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AIR POLLUTION STUDIES IN MACEDONIA
USING THE MOSS BIOMONITORING TECHNIQUE,
NAA, AAS AND GIS TECHNOLOGY

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Впервые метод мхов-биомониторов был применен к изучению воздушных загрязнений в Республике Македонии, в центре Балканского полуострова. Образцы мхов *Hypnum cupressiforme*, *Campothecium lutescens* и *Homolothecium sericium* были собраны в сентябре–октябре 2002 г. в соответствии с правилами Европейской программы одновременного сбора мха. Сеть пробоотбора включала в себя 73 площадки, равномерно распределенных на территории страны. В целом 43 элемента (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Ag, Cd, In, Sb, I, Cs, Ba, La, Ce, Sm, Eu, Tb, Hf, Ta, W, Au, Hg, Pb, Th и U) были определены с помощью инструментального эпитеплового нейтронного активационного анализа и пламенной атомной абсорбционной спектрометрии в широком интервале концентраций — от 10000 мг/кг Al и K и 0,001 мг/кг некоторых редкоземельных элементов. Метод главных компонент (факторный анализ) использовался для идентификации и характеристики. Было выявлено девять факторов различных источников загрязнения. Происхождение трех факторов связано с элементами земной коры, морскими и растительными элементами. Остальные отражают антропогенное происхождение выпадения ряда следовых элементов: черная и цветная металлургия, нефтеперерабатывающая промышленность, производство удобрений и станции центрального отопления. Четыре области испытывают экологический стресс: Велес, Скопье, Тетово и Кавадарци, в то время как сельскохозяйственный юг, юго-запад и юго-восток характеризуются среднеевропейскими значениями для большинства тяжелых металлов и других элементов-загрязнителей. Технологии ГИС (географическая информационная система) использовались для построения черно-белых карт распределений значений факторов (factor scores) и цветных контурных карт распределений некоторых элементов, соответствующих этим факторам на исследованной территории.

Работа выполнена в Лаборатории нейтронной физики им. И. М. Франка ОИЯИ и в Университете им. Св. Кирилла и Мефодия в Скопье.

For the first time the moss biomonitoring technique was applied to air pollution studies in the Republic of Macedonia, in the central part of the Balkan Peninsula. Samples of the terrestrial mosses *Hypnum cupressiforme*, *Campothecium lutescens*, and *Homolothecium sericium* were collected in September–October 2002 in accordance with the sampling strategy of the European moss survey programme. The sampling network included 73 sites evenly distributed over the territory of the country. A total of 43 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Ag, Cd, In, Sb, I, Cs, Ba, La, Ce, Sm, Eu, Tb, Hf, Ta, W, Au, Hg, Pb, Th, and U) were determined by instrumental epithermal neutron activation analysis and flame atomic absorption spectrometry in the large-scale concentration range — from 10.000 mg/kg for Al and K to 0.001 mg/kg for some rare earths. Principal component factor analysis was used to identify and characterize different pollution sources and to point out the most polluted areas. Nine factors were identified. The interpretation of the factor analysis findings points to natural crustal, marine, and vegetation components. Other factors reflect anthropogenic origin of trace element deposition in the Macedonian moss samples: ferrous and non-ferrous industries, oil refining, fertilizer production and central heating stations. Four areas are experiencing environmental stress: Veles, Skopje, Tetovo and Kavadarci-Negotino, whereas the predominantly agricultural regions in the south, south-west and south-east show median European values for most of heavy metals and other element-pollutants. GIS technology (geographic information system) is used for constructing black-and-white maps based on factor scores along with coloured maps of the distribution of some relevant elements for these factors over the investigated territory.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR, and at Sts. Cyril and Methodius University, POB 162, 1000 Skopje.

INTRODUCTION

The use of mosses as biomonitors was introduced in Scandinavian countries more than three decades ago, and it is presently widely accepted as a method to assess the atmospheric deposition of metals [1, 2]. Mosses have only a rudimentary root system and readily take up elements from the atmosphere. The advantage of the method is in the simplicity of sample collection, although the determination of the species needs an experienced hand. Data from existing surveys of heavy metal concentrations in mosses are an invaluable resource for international negotiations on heavy metal pollution. Results from moss surveys allow examination of both spatial and temporal trends in heavy metal concentration/deposition, and identification of areas where there is high deposition of heavy metals from long-range transport and local sources.

The Task Force on Heavy Metals was established by the United Nations Economic Commission for Europe Convention on Long-Range Transboundary Air Pollution (UNECE — CLRTAP) as a response to the concern over the accumulation of heavy metals in ecosystems, and their impacts on the environment and human health. The heavy metals moss project is coordinated by the Co-ordination Centre of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation) [3].

In the Republic of Macedonia the first systematic study of atmospheric pollution from heavy metals and

other toxic elements based on moss analysis was undertaken in the framework of Macedonian–Russian collaboration in order to assess the general situation regarding heavy metal pollution and to jointly report these results to the European Atlas of Heavy Metal Atmospheric Deposition issued by UNECE ICP Vegetation [3, 4].

