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AIR POLLUTION STUDY IN MACEDONIA USING A MOSS BIOMONITORING TECHNIQUE, ICP-AES AND AAS

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In the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops under the auspices of the United Nations Economic Commission for Europe (UNECE-ICP Vegetation) Convention on Long-Range Transboundary Air Pollution (LRTAP), in 2002 and 2005, a moss biomonitoring technique was applied to air pollution studies in the Republic of Macedonia. The third moss survey took place in August and September 2010 when 72 samples of the terrestrial mosses *Homalothecium lutescens* and *Hypnum cupressiforme* were collected over the territory of the Republic of Macedonia, using the same sampling network grid as for the previous surveys. Using inductively coupled plasma-atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS), a total of 19 elements (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Ni, P, Pb, Sr, V and Zn) were determined. To reveal hidden multivariate data structures and to identify and characterize different pollution sources Principal Component Analysis was used. Distributional maps were prepared to point out the regions most affected by pollution and related to known sources of contamination. As in the previous surveys, the regions near the towns of Skopje, Veles, Tetovo, Radoviš and Kavadarci were found to be most affected by pollution, even though the median elemental content in the mosses in 2010 for Cd, Cr, Cu, Ni, Pb and Zn was slightly lower than in the previous surveys. For the first time, P content in the moss samples was analyzed, and a higher content of this element as well as K in the mosses was observed in the agricultural regions of the country.

Keywords: Moss; biomonitoring; air pollution; heavy metals; Macedonia

ПРОУЧУВАЊЕ НА ЗАГАДУВАЊЕТО НА ВОЗДУХОТ ВО МАКЕДОНИЈА СО ПРИМЕНА НА БИОМОНИТОРИНГ НА МОВ, ICP-AES И AAS

Во рамките на меѓународната програма за изучување на ефектите од загадувањето на воздухот врз природната вегетација и житните култури, под покровителството на Економската комисија за Европа на Обединетите Нации (UNECE-ICP Vegetation) и Конвенцијата за следење на прекуграничното загадување (LRTAP), во 2002 и 2005 година беше извршен биомониторинг на мов заради проучување на загадувањето на воздухот во Република Македонија. Третото по ред собирање на примероците беше направено во август и септември 2010 година кога од целата територија на Република Македонија беа собрани 72 примерока од терестријалните видови мов *Homalothecium lutescens* и *Hypnum cupressiforme,* користејќи идентична мрежа за собирање на примероците како и во претходните испитувања. Со примена на атомската емисиона спектрометрија со индуктивно спрегната плазма (ICP-AES) и атомската апсорпциона спектрометрија (AAS) е определена содржината на 19 елементи (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Ni, P, Pb, Sr, V и Zn). За да се откријат скриените мултиваријантни структури на податоците, како и да се одредат различните извори на загадувањето, беше применет методот на главни компоненти. Со цел да се одредат местата со најголемо загадување и тие да се поврзат со познатите извори на загадувањето, беа изработени карти на кои е прикажана дистрибуцијата на одделните елементи. Како и во претходните истражувања, најголемо загадување на воздухот е во регионите во близина на Скопје, Велес, Тетово, Радовиш и Кавадарци, иако медијаните на Cd, Cr, Cu, Ni, Pb и Zn во примероците од мов анализирани во 2010 година се помали од оние добиени во претходните истражувања. За првпат во примероците од мов е извршено определување на содржината на P и највисоки вредности на овој елемент и на K се забележани во примероците собрани од земјоделските региони.

Клучни зборови: мов; биомониторинг; загадување на воздух; тешки метали; Македонија

1. INTRODUCTION

Biomonitoring in the most general sense can be defined as the use of organisms (biomaterials) to obtain quantitative information and some characteristics of the biosphere. Bioindicator or biomonitor are terms used to refer to an organism (or a part of the organism), that reacts on the occurrence of pollutants on the basis of specific symptoms, reactions, morphological changes or concentrations. Usually, organisms can be classified according to the way in which the reaction is manifested: reaction indicators, which have a sensitive reaction to air pollutants and which are used especially in studying the effects of pollutants on their physiological and ecological functioning, and accumulation indicators that readily accumulate a range of pollutants and therefore are used especially when monitoring the amount of pollutants and their distribution [1]. A general advantage of the biomonitoring approach is related primarily to the permanent and common occurrence of the organism in the field even in remote areas, the ease of sampling and the absence of any expensive technical equipment, if proper selection of an organism has been made. Due to their common occurrence, lichens and mosses are two biological species that are most commonly used as biomonitors [2].

Terrestrial mosses as biomonitors of atmospheric deposition of trace elements were introduced in Scandinavian countries [2, 3] and shortly after that, usage of the mosses to assess the atmospheric deposition of metals was widely accepted in Europe [1, 4, 5], North America, and some of the countries in Latin America and Asia [6-10]. Although the passive biomonitoring technique is commonly used, there is a growing interest in using the active technique, particularly in heavily polluted areas and urban areas where mosses are not often found in sufficient quantities or are absent [10–13]. Carpet-forming moss species have many advantages as biomonitors compared to higher plants and lichens [14–17].

Pleurozium schreberi (Brid.) Mitt. and *Hylocomium splendens* (Hedw.) Schimp. are the moss species that are most commonly used for biomonitoring of atmospheric deposition of trace elements and were suggested by the guidelines of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation) monitoring manual for the 2005/2006 survey, as well as the procedure used in the previous European moss surveys [4, 18]. However, in areas where these two species cannot be found, alternative moss species are used like *Hypnum cuppressiforme* (Hedw.), *Homalothecium lute-*

scens (Hedw.) Robins., *Hylocomium splendens* (Hedw.) Schimp. BS&G., *Sphagnum girgensohnii* Russow, *Brachythecium salebrosum* (Web. & Mohr) BS&G., *Scleropodium purum* (Hedw.) Limpr., etc. [12–14, 18, 19].

The Republic of Macedonia was involved in the UNECE ICP Vegetation – Heavy Metals in European Mosses, for the first time in 2002 (survey 2000/2001) and again in 2005 when atmospheric deposition of trace elements was studied over the entire territory of the country using samples of terrestrial mosses *Hypnum cupressiforme* and *Homalothecium lutescens* [20–22] (given as *Camptothecium lutescens* in previously published papers [20, 21]). Analysing the results from the first survey, the most important emission sources were determined (mines and drainage systems and smelters near the towns of Veles, Tetovo, Kavadarci and Radoviš), and some uranium deposition patterns were described by the activity of power plants using lignite coal as fuel. A comparison of the results was made with results obtained from similar studies performed in neighboring countries [23–27], as well as a comparison with more pristine territories in other parts of Europe [5, 28–30]. The results from the second survey showed increasing trends of elemental content in mosses that are connected with anthropogenic sources, such as Cd, Co, Pb, Hg and Ni in 2005 compared with the previous survey, but also a decreasing trend in the content of some elements in mosses such as As, Cr, Cu, Sb and Se.

The aim of this paper was (1) to present the results obtained from the 2010 deposition survey in the Republic of Macedonia based on terrestrial moss analysis, using atomic absorption spectrometry (AAS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) as analytical techniques, (2) to report on temporal trends in the heavy metal content in mosses in the Republic of Macedonia between 2002 and 2010, and (3) to classify data and to identify possible sources of the elements and their deposition patterns.

