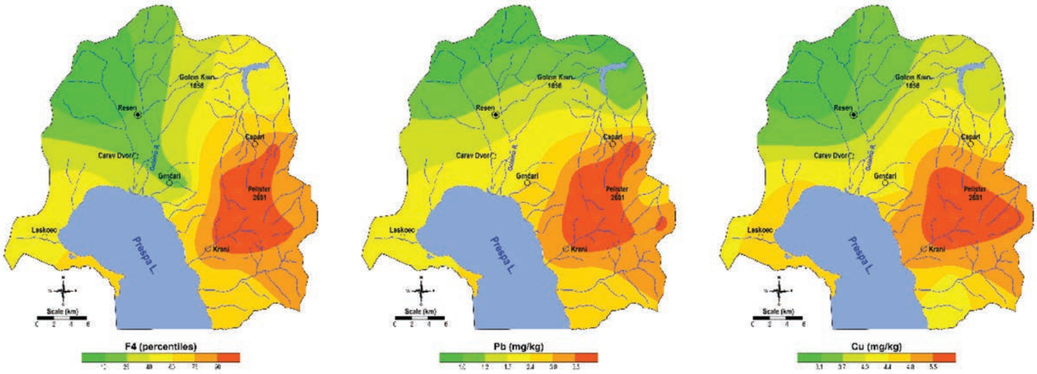


Figure 8. Maps of the spatial distribution of the factor scores of Factor 4 and the content of the elements of Factor 4 (Pb-Cu)

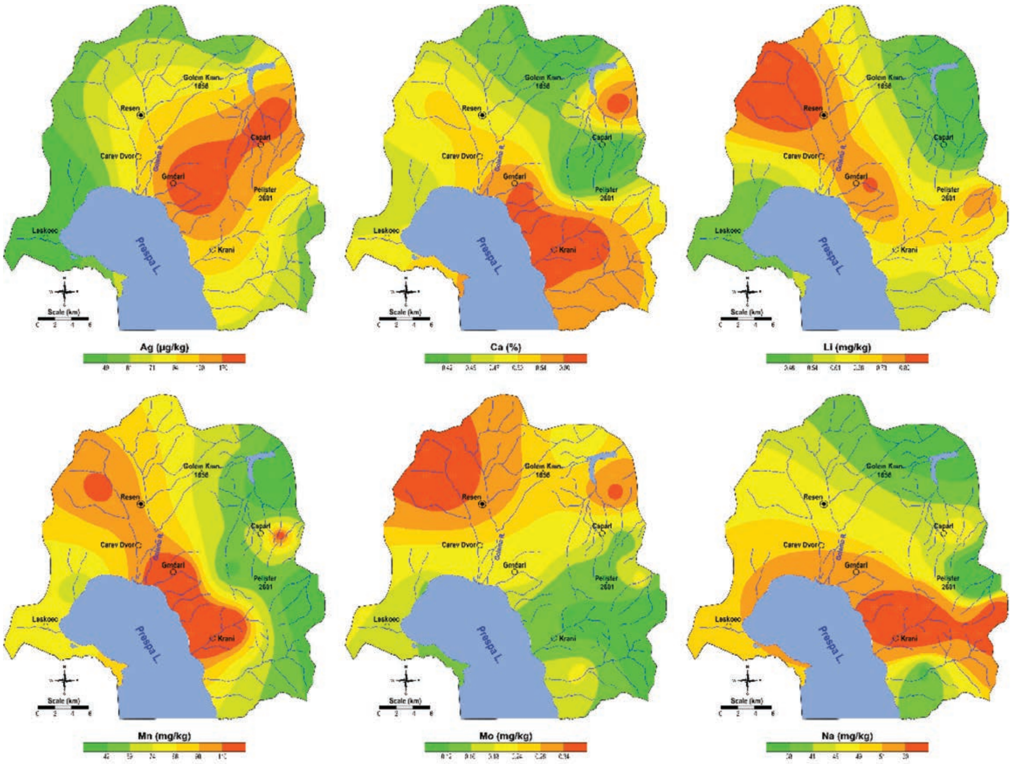


Figure 9. Maps of spatial distribution of the content of Ag, Ca, Li, Mn, Mo and Na

Conclusion

The moss biomonitoring technique was used to determine the distribution of 19 chemical elements (Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V and Zn) in the air in the region of Polog, North Macedonia. The moss samples were analysed by inductively coupled plasma – atomic emission spectrometry (ICP-AES) after microwave digestion. Factor analysis was performed to identify and characterise the elemental associations and five elemental associations were determined: Factor 1, which includes Fe, Al, Cr, V and Ni; Factor 2 with Sr, Ba and Mg; Factor 3 with K, P and Zn; and Factor 4, which includes Pb and Cu. Silver, Ca, Li, Mn, Mo and Na were excluded from further analysis as they tend to form their own factors that are not associated with other elements. All associations of elements were found to be typical geochemical associations, except for the distribution of K and P in the agricultural areas of the study area where fertilisers are used over a long period of time.

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