The presence of heavy metals in air within the Macedonian territory had been previously studied only for some particular locations such as the towns of Veles and Skopje, using atomic absorption spectrometry (AAS) for determination of a limited number of elements [5–9]. In 2002 moss samples were collected over the entire territory of Macedonia and subsequently analyzed by multi-element instrumental epithermal neutron activation analysis, previously successfully used by the authors in similar studies in Russia [10–12] and in some Balkan countries: Romania [13, 14], Bulgaria [15], Northern Serbia and Bosnia [16]. The primary task of the present study was to reveal unknown pollution sources and to depict the geographical deposition patterns in the areas affected by anthropogenic impact of heavy metals.

In addition, the results obtained might be useful for elucidating different endemic health problems existing in the Balkans, such as Balkan endemic nephropathy, endemic arsenosis, and diseases caused by iron and selenium deficiency, which are hypothetically connected with the environmental contamination with toxic substances [17].

Although the most obvious reason for this kind of study concerns human health problems and environmental problems from air pollution, a possible

economic impact of the pollution is also an important issue, having in mind that Macedonia is an exporter of food products.



Fig. 1. Study area — Republic of Macedonia



Fig. 2. Sampling network in Macedonia

STUDY AREA

The Republic of Macedonia, located in the central part of the Balkan Peninsula (Fig. 1), is a landlocked country with an area of 25.713 km² and approximately 50% of the territory in mountainous regions. The climate is continental in the north and Mediterranean in the south. The population of the country is around 2 million people, of which about 60% live in urban areas. The major urban areas are Skopje, Bitola, Tetovo, Kumanovo,

Veles, Prilep, Štip, Ohrid, Strumica, and Gostivar. The largest industries (by value of annual output) are coal production, metal production (chromium in the recent past, lead, zinc, steel, ferronickel, and ferrosilicon), and textiles. Industry and mining constitute 35% of the gross national income [18].

The sampling network with numbered sampling sites is shown in Fig. 2.

EXPERIMENTAL

Sampling. Samples of the three moss species *Hypnum cupressiforme*, *Camptothecium lutescens* and *Homolothecium sericium* (Fig. 3) were collected at 73 localities evenly distributed over the country during the period September–October, 2002.

The sampling was carried out in accordance with the strategy of the European moss survey programme [1]. Samples were collected at least 300 m from main roads, at least 100 m from local roads and at least 200 m from villages, in forest glades or on open heath to reduce through-fall effects from the forest canopy. In order to make the moss samples representative for a reasonably large area, each sample was composed of five to ten sub-samples collected within an area of 50 × 50 m. Collected material was stored in paper bags. A separate set of dis-

posable polyethylene gloves was used for collection of each sample. *Hypnum cupressiforme* — both *epigeic* and *epiphytic* — was the dominant moss type (80% of all collected samples). Interspecies comparison (possible in a limited number of cases) did not reveal great difference in the elemental concentrations. It was mostly within the error estimations.

Analysis. NAA. Neutron activation analysis (NAA) was performed at the pulsed fast reactor IBR-2 in the Frank Laboratory of Neutron Physics, Dubna, Russia.

In the laboratory the samples were cleaned from extraneous plant material and air-dried to constant weight at 30–40°C for 48 h. The samples were neither washed nor homogenised. Green-brown moss shoots represent-

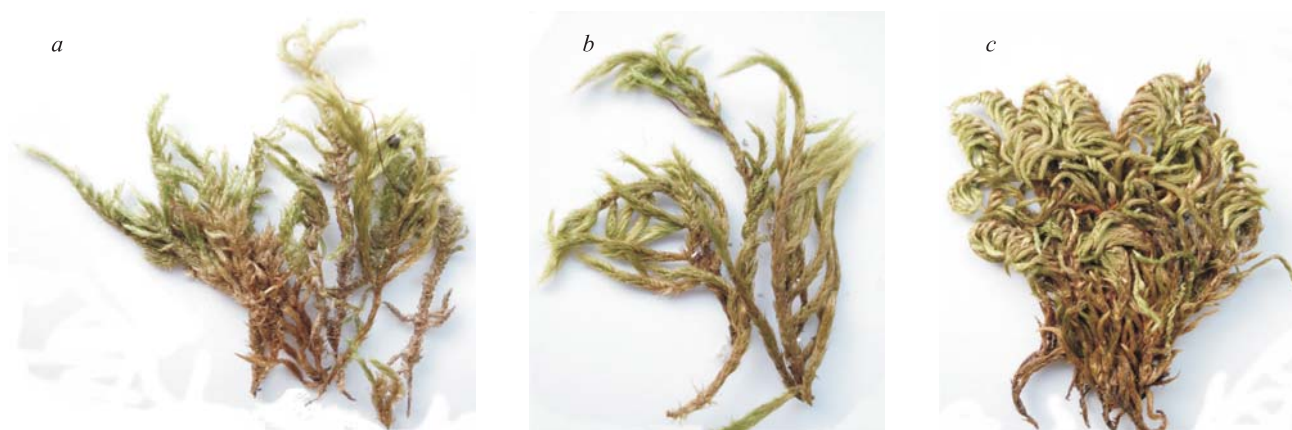


Fig. 3. Moss species used in the present study: a) *Hypnum cupressiforme*; b) *Camptothecium lutescens*; c) *Homolothecium sericium*