2. EXPERIMENTAL

2.1. *Study area*

The Republic of Macedonia is a landlocked country situated in the central part of the Balkan Peninsula and it has a total area of 25,713 km^2. The total population of the country is two million and around 60% of the population lives in urban areas [31].

The climate is unique, and it is transitional from Mediterranean to the south of the state to continental in the north. Annual precipitation varies from 1400 mm in the western mountainous area to 500 mm in the eastern parts of the country. The wind direction in different parts of Macedonia depends on the orographic conditions. The main industrial capacities in the country are located in Skopje (steel and ferroalloy production and steel processing), Veles (lead, zinc and cadmium smelter and refinery), Radoviš (copper mine and flotation), Kavadarci (ferro-nickel smelter), Tetovo (previously active ferro-chromium smelter and at present ferro-silicon smelter) and Kičevo and Bitola (thermoelectric power plants using lignite as fuel). There are three mines with flotation plants for lead and zinc and one for copper in the eastern part of the Republic of Macedonia. All these industrial activities affect environmental pollution in the mentioned areas with different heavy metals [21, 32–37].

The Macedonian basement consists of four major tectonic units: the Serbo-Macedonian massif (SMM), the Vardar zone (VZ), the Pelagonian massif (PM) and the West-Macedonian zone (WMZ) [38, 39]. A detailed description of the study area and a lithological map of the Republic of Macedonia are given elsewhere [22].

2.2. *Moss species and sampling*

Moss sampling was performed according to the guidelines of the UNECE-ICP Vegetation monitoring manual for air pollution monitoring of the atmospheric deposition of heavy metal deposition using bryophytes, as well as the procedure used in the previous European moss surveys [40]. At 72 locations over the entire territory of the Republic of Macedonia during August and September 2010, samples from the species *Homalothecium lutescens* (Hedw.) Robins. and *Hypnum cupressiforme* (Hedw.) were collected. To aid the analysis of temporal trends in the concentration of heavy metals in mosses, samples were collected from the same sites as in the previous surveys. Both moss species were present at some sampling sites, but no single species was present at all sampling sites due to the large number of types of soil as well as the different climatic conditions over the country. Interspecies comparison performed for the sampling sites where both moss species were present showed an equal content of elements within the error estimates. The distribution of the sampling sites is shown in Figure 1.

Samples were collected at least 300 m from main roads and populated areas and at least 100 m from local roads, and 200 m from villages or single houses. As much as possible, the samples were taken from small forest clearings to reduce the through-fall effects. Sampling below a forest canopy of shrubs and large-leafed herbs was avoided. Five to ten sub-samples were collected within an area of 50 m × 50 m and combined in one sample in order to make the moss samples representative for the site. To prevent any contamination, sampling and sample handling was performed using disposable polyethylene gloves for each sample.

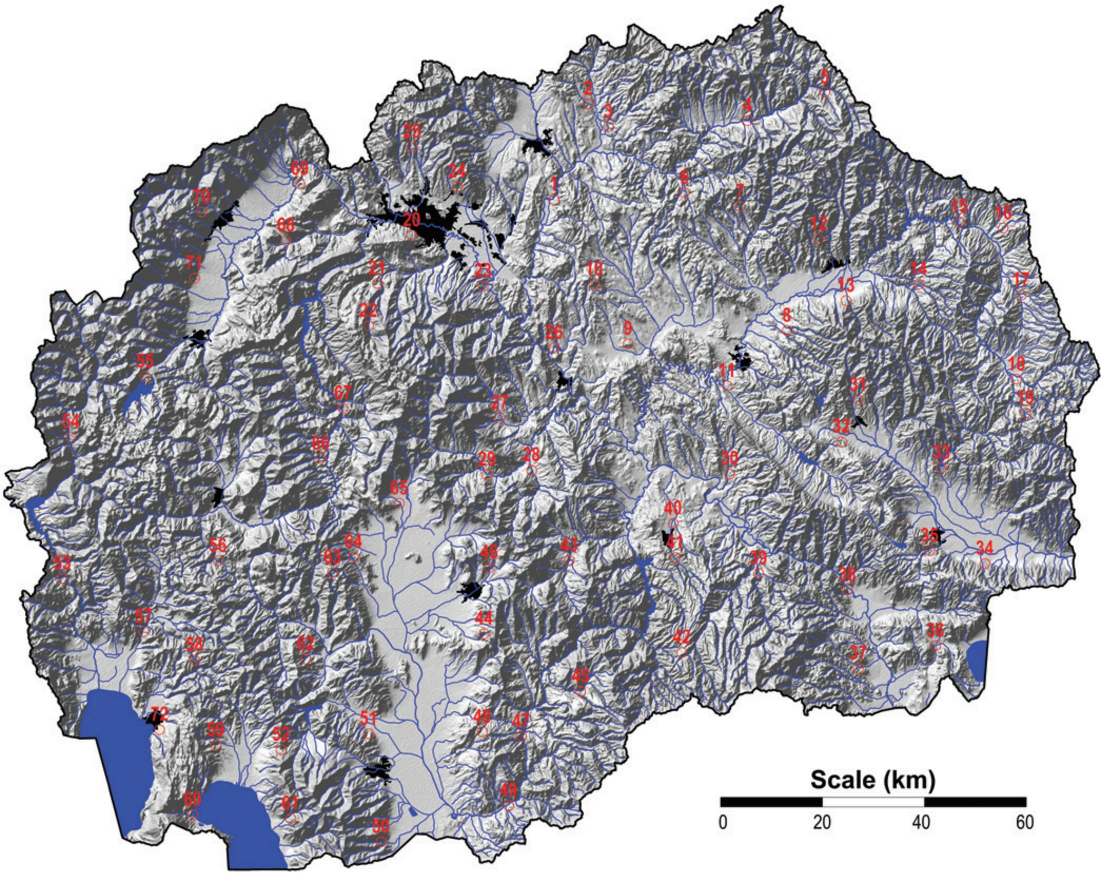

Fig. 1. Sampling network points in the Republic of Macedonia

All the collected samples, after they were cleaned of extraneous material (litter and dead leaves), were stored in paper bags, carefully closed to prevent contamination during transportation and transferred to the analytical laboratory. For each sampling site, longitude, latitude and altitude were noted using GPS (Greenwich co-ordinates, 360º system) as well as details about the sampling site: date and time of sampling, weather conditions, nearby vegetation topography and land use.

2.3. *Sample preparation and digestion*

In the laboratory, the samples were cleaned but not subjected to any further washing and dried to a constant weight for 48 hours at room temperature. Green and green-brown parts of the moss that correspond to three years of moss growth were sorted and prepared for analysis.

For digestion, moss samples (0.5000 g) were placed in Teflon digestion vessels, and 7 ml of trace pure HNO_3 (Merck, Germany) and 2 ml H_2O_2 *p.a*. (Alkaloid, Macedonia) were added, and the vessels were capped closed, tightened and placed in the rotor of a Mars microwave digestion apparatus (CEM, USA). Plant samples were digested at 180 ºC. After cooling, the digested samples were quantitatively transferred into 25 ml calibrated flasks.