Table 1. Flux parameters of irradiation positions [20]

Irradiation position	$\Phi_{th} \cdot 10^{12}, \text{cm}^{-2} \text{s}^{-1}$ ($E = 0 \div 0.55 \text{ eV}$)	$\Phi_{th} \cdot 10^{12}, \text{cm}^{-2} \text{s}^{-1}$ ($E = 0.55 \div 10^5 \text{ eV}$)	$\Phi_{th} \cdot 10^{12}, \text{cm}^{-2} \text{s}^{-1}$ ($E = 10^5 \div 25 \cdot 10^6 \text{ eV}$)
Ch1 (Cd-screened)	0.023	3.3	4.2
Ch2	1.23	2.9	4.1

ing the last three years' growth were subjected to analysis, as they correspond approximately to the deposition over the last three years. Previous experience from the use of NAA in moss biomonitoring has shown that samples of 0.3 g are sufficiently large to be used without homogenization [19]. The samples were pelletized before irradiation using simple press-forms. For short irradiation

unwashed samples of about 0.3 g were heat-sealed in polyethylene bags. For long irradiation samples of the similar weight (about 0.3 g) were packed in aluminium cups. Characteristics of neutron flux density in the channels equipped with the pneumatic system are given in Table 1.

To determine short-lived isotopes the samples were irradiated for 3 min. After irradiation two gamma-spectrometric measurements were performed; the first one for 5 min after 2–3 min of decay, and the second one for 20 min after 9–10 min of decay.

Long-lived isotopes were determined after irradiation for 100 h in the cadmium-screened channel 1. After irradiation samples were repacked into clean containers and measured after 4–5 and 20–23 d for 45 min and for 3 h, respectively. Gamma-spectra were registered as described elsewhere [21].

Table 2 lists selected peak energies for NAA and method of analysis. The gamma-spectra of the induced activity were analyzed using software developed in the Frank Laboratory of Neutron Physics [22].

AAS. The environmentally important element lead cannot be determined by INAA, and mercury Hg is difficult at low concentration levels. These elements were

Table 2. List of selected peak energies for NAA and method of analysis

Element	Isotope	Half life	Gamma peak, keV	Method of analysis*
Na	²⁴ Na	14.7 h	2753.6	3
Mg	²⁷ Mg	9.5 m	1014.1	2
Al	²⁸ Al	2.2 m	1778.9	1
Cl	³⁸ Cl	37.2 m	2168.8	2
K	⁴² K	12.4 h	1524.7	3
Ca	⁴⁹ Ca	8.7 m	3084.4	2
Sc	⁴⁶ Sc	83.8 d	889.2	4
Ti	⁵¹ Ti	5.8 m	320.1	1
V	⁵² V	3.8 m	1434.1	1
Cr	⁵¹ Cr	27.7 d	320.1	4
Mn	⁵⁶ Mn	2.6 h	1810.7	2
Fe	⁵⁹ Fe	44.5 d	1099.2	4
Co	⁶⁰ Co	5.3 y	1173.1	4
Ni	⁵⁸ Co	70.9 d	810.8	4
Zn	⁶⁵ Zn	244.0 d	1116.0	4
As	⁷⁶ As	26.3 h	559.1	3
Se	⁷⁵ Se	119.8 d	264.7	4
Br	⁸² Br	35.3 h	776.5	3
Rb	⁸⁶ Rb	18.7 d	1076.6	4
Sr	⁸⁵ Sr	64.8 d	514.0	4
Mo	⁹⁹ Mo	66.0 h	140.5	3
Ag	^{110m} Ag	249.8 d	657.7	4
Cd	¹¹⁵ Cd	53.5 h	527.7	3
In	^{115m} In	4.5 h	336.2	3
Sb	¹²⁴ Sb	60.2 d	1691.0	4
I	¹²⁸ I	25.0 m	442.9	2
Cs	¹³⁴ Cs	2.1 y	795.8	4
Ba	¹³¹ Ba	11.8 d	496.8	4
La	¹⁴⁰ La	40.2 h	1596.5	3
Ce	¹⁴¹ Ce	32.5 d	145.4	4
Eu	¹⁵² Eu	13.3 y	1407.5	4
Tb	¹⁶⁰ Tb	72.3 d	879.4	4
Hf	¹⁸¹ Hf	42.4 d	482.0	4
Ta	¹⁸² Ta	114.4 d	1221.4	4
W	¹⁸⁷ W	23.9 h	685.8	3
Au	¹⁹⁸ Au	2.7 d	411.8	3
Th	²³³ Pa	27.0 d	312.0	4
U	²³⁹ Np	2.4 d	228.2	3

*Method 1: conventional NAA, measured after 2–3 min of decay;
 Method 2: conventional NAA, measured after 9–10 min of decay;
 Method 3: epithermal NAA, measured after 4–5 d of decay;
 Method 4: epithermal NAA, measured after 20–23 d of decay.