2.4. *Reagents and standards*

Stock solutions (11355-ICP Multi Element Standard IV, Merck) of 23 elements with a concentration of 1000 mg l^{-1} served for further dilutions. All chemical reagents used were of analytical grade: HF, *p.a*. (Fluka, Germany); perchloric acid, *p.a.* (Alkaloid, Macedonia); HCl, *p.a.* (MERCK, Germany); H_2O_2, *p.a.* (MERCK, Germany), and HNO_3, *p.a.* (MERCK, Germany). All vessels used were precleaned by leaching for 24 h each in proportions of 1 part HNO_3 and 3 parts HCl, followed by rinsing with double distilled water.

2.5. *Instrumentation*

The analyses were performed at the Institute of Chemistry, Faculty of Natural Sciences and Mathematics in Skopje. All analyzed elements (Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Ni, P, Pb, Sr, V and Zn) were determined by the application of ICP-AES (Varian, 715-ES) applying an ultrasonic nebulizer CETAC (ICP/U-5000AT$^+$) for better sensitivity, electrothermal AAS, ETAAS (Varian SpectrAA 640Z) for the analysis of Cd and Pb, and CV-AAS for Hg. The optimal instrumental parameters for these techniques are given in our previously published paper [41].

2.6. *Quality control*

Quality control was ensured using standard moss reference materials M2 and M3, which were prepared for the European Moss Survey [42]. There was good agreement between the measured concentrations and the recommended values. The method of standard addition was also applied and quantitative recoveries were achieved for most of the elements.

2.7. *Data processing and statistical analysis*

Data processing was performed using the statistical software Stat Soft (Version 9) after all field observations, analytical data and measurements were entered into a data matrix. Parametric and non-parametric statistical methods were used, and normality tests of data distributions were performed [43, 44]. For the set of the samples, the arithmetical mean, geometrical mean, median, minimum, maximum, 10th percentile, 90th percentile, arithmetic standard deviation, geometric standard deviation, coefficient of variance, skewness and kurtosis were calculated, for the content of all 19 elements.

On the basis of normality tests and visual inspection of individual histograms of the distribution of the content of 18 analyzed elements in the samples (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Ni, P, Pb, Sr, V and Zn), logarithms of content values were considered as normally distributed for all the elements except for Ca, K and P, where normality was assumed for the natural values. The degree of association of chemical elements was assessed using the linear coefficient of correlation. Absolute values $r>0.50$ indicated a good relation between the variables [45].

To explain the variation and to reveal associations between chemical elements, all moss samples were examined by multivariate analysis. Multivariate cluster and R-mode factor analyses were used [46–48] The multivariate statistical cluster and factor analyses were performed on 15 selected chemical elements (Al, Ba, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Pb, Sr, V and Zn). Other elements were eliminated from further analysis to satisfy the criteria of dimension variables based on the number of observations and because of their tendency to form their own clusters, not showing a reasonable connection with other chemical elements. Factor analysis (FA) was performed on variables standardized to zero mean and unit standard deviation. For orthogonal rotation, the varimax method was used. With FA, the characteristics of the 15 individual elements were reduced to four synthetic variables, i.e. factors (F1 to F4), which accounted for 78.6% of the total variability of the treated elements.

Universal kriging with the linear variogram interpolation method was applied for the construction of maps showing the spatial distribution of factor scores, as well as maps displaying the distribution of heavy metals in moss samples [46, 49]. The basic grid cell size for interpolation was 1 × 1 km. For class limits, the percentile values of distribution of interpolated values were chosen with following percentile values: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100.

3. RESULTS AND DISCUSSION

The descriptive statistics of the 19 analyzed elements in all collected moss samples ($n = 72$) is shown in Table 1. All values in Table 1 are given in mg kg^{-1}, dry weight. In Table 2, the median values and minimum-maximum ranges for the contents of all elements are compared with the data obtained in the 2005 and 2002 moss surveys in the Republic of Macedonia (number of sampling sites $n = 73$ in 2002 and $n = 72$ in 2005) [21, 22], the data obtained from the European Moss Survey program in 2005/2006 ($n = 6049$) [29], as well as the data from 2010 moss survey in Norway ($n = 464$) [50].

As it can be seen from the results presented in Table 2 and the reported results for other European countries, for median values and minimum–maximum ranges, most of the European countries reported lower median data for As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn in the mosses analyzed in 2005 than those analyzed in 2002 [30]. The situation in the Republic of Macedonia concerning the content of Cd, Ni, Pb was the opposite. The higher content of Cd and Pb in the mosses was explained by pollution from the lead-zinc smelter in Veles which operated until 2003, as well as the pollution that comes from the open slag waste dump of this smelter in the vicinity of Veles and the usage of leaded gasoline in the country in that period. The most evident difference was for the Ni content, which was 2.5-fold higher than its content in moss samples from the 2002 survey, which was explained by the increase in production capacity of the ferro-nickel smelter near Kavadarci beginning in 2004. The median content of As, Cu, Fe, Hg, V and Zn in the mosses in Macedonia were not significantly changed in the two surveys, although slightly lower median values were observed in 2005 compared to 2002 for As, Cu, Fe, V and Zn. The comparison of the median values for Cr, from the two previous surveys in Macedonia, showed a decrease in the content in the mosses. A comparison of the results from the surveys in

Table 1

Descriptive statistics of measurements for moss samples (in mg kg^{-1})

	n	Dis	X_a	X_g	Md	P_{10}	P_{90}	min	max	s_a	s_g	CV	A	E
Al	72	log	2200	1900	1900	1100	3400	540	8700	1400	160	64	0.43	0.48
B	72	log	7.9	3.2	6.6	0.20	14	0.010	94	12	1.4	150	–1.33	1.85
Ba	72	log	41	33	34	13	76	7.1	240	32	3.7	78	–0.03	0.34
Ca	72	N	7300	7100	7100	5500	9800	2900	12000	1700	210	24	0.26	–0.08
Cd*	72	log	0.29	0.23	0.22	0.088	0.44	0.068	2.2	0.29	0.034	100	0.59	1.28
Cr	72	log	4.7	3.8	3.5	2.2	7.5	1.0	40	5.0	0.59	107	1.41	3.99
Cu	72	log	4.0	3.8	3.5	2.6	6.2	2.0	11	1.6	0.19	40	0.71	0.64
Fe	72	log	1700	1500	1500	800	2900	510	6300	1100	130	61	0.39	0.06
Hg	72	log	0.11	0.09	0.09	0.05	0.16	0.01	0.59	0.09	0.01	0.01	3.57	14.2
K	72	N	4800	4700	4600	3800	6100	2100	7600	960	110	20	0.47	0.98
Li	72	log	1.2	1.0	1.0	0.52	2.0	0.29	5.1	0.75	0.088	63	0.29	0.68
Mg	72	log	2000	1900	1900	1500	2800	610	4900	630	74	31	–0.30	3.42
Mn	72	log	150	130	130	56	300	30	440	96	11	63	–0.15	–0.77
Ni	72	log	6.4	4.1	3.5	2.5	11	1.3	52	9.8	1.2	152	1.40	2.76
P	72	N	1100	1100	1100	800	1600	420	2000	310	37	27	0.38	0.35
Pb*	72	log	5.4	4.7	4.6	2.4	8.4	1.9	22	3.3	0.39	62	0.43	0.25
Sr	72	log	28	24	24	11	49	5.6	100	16	1.9	59	–0.15	0.13
V	72	log	3.9	3.3	3.5	1.5	6.2	1.0	17	2.7	0.32	69	0.22	0.47
Zn	72	log	30	20	20	8.0	49	1.0	360	45	5.3	151	–0.23	2.86

* – determined by AAS; n – number of samples; Dis – distribution (log – lognormal, N – normal); X_a – arithmetical mean; X_g – geometrical mean; Md – median; P_{10} – 10 percentile; P_{90} – 90 percentile; min – minimum; max – maximum; s_a – standard deviation; s_g – geometric standard deviation; CV – coefficient of variance; A – skewness; E– kurtosis.

2002 and 2005 with the median values reported for Europe showed that the median values for the Republic of Macedonia were higher for all elements.

The comparison made for the median values calculated for the results obtained from the moss samples in Macedonia in 2010 with the median values for Europe calculated on the basis of the content of the elements in 6049 moss samples collected in 34 European countries shows that Macedonia had higher median values for Cd (1.5), Cr (2.9), Fe (2.8), Ni (2.6), Pb (4.3), V (2.3) and Zn (1.1) and only lower median value for Cu (0.9). The number in the brackets represents the ratio between the median values for Macedonia and the median values for 34 European countries.

Analysing the trend of the median values calculated for the three moss surveys in Macedonia, it can be seen that in the last survey, lower median values were observed for all elements that were analyzed for the moss survey in 2010. The analysis with AAS as well as ICP-AES (for the 2010 survey) was based on nitric acid digestion, using non-destructive NAA determination (for 2002 and 2005 surveys), the entire amount of the elements in question was analyzed. The lower median values for Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Sr, V and Zn can be explained by the difference in the analytical techniques and potentially leaving out a fraction of the elements due to their refractory minerals [51].

In the 2002 and 2005 surveys, Cd, Cu and Pb were analyzed by AAS and all other elements were analyzed by NAA. In 2010, Pb was also analyzed by AAS, but Cd and Cu were analyzed by ICP-AES (Table 2). Both

T a b l e 2

Comparison of the median values and ranges of element content in moss from Macedonia between data of the moss survey 2010 and moss surveys in 2002 and 2005 and European moss survey program (all data are given in mg kg^{-1})

	Macedonia moss survey 2010 (Present work)		Macedonia moss survey 2005 [22]		Macedonia moss survey 2002 [21]		European moss survey 2005/2006 [29]		Norway moss survey 2010 [50]	
No of samples	*n* = 72		*n* = 72		*n* = 73		*n* = 6049		*n* = 464	
Element	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
Al	1900	540–8700	3600	1466-25860	3736	825–17600	–	–	238	46–4581
B	6.6	0.010–94	–	–	–	–	–	–	3.3	<0.2–19.4
Ba	34	7.1–240	52	18–184	54	14–256	–	–	25	4–325
Ca	7100	2900–12000	8547	5237–16280	5593	1207–23640	–	–	2787	873–8515
Cd	0.22*	0.068–2.2*	0.29*	0.015–3.01*	0.16*	0.016–2.95*	0.20	0.07–1.26	0.081	0.009–1.875
Cr	3.5	1.0–40	6.79	2.09–82	7.47	2.33–122	2.32	0.72–29.33	0.59	0.16–47.87
Cu	3.5	2.0–11	6.7*	0.7–21.4*	7.65*	2.9–29.4*	6.80	3.07–91.20	4.0	1.4–443.4
Fe	1500	510–6300	2238	998–8130	2458	424–17380	799	233–6147	278	27–24684
Hg	0.09	0.01–0.59	0.07	0.01–0.42	0.06	0.02–0.26	0.06	0.01–0.42	0.06	0.02–0.34
K	4600	2100–7600	7510	4652–13530	8615	2861–18190	–	–	3867	1763–8659
Li	1.0	0.29–5.1	–	–	–	–	–	–	0.117	0.011–1.277
Mg	1900	610–4900	1311	658–3351	2377	674–7421	–	–	1335	502–3128
Mn	130	30–440	188	54–595	186	37–1475	–	–	292	19–2653
Ni	3.5	1.3–52	5.8	1.80–43	2.4	0.09–24	2.26	0.71–63.39	1.16	0.15–856.66
P	1100	420–2000	–	–	–	–	–	–	–	–
Pb	4.6*	1.9–22*	7.6*	0.1–46.1*	6.0*	1.5–37.2*	1.76	1.76–46.94	1.54	0.33–20.83
Sr	24	5.6–100	34	13–140	31	12–136	–	–	15.1	1.9–72.0
V	3.5	1.0–17	6.4	2.50–32	6.9	1.79–43	2.82	0.80–21.56	1.41	0.29–25.88
Zn	20	1.0–129	36	16–91	39	14–203	33.6	15.2–176.8	30.7	7.4–368.4

* - determined by AAS

techniques are based on nitric acid digestion and the comparison of the median values shows that the content of Cd, Cu and Pb in mosses in 2010 was lower than the content of the elements in the mosses in the two previous surveys. This result can be explained by the closing of the lead-zinc smelter in the town of Veles in May 2004 and a significant reduction in the use of leaded gasoline in the past few years.

In comparison with the only published results from the moss survey in 2010, the results from Norway, which is usually considered one of the most pristine areas in Europe, Macedonia had a higher median value for the element content in mosses for all elements except for Mn and Zn. A comparison of the maximum values obtained for the two surveys shows that maximum values were higher in Macedonia for Al, B, Ba, Ca, Cd, Li, Mg, Na, Ni, Pb and Sr. The opposite situation was observed for the maximum values of Cr, Cu, Fe, K, Mn V, and Zn. The much higher median content of crustal elements such as Al, Ba, Ca, Fe, Li can be explained by the drier climate in Macedonia than Norway and the high influence of the content of these elements in mosses due to wind erosion, especially in the dry periods of the year. The lower median value for Mn can be explained by the lower density of higher plants in Macedonia than in Norway, since it is believed that there is an influence of uptake and secretion by higher plants on the content of Mn in mosses. Some conclusions can also be extracted from the observation of the maximum values for this element. The higher maximum values in Norway for some elements but lower median values than the median values for Macedonia can be explained by the small influence of local industries in Mo, Rana and Odda (Norway) to air pollution in the entire country.

3.1. *Associations between chemical elements*

The matrix of rotated factor loadings is given in Table 3. 78.6% of the variability of the treated elements was explained by four identified factors. These factors were identified by a visual inspection of similarities in the spatial distribution of element patterns, the correlation coefficients, a comparison of basic statistical parameters and the results of multivariate analyses.