Table 3. Optimal instrumental parameters for lead determination by ZETAAS

Wavelength, nm	283.3
Slit width, nm	0.5
Lamp current, mA	10
Calibration mode	Absorbance, peak area
Correction	Zeeman
Gas	Argon
Drying	
Temperature, °C	120
Ramp time, s	45
Hold time, s	10
Pyrolysis	
Temperature, °C	400
Ramp time, s	5
Hold time, s	15
Atomization	
Temperature, °C	2100
Ramp time, s	0
Hold time, s	2
Internal gas flow, mL·min ⁻¹	0
Cleaning	
Temperature, °C	2500
Ramp time, s	1
Hold time, s	2

therefore determined by atomic absorption spectrometry (AAS) at the Sts. Cyril and Methodius University, Scopje, Macedonia.

Moss samples (0.5 g) were placed in a Teflon digestion vessels, 5 mL concentrated nitric acid and 2 mL H₂O₂ (30%, m/V) were added, and the vessels were capped closed, tightened and placed in the rotor of the microwave digestion system Milestone, Ethos Touch Control. The digestion was carried out with the following digestion program: (1) temperature 180°C, 5 min ramp time, 500 W and 20 bar; (2) temperature 180°C, 5 min hold time, 500 W and 20 bar. Finally, the vessels were cooled, carefully opened, and digests were quantitatively transferred to 10 mL calibrated flasks.

Copper was determined by flame AAS (Thermo So-laar S4), whereas lead was determined by Zeeman electrothermal AAS (Varian SpectrAA 640 Z) applying pyrolysis and atomizing temperatures of 400 and 2000°C, respectively. Mercury was determined by cold vapour AAS using a continuous flow vapour generation accessory (VGA-76, Varian) connected to an atomic absorption spectrometer (SpectrAA 55B, Varian). The reaction medium used was a mixture of HCl and NaBH₄.

Optimal instrumental conditions for lead and mercury determination are given in Tables 3 and 4.

Quality control. The QC of NAA results was ensured by simultaneous analysis of the examined samples and reference materials (RM) Lichen 336 IAEA (International Atomic Energy Agency) and NORD DK-1 (moss reference sample prepared for intercomparison in 1990 [23]). The NAA data and certified values of reference materials are given in Table 5. The QC of AAS determinations was based on the standard addition method and it was found that the recovery of the investigated elements ranged between 98.5 and 101.2%. Beside standard addition method, blanks parallel to the decomposition of

Table 4. **Optimal instrumental parameters for mercury determination by CV-AAS**

Instrument mode	Absorbance
Calibration mode	Concentration
Measurement mode	Integration
Wavelength, nm	253.7
Slit width, nm	0.5
Integration time, s	3
Delay time, s	40
Replicates	3
Sample flow rate, mL·min ⁻¹	7
Reaction media	HCl–NaBH ₄
HCl flow rate, mL·min ⁻¹	1
NaBH ₄ flow rate, mL·min ⁻¹	1

samples and preparation of sample solutions for analysis were analyzed. The loss of Hg was checked by standard additions. The same sample was decomposed with and without addition of Hg. The added content of Hg was recovered in the solution obtained after microwave digestion.

Mapping. The program GRINVEIW from the geographical information system software package GIS-INTEGRO with raster and vector graphics was used to generate raster-based pollution contour maps for the elements of interest for the entire study area. The system is supplied with interfaces for all international standard GIS: ARC-info, MAP-info, etc.

RESULTS AND DISCUSSION

Median values and ranges for the elements studied are presented in Table 6, along with the corresponding data from similar studies in the neighbouring Balkan countries. For comparison with a pristine territory the corresponding data for northern Norway [24] are shown in the right-hand column. The Norwegian values are from ICP-MS analysis and are based on nitric-acid solutions, possibly leaving out fractions of the elements in moss samples contained in silicate minerals (attached soil particles).

Taking the values of the data in Table 6 one can range countries according to the median values for each element. This presents a generally favourable picture for Macedonia in comparison with the other three Balkan

countries. Macedonia is characterized with the highest median for four elements: K, Ti, Cu, and In (data for In and Ti are not available for all of the countries). It has the second highest median for Cr, Sr, Cd, Eu, W, Au and Hg (data for Cd and Eu are not complete) and the third highest median for Mg, Sc, Fe, Co, Ba, Ce, Ta, Pb, Th, and U (data for Ce and Pb are not complete). Lowest median for the Macedonian data is observed for Na, Al, Cl, Ca, V, Mn, Ni, Zn, As, Se, Br, Rb, Mo, Ag, Cd, Sb, I, Cs, La, Ce, Tb, and Hf (data for Ag are incomplete). There are no available data for comparisons for mercury.