Table 3

Matrix of rotated factor loadings (n = 72, 15 selected elements, F > 0.55)

Element	F1	F2	F3	F4	Com (%)
Al	**0.86**	0.21	0.36	–0.01	91.0
V	**0.83**	0.24	0.33	–0.11	87.4
Fe	**0.81**	0.24	0.46	–0.09	93.3
Ba	**0.77**	0.04	–0.09	0.29	68.1
Li	**0.76**	0.20	0.47	0.02	83.4
Sr	**0.75**	0.09	0.05	0.21	61.9
Cu	0.39	**0.56**	0.30	0.20	60.5
Zn	0.17	**0.88**	0.12	0.08	82.8
Pb	0.15	**0.77**	0.16	–0.36	76.8
Cd	0.06	**0.88**	0.02	0.14	80.6
Mg	0.51	-0.03	**0.57**	0.22	63.8
Cr	0.36	0.19	**0.86**	–0.09	91.3
Ni	0.11	0.17	**0.87**	–0.15	82.6
P	0.20	0.04	–0.18	**0.82**	74.4
K	0.04	0.04	0.06	**0.89**	80.8
Var (%)	29.7	18.3	17.9	12.7	78.6

F1, F2, F3 and F4 – Factor loading; Var – Variance (%); Com – Communality (%)

Factor 1 (Al, V, Fe, Ba, Li, Sr) is the strongest factor, representing nearly 30% of the total variability. This group represents chemical elements that are probably naturally distributed. The content of these elements in mosses is significantly influenced by mineral particles released into the atmosphere by wind erosion of local sources or particles attached to the moss in the periods when the soil surface is covered by water. The distribution of these elements is independent of populated and industrialized areas, and these elements are usually not connected to air pollution. The spatial distribution of Factor 1 scores is presented in Figure 2. The highest contents of the elements were found in moss samples which were collected on Precambrian and Paleozoic shists or close to them. The presence of Sr in this group can be explained by the influence of the volcanic rocks in some areas of the country, especially in the area of Kratovo. The high content of these elements in the region of Bitola (Pelagonia valley) can be explained by fly ash emission from the lignite-burning power plant. Usually, the content of this element in mosses collected in northern European countries is much lower [50], but reported values for the same element in other Balkan countries [52-54], which are close to the values for Macedonia, indicate that a dry climate has a significant impact on the distribution.

Second strongest factor was Factor 2, explaining 18.3% of the total variability. The presence of Cu, Zn, Cd and Pb in this group (Figure 3) indicates that this is an anthropogenic geochemical association of elements. This factor is connected to industrial activity in Macedonia. A high content of these elements in mosses was observed near the towns of Skopje, Veles and Radovis, as well as in the eastern part of the country. By May 2003, a lead and zinc smelter plant was operational in the city of Veles. The open slag waste dump of this smelter in Veles still is contributing to pollution with Cd, Zn and Pb in this region (Figures 4–6). The wind of Vardarec also contributes to pollution with these elements along the river of Vardar. The high density of road traffic in the region of Skopje, the presence of a central heating station in the town and an oil refinery in the vicinity of the town also contribute to the presence of these elements in the Skopje region. A zone with high values of Cd, Pb and Zn (Figure 3) was found in the eastern parts of Macedonia as well, because of the operation of three lead and zinc mines (Sasa, Toranica and Zletovo) [55, 56] as well as one open pit copper mine on the southeast, near the city of Radoviš [34, 35] (Figure 7).

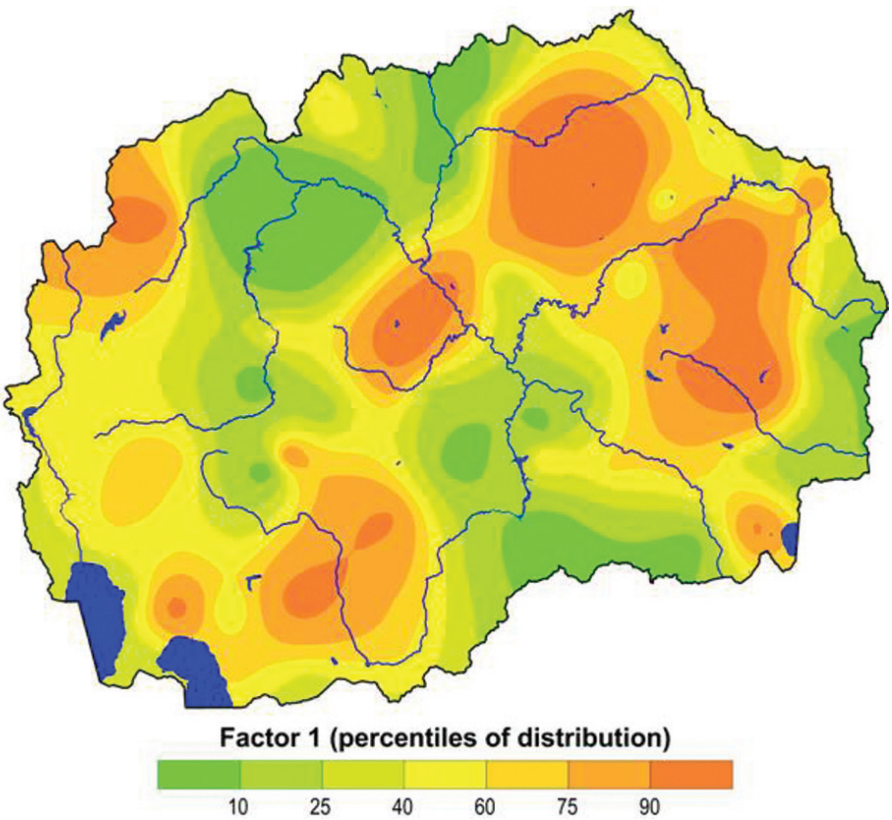

Fig. 2. Spatial distribution of Factor 1 scores (Al-Ba-Fe-Li-Sr-V)

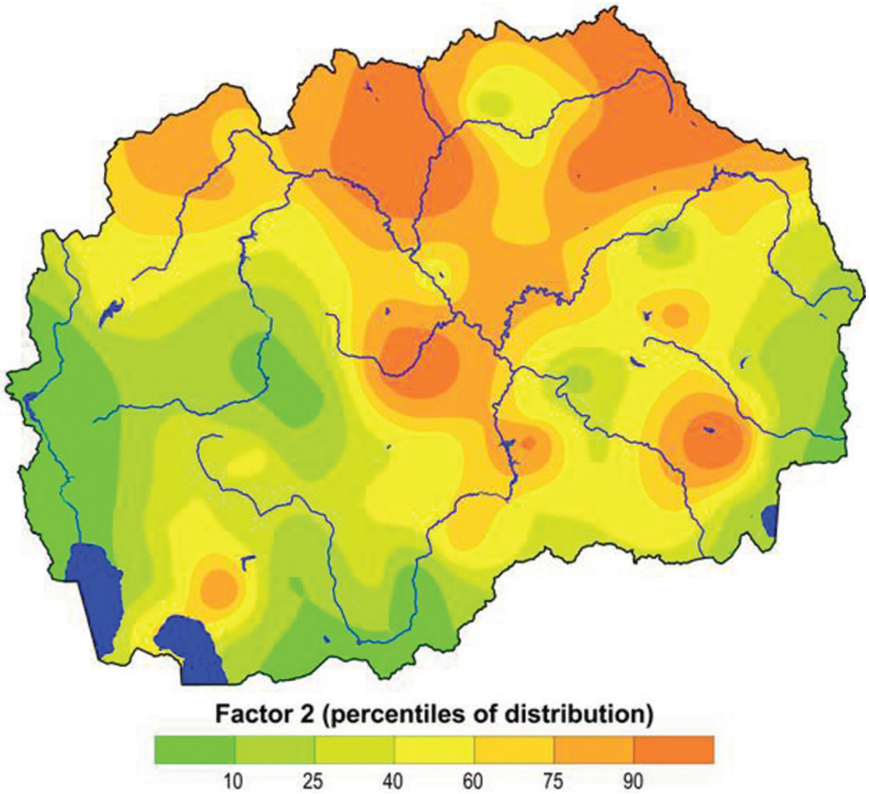

Fig. 3. Spatial distribution of Factor 2 scores (Cd-Cu-Pb-Zn)