In comparison with Norway, Macedonia has the lower median only for Mn and a very close value for Hg. For the «marine» elements (halogens) the Norwegian

Table 5. NAA data and certified values of reference materials, mg/kg

Element	DK-1 (determined)	DK-1 (certified)	Lichen-336 (determined)	Lichen-336 (certified)
Na	303 ± 25	315 ± 31	304 ± 26	320 ± 40
Mg	850 ± 150	910 ± 91	–	–
Al	830 ± 84	810 ± 81	720 ± 65	680 ± 109
Cl	328 ± 35	328 ± 33	1927 ± 288	1900 ± 304
K	3350 ± 165	3300 ± 297	1910 ± 90	1840 ± 202
Ca	1604 ± 180	1630 ± 40	–	–
Sc	0.16 ± 0.02	0.16 ± 0.02	0.176 ± 0.014	0.17 ± 0.20
V	4.12 ± 0.31	3.8 ± 0.3	1.38 ± 0.19	1.47 ± 0.22
Cr	1.94 ± 0.15	1.7 ± 0.4	1.10 ± 0.17	1.06 ± 0.17
Mn	143 ± 10	120 ± 10	69 ± 5.1	63 ± 7
Fe	575 ± 53	550 ± 50	430 ± 8.5	430 ± 51
Co	0.26 ± 0.01	0.23 ± 0.01	0.303 ± 0.070	0.29 ± 0.05
Ni	1.58 ± 0.33	1.8 ± 0.2	–	–
Cu	87 ± 2.5	85 ± 5	3.7 ± 0.5	3.6 ± 0.5
Zn	30.8 ± 4.0	29 ± 2	28.2 ± 2.3	30.4 ± 3.3
As	0.64 ± 0.02	0.64 ± 0.02	0.54 ± 0.71	0.63 ± 0.08
Se	0.43 ± 0.04	0.43 ± 0.04	0.22 ± 0.033	0.22 ± 0.04
Br	13.5 ± 0.94	12.8 ± 1.0	14.2 ± 2.3	12.9 ± 1.6
Rb	12.9 ± 0.86	12.6 ± 0.9	1.7 ± 0.17	1.76 ± 0.22
Sr	15.1 ± 3.0	10 ± 0.1	11.4 ± 0.55	9.3 ± 1.1
Zr	11.0 ± 1.2	11 ± 1.2	–	–
Mo	0.21 ± 0.02	0.2 ± 0.02	–	–
Ag	0.05 ± 0.004	0.05 ± 0.004	–	–
Cd	0.3 ± 0.11	0.3 ± 0.02	0.13 ± 0.015	0.117 ± 0.0006
Sb	0.347 ± 0.02	0.347 ± 0.02	0.078 ± 0.01	0.073 ± 0.0067
I	3.8 ± 0.07	3.8 ± 0.3	–	–
Cs	0.285 ± 0.02	0.30 ± 0.02	0.12 ± 0.024	0.110 ± 0.013
Ba	12.5 ± 0.12	12 ± 2	6.6 ± 0.7	6.4 ± 1.1
La	1.22 ± 0.34	1.22 ± 0.1	0.70 ± 0.06	0.66 ± 0.10
Ce	2.92 ± 0.53	2.92 ± 0.22	1.3 ± 0.25	1.28 ± 0.17
Sm	0.231 ± 0.05	0.231 ± 0.01	0.106 ± 0.06	0.106 ± 0.014
Eu	0.042 ± 0.01	0.042 ± 0.01	0.021 ± 0.003	0.023 ± 0.003
Tb	0.0218 ± 0.01	0.0216 ± 0.002	0.015 ± 0.002	0.014 ± 0.002
Hf	0.21 ± 0.06	0.21 ± 0.009	–	–
Ta	0.026 ± 0.005	0.026 ± 0.0036	–	–
W	0.73 ± 0.11	0.73 ± 0.21	–	–
Au	0.00074 ± 0.0014	0.00074 ± 0.00004	–	–
Th	0.16 ± 0.08	0.15 ± 0.0011	0.14 ± 0.01	0.14 ± 0.02
U	0.192 ± 0.02	0.192 ± 0.015	–	–

values are equal to or higher than the other data, as might be expected because of the stronger marine influence [25].

For elements where the local micro-environment is known to be a more dominant source to the moss than atmospheric deposition (Mg, Ca, Mn, Rb, Sr, Cs, Ba, partly Zn) the Norwegian data are of the same order of magnitude as the Balkan values. For typical air pollution elements (V, Cr, As, Ag, Cd, Sb, Pb) the Norwegian data are

orders of magnitude lower. The Norwegian data are also much lower for elements that we previously have normally ascribed mainly to geogenic factors associated with soil particles (Sc, Ti, Fe, REE, Th, U). In this case, obviously the fact that INAA determines the whole content could be one reason for the large difference.

Similar comparison with the data from the European Moss Atlas [4] appears to be less favourable. Examples of an approximate ordering of the atmospheric environ-

Table 6. Comparison of the results obtained in the present study with other Balkan countries and Norway, mg/kg