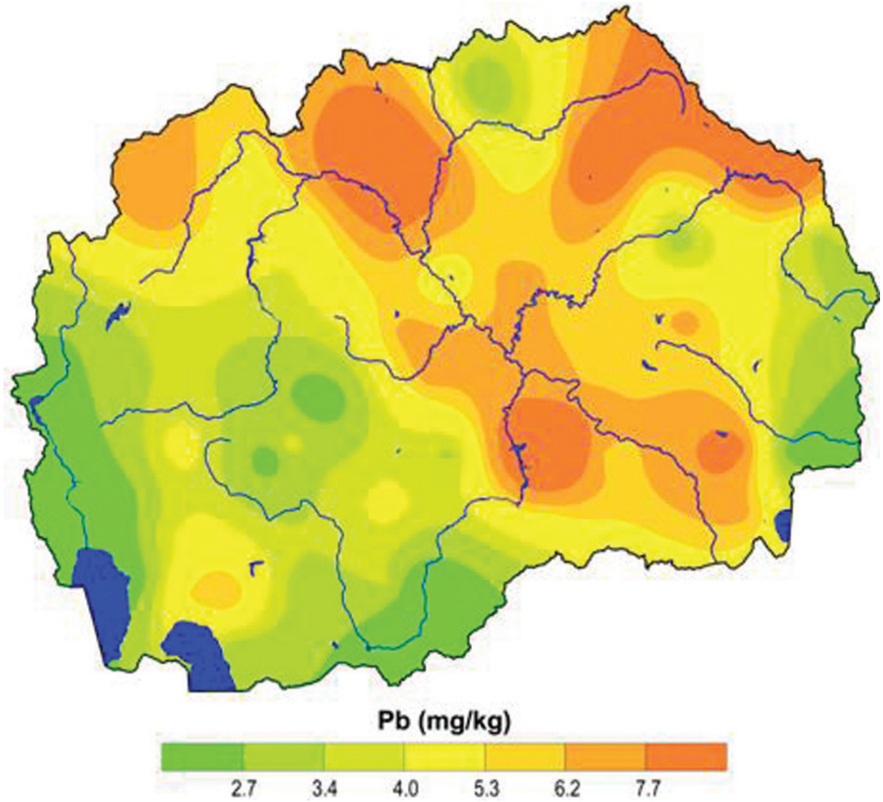

Fig. 4. Spatial distribution of lead

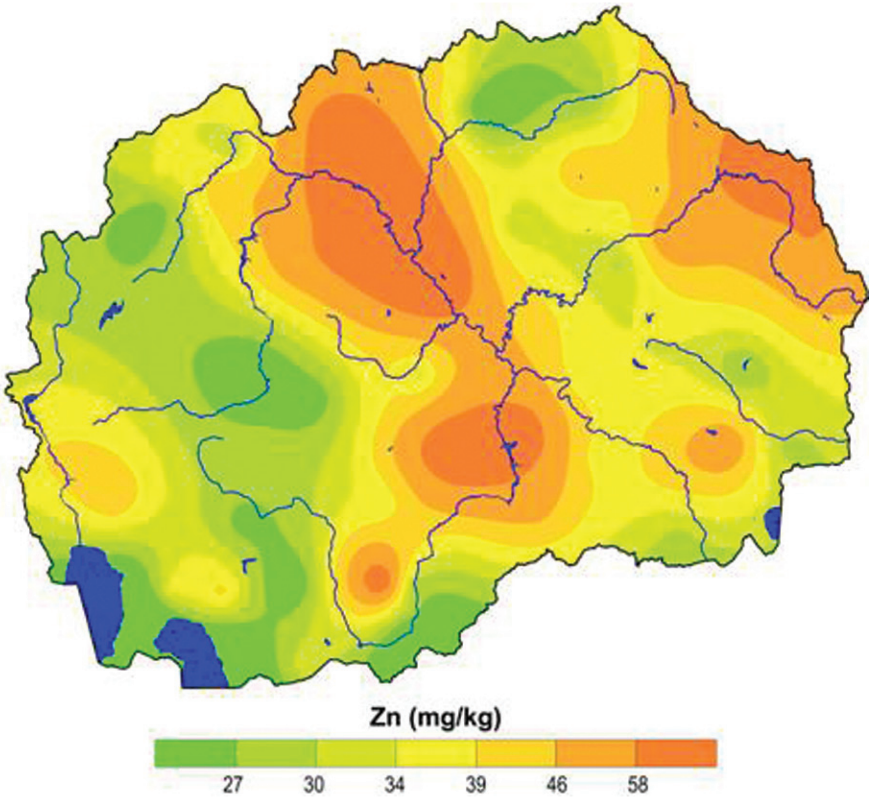

Fig. 5. Spatial distribution of zinc

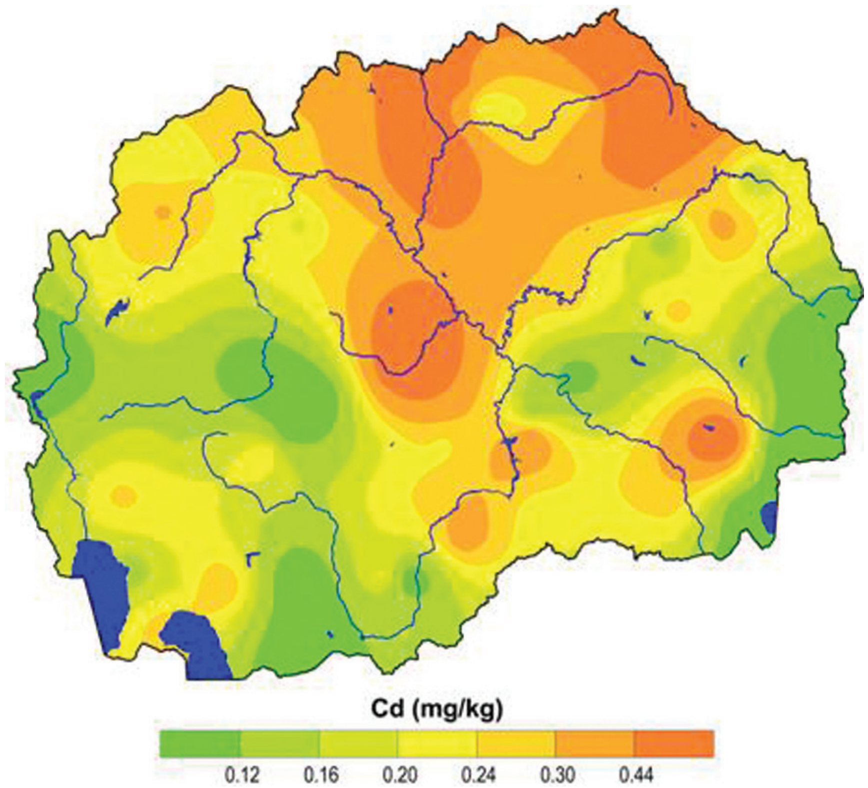

Fig. 6. Spatial distribution of cadmium

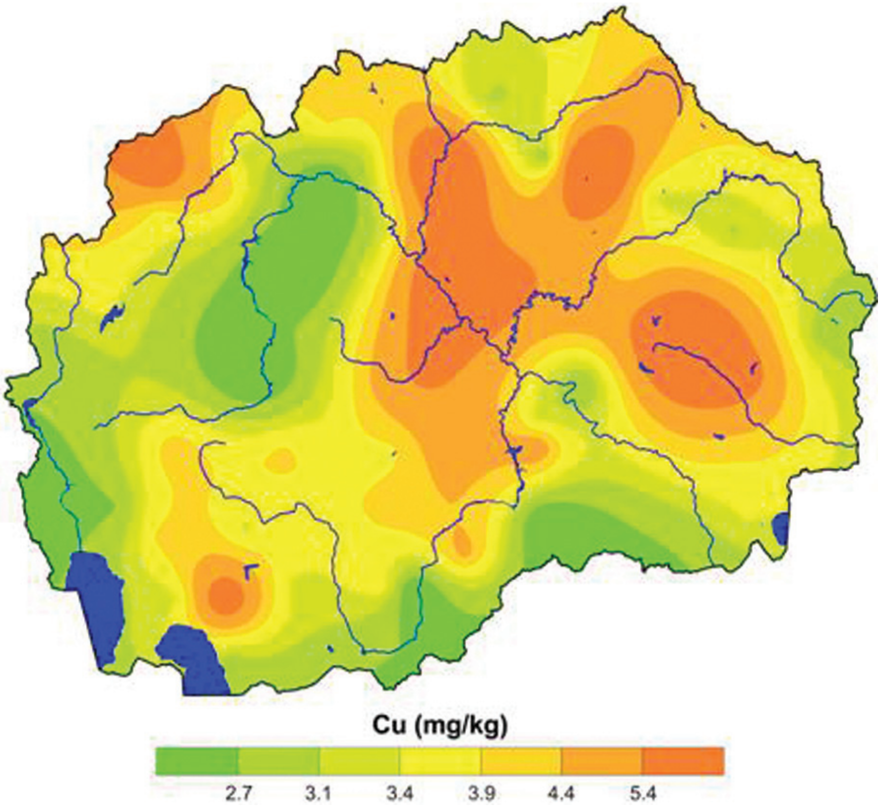

Fig. 7. Spatial distribution of copper

Factor 3 (Mg, Cr and Ni) represents a mixed (geogenic-anthropogenic) association of elements. The specific content of these elements is primarily affected by natural factors such as lithological background, but there is an anthropogenic influence as well. High values of aforementioned elements were clearly isolated in the Vardar zone (Figure 8), where Paleogene (Pg) flysch sediments and Ng sediments occur that have been repeatedly demonstrated in Macedonia [33–37]. The geogenic influence of nickel, reaching the locality of Groot near the town of Veles (central part), is also present [55, 56]. High contents of these elements were found in mosses along the Vardar and Crna river valleys (Figure 8), where the constant flow of air masses is present in both directions [57]. High concentrations of Ni were present near the ferro-nickel smelter in the town of Kavadarci (Figs. 9 and 10) situated in the south-central part of the country [36, 37, 58, 59], and near the former ferro-chromium smelter near Tetovo (northern part). The marine influence from the Aegean sea was most dominant along the Vardar river, which explains the high content of Mg in the mosses in this region.

Factor 4 (P and K) represents the second anthropogenic geochemical association of elements (Figure 11). It was the weakest factor, explaining 12.7% of total variability. For the first time, the content of P in moss samples collected from Macedonia was determined since the ICP-AES analytical technique was used. NAA is not suitable for P due to interference from a ^{30}Si (n, γ) ^{31}Si (β^{-}) ^{31}P reaction and the (n, α) decay of phosphorus to aluminum via a ^{31}P (n, α) ^{28}Al reaction [60]. High values of these elements were found in the regions where agricultural activities are present in the country, i.e. near the towns of Bitola and Prilep (Pelagonia region), in the southwest of the country, Strumica in the southeast of the country, and the region of Polog, near the towns of Tetovo and Gostivar in the northwest of the country. An apparent reason for the high content of K and P in the moss samples collected in these regions is the usage of potassium and phosphorus fertilizers in agricultural activities. This conclusion

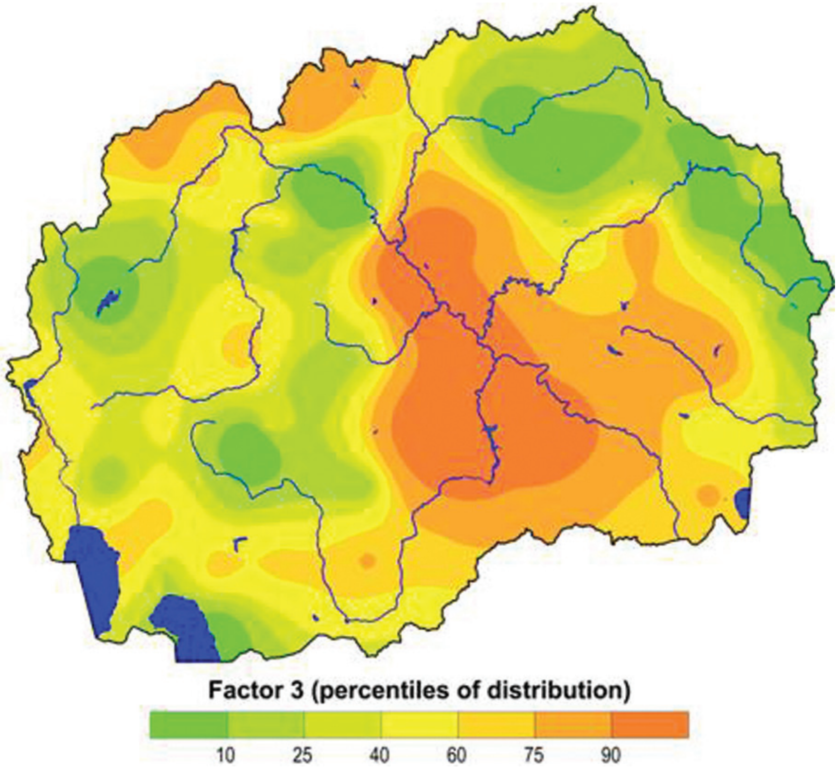

Fig. 8. Spatial distribution of Factor 3 scores (Cr-Mg-Ni)