	Macedonia (present work)		Northern Serbia [16]		Romania (Transilvania) [13]		Bulgaria (West and South) [15]		Norway [24]	
№ of samples	73		92		70		103		100	
Element	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
Na	419	118-8673	694	178-2440	902	192-4330	523	155-5573	–	–
Mg	2377	674-7421	2780	1100-8130	2850	480-6840	2026	748-12500	1730	940-2370
Al	3736	825-17600	6800	1280-22090	5545	830-23000	3843	1111-46350	200	67-820
Cl	149	43-693	256	105-1030	370	160-1300	161	59-1180	–	–
K	8615	2861-18190	5090	2710-11750	7770	4770-19980	5764	3274-20490	–	–
Ca	5593	1207-23640	7720	2890-18120	5770	1250-23500	7283	2266-19650	2820	1680-5490
Sc	0.81	0.12-6.79	1.31	0.27-4.13	0.94	0.21-6.13	0.65	0.2-6.4	0.052	0.009-0.220
Ti	163	12-1365	71	11-297	–	–	–	–	23.5	12.4-66.4
V	6.9	1.79-43	11	2.85-39	8.7	1.95-32	8.4	2.2-112.6	0.92	0.39-5.1
Cr	7.47	2.33-122	6.51	1.14-22	13.8	2.72-51.9	3.2	0.5-26.9	0.55	0.10-4.2
Mn	186	37-1475	217	30-2340	265	27-1470	251	32-986	256	22-750
Fe	2458	424-17380	3110	720-9230	3290	815-21340	2314	692-14700	209	77-1370
Co	1.09	0.24-13.6	8.24	1.42-39	1.41	0.32-7.0	1.08	0.23-10.6	0.202	0.065-0.654
Ni	2.4	0.09-24	6.73	1.96-26	5.4	0.6-32	4.1	0.5-18.6	1.14	0.12-6.6
Cu	22	3-83	16.9	6.31-3140	21.5	2.21-2420	14.5	5.34-1860	3.6	2.1-9.2
Zn	39	14-203	44	14-415	135	39-2950	41	19-379	26.5	7.9-173
As	0.80	0.12-8.0	3.35	0.46-61	2.2	0.59-45.1	1	0.3-59.0	0.093	0.020-0.505
Se	0.18	0.013-0.61	0.39	0.046-10	0.36	0.08-5.01	0.24	0.01-1.18	0.33	0.05-1.30
Br	2.16	0.06-7.7	5.75	1.83-18	8.6	2.03-20.9	3.6	1.1-11.6	4.5	1.4-20.3
Rb	10.9	5-47	13	3-47	15.0	5.8-135	12	3.0-69	7.7	1.3-51.5
Sr	31	11.8-136	22	6.8-95	37.4	1.8-290	25	7-106	15.8	3.6-43.3
Zr	15	2-142	–	–	40	5-797	–	–	0.50	0.25-1.34
Mo	0.19	0.03-1.12	0.85	0.12-23	0.65	0.13-10	0.99	0.16-3.36	0.135	0.065-0.70
Ag	0.040	0.007-0.20	0.078	0.012-1.5	0.13	0.03-4.54	–	–	0.014	< 0.003-0.035
Cd	0.16	0.016-2.95	< 0.4	< 0.4-6.5	–	–	–	–	0.058	0.025-0.171
In	0.043	0.0032-0.16	0.025	0.0036-0.34	–	–	–	–	–	–
Sb	0.2	0.039-1.4	0.52	0.13-7	0.88	0.16-51	0.23	0.07-20.2	0.033	0.004-0.240
I	1.18	0.36-2.8	2.09	0.87-4	2.17	0.76-5.55	1.4	0.6-4.4	2.5	0.6-41.7
Cs	0.39	0.097-1.7	0.76	0.11-18.2	0.51	0.12-3.4	0.40	0.10-2.96	0.072	0.016-0.88
Ba	54	14-256	39	13-130	101	20-658	68	17-517	17.1	5.6-50.5
La	2.32	0.50-22	4.66	1.09-13	2.4	0.4-15.2	2.9	0.8-23.7	0.189	0.045-2.56
Ce	5.60	0.83-42	9.2	1.84-28	6.1	0.9-42.5	–	–	0.342	0.095-4.61
Sm	0.46	0.07-3.4	–	–	0.59	0.01-2.51	0.62	0.07-2.86	0.33	0.05-1.34
Eu	0.110	0.03-0.48	0.08	0.02-0.48	–	–	–	–	0.017	0.008-0.061
Tb	0.06	0.01-0.56	0.11	0.02-0.36	0.07	0.01-0.42	0.068	0.016-0.610	0.003	< 0.002-0.030
Hf	0.26	0.05-3.8	0.78	0.15-2.6	0.56	0.12-4.66	0.46	0.11-4.78	–	–
Ta	0.09	0.013-0.79	0.11	0.024-0.29	0.10	0.01-0.66	0.076	0.018-0.563	0.01	< 0.01-0.07
W	1.21	0.25-3.9	1.34	0.19-3.3	1.02	0.12-8.74	0.193	0.03-1.39	0.127	0.009-1.23
Au	0.0061	0.001-0.034	0.0041	0.00029-0.087	0.025	0.003-0.114	0.0042	0.0009-0.0465	–	–
Hg*	0.056	0.018-0.264	–	–	–	–	–	–	0.046	0.026-0.166
Pb*	6.0	1.5-37.2	–	–	14.3	6.45-31.5	18.9	4.55-887	1.17	0.64-6.12
Th	0.67	0.12-7.6	0.82	0.18-2.4	0.81	0.21-4.16	0.56	0.11-4.53	0.033	0.004-0.240
U	0.21	0.03-1.45	0.32	0.08-1.03	0.28	0.04-1.36	0.20	0.03-1.87	0.015	0.001-0.138

*Determined by AAS.