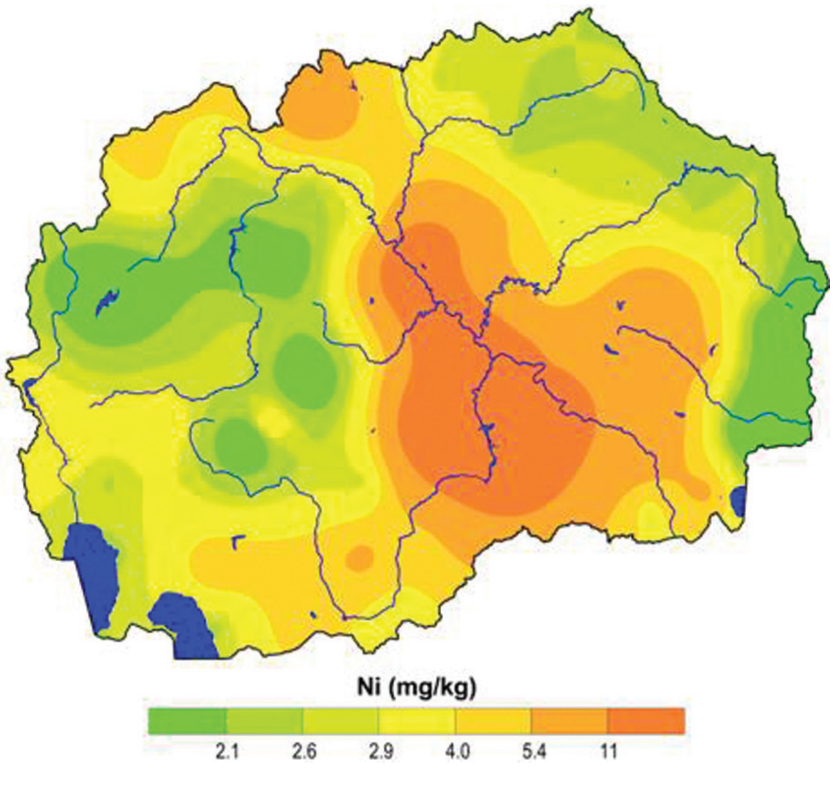

Fig. 9. Spatial distribution of nickel

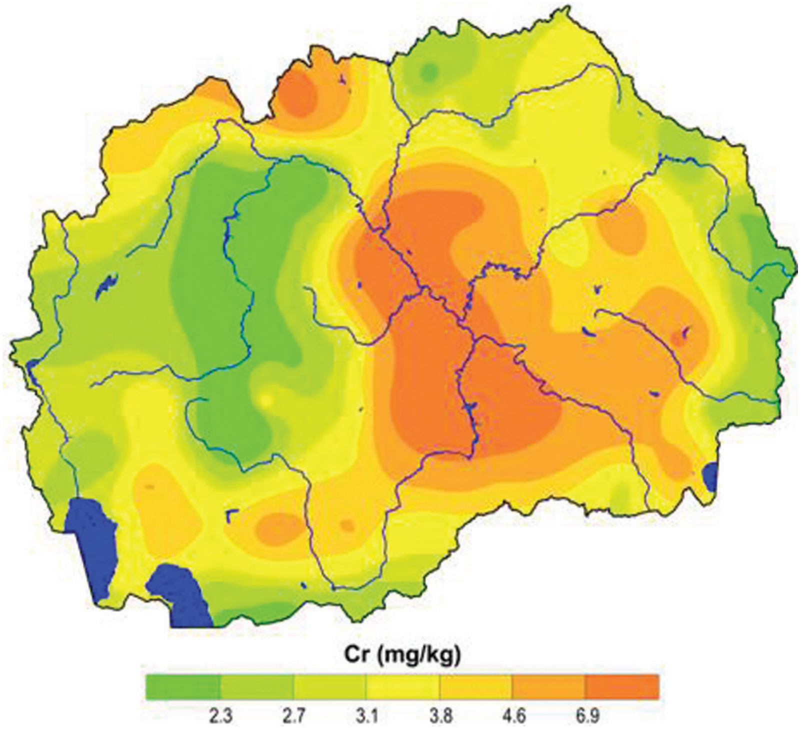

Fig. 10. Spatial distribution of chromium

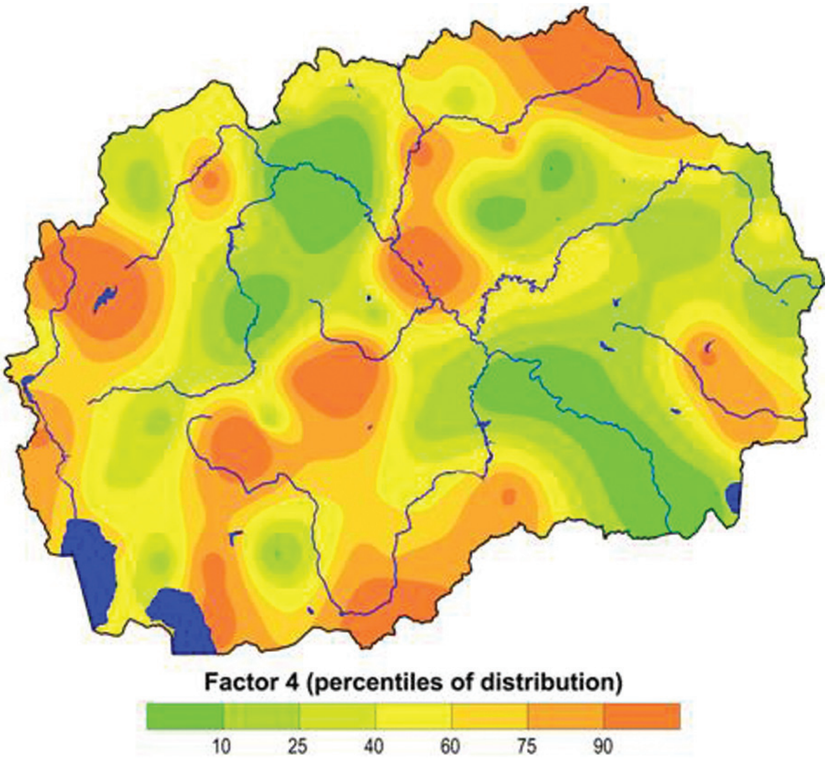

Fig. 11. Spatial distribution of Factor 4 scores (K-P)

indicates the releasing of soil particles into the atmosphere, not just by wind erosion of local soils, but also by agricultural activities in some regions.

4. CONCLUSION

While most European countries have reported decreasing trends in the elemental content in mosses that are connected with anthropogenic sources, such as Cd, Pb, Cr, Ni and Zn, in the period from 2000 to 2005, the data obtained for Macedonia show the opposite trend for the mentioned elements, except for Cr. The results from 2010 showed a lower elemental content in the mosses for the mentioned elements than the results obtained in 2005. Again, the most important pollution sources appear to be smelters of Skopje and Kavadarci, open slag dumps in Veles and Tetovo, the Pb-Zn mines of Sasa, Toranica and Zletovo and the Cu mine of Bučim. Agricultural activities and the use of artificial fertilizers in some areas of the country have an influence on the content of K and P in mosses, indicating that emission of soil particles in these regions is higher due to this activity. In comparison with the results obtained in the 2010 moss survey in Norway, Macedonia has a higher median value for the elemental contents of practically all elements that are usually connected with air pollution. Higher maximum but lower median values for some of these elements in Norway indicate that the local pollution sources in Norway have a small or no effect on the air pollution of the entire country, which is not the situation in the Republic of Macedonia.

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