ment of Macedonia relative to other countries for Cu, Fe, Cr, As, V, and Zn are given in Fig. 4 (a-f). Among 29 sets of data, Macedonia has the highest median for Cu

(present data) whereas the maximum value for copper (3140 mg/kg) was determined for the copper basin in Bor, in neighboring Serbia. The worse pollution in Mace-

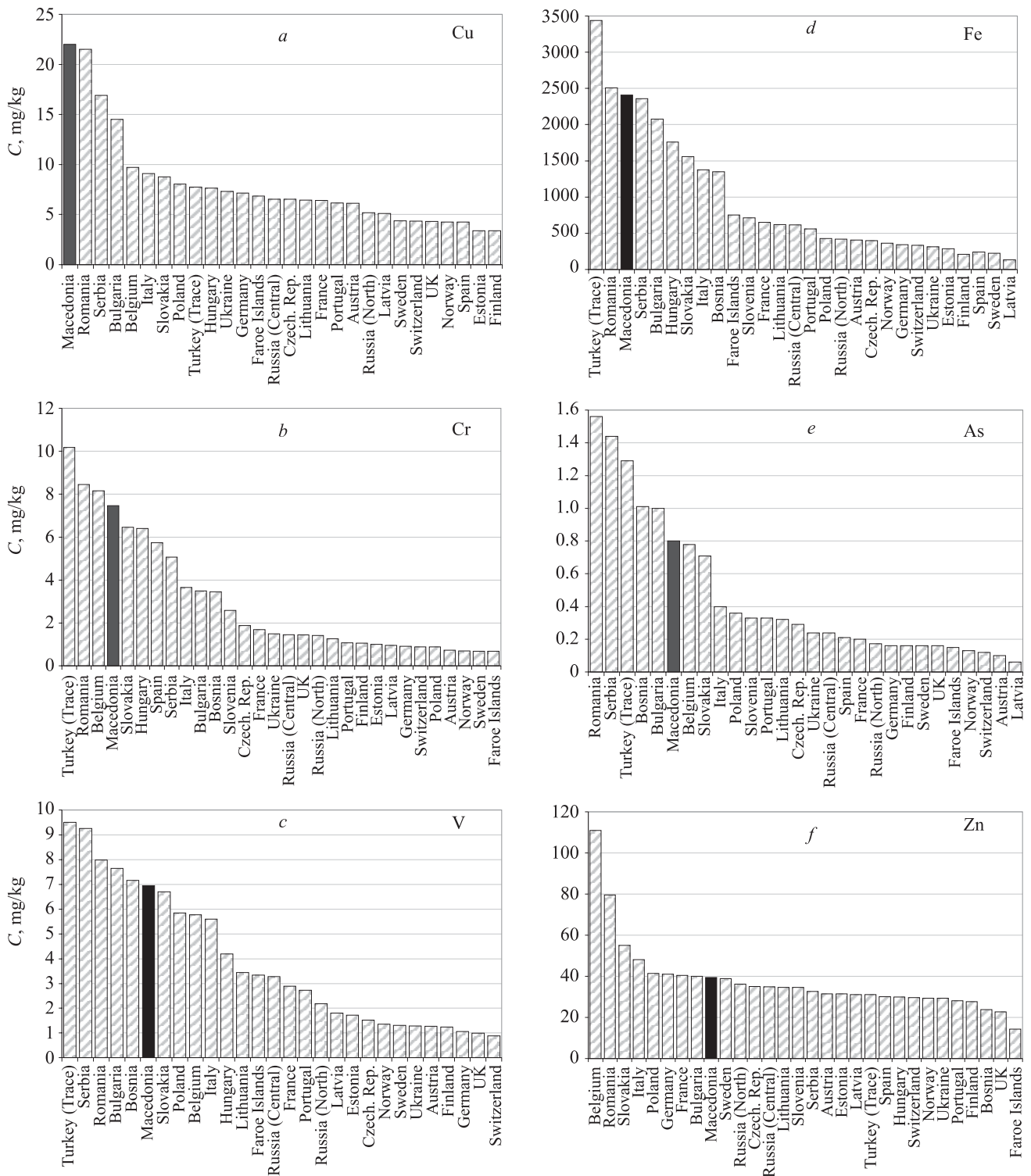


Fig. 4. Range of median values for selected elements in moss according to moss surveys in different European countries [4]. Data for Turkey (Thrace Region) are taken from [26]

donia comes from a previous chromium production facility and related dump site northwest of Skopje.

A distinct outcome of this comparison is in the fact that all Balkan countries show considerably higher concentrations of the above elements in moss than in other sampled European countries where moss sampling has

been employed. It should be pointed out that for such elements as Hg, Ni, and Pb, the number of countries with lower/higher median than the Macedonian is as follows: Hg (12 8 8); Ni (18 8 2); Pb (16 9 3). (The last number gives the number of countries for which the corresponding data are unavailable).

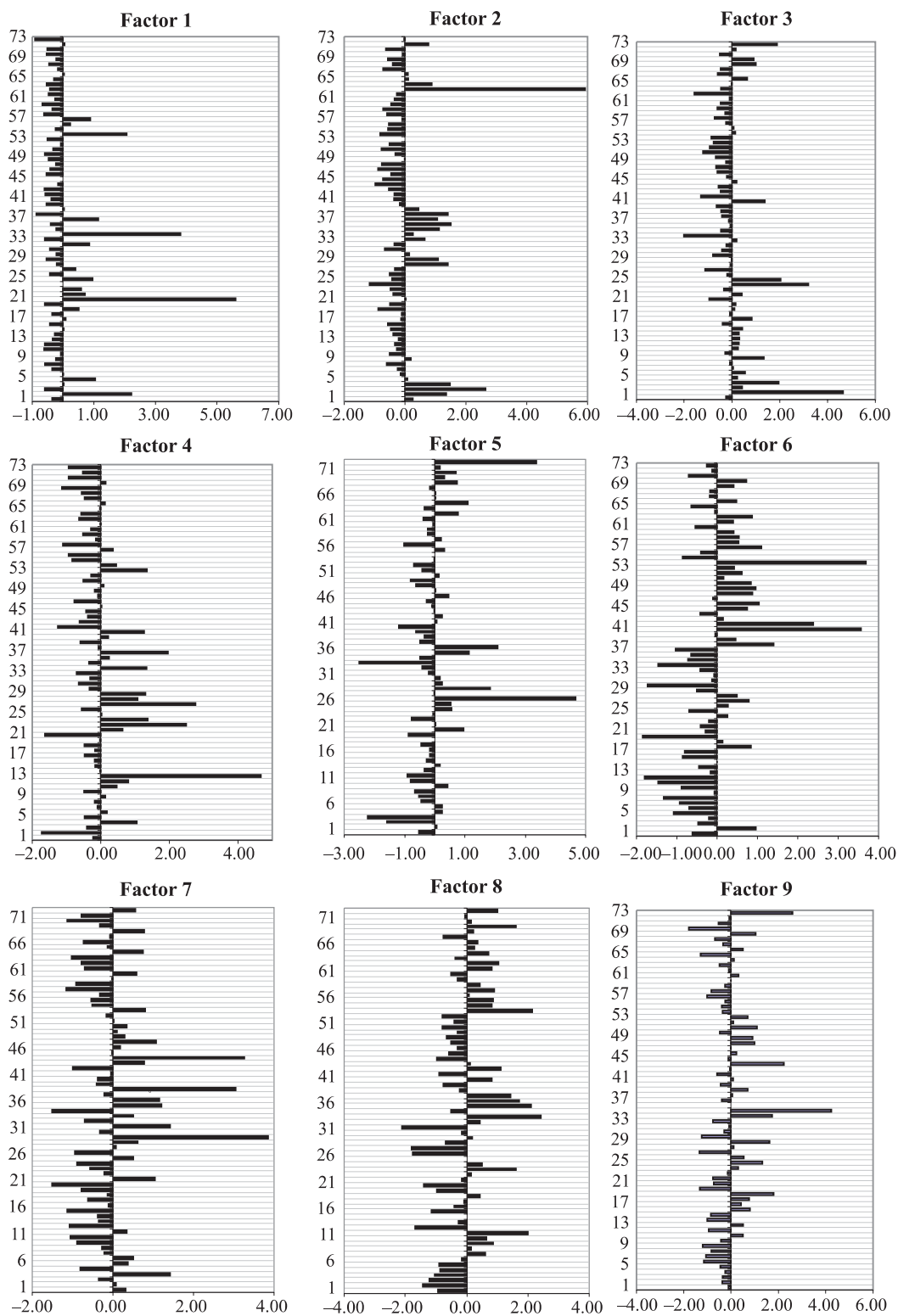


Fig. 5. Plots of factor scores for moss samples from Macedonia

This simple comparison is obvious evidence that the East and the West of Europe differ greatly by the level of contaminants in the atmospheric deposition. High levels of Cu, Cr, V and Zn in Belgian moss are explained by smelter emissions in this industrialized country.

Principal component analysis (factor analysis) was used to identify and characterise different pollution sources and to point out the most polluted areas. The results of factor analysis are given in Table 7. Factor scores representing the contributions of individual sampling sites to the relevant factor are given in Fig. 5.

Table 7. Factor analysis of NAA and AAS data on moss samples from Macedonia

Factor	Rotated Matrix Component								
	1	2	3	4	5	6	7	8	9
% of expl. variance	43.1	11.4	5.6	4.8	4.3	3.7	3.1	2.7	2.4
Na	0.79	-0.01	-0.08	0.13	0.35	0.00	-0.18	-0.16	-0.13
Mg	0.46	0.25	0.07	0.71	0.05	0.07	0.20	0.15	0.03
Al	0.69	0.04	0.05	0.63	0.07	0.07	0.12	0.08	0.05
Cl	-0.05	0.09	-0.08	-0.05	0.07	0.79	0.05	0.03	-0.03
K	0.38	0.12	0.01	-0.05	0.10	0.27	-0.30	0.65	-0.07
Ca	0.04	0.10	0.02	0.07	0.09	0.01	0.89	-0.03	-0.02
Sc	0.60	0.17	0.15	0.48	0.50	0.01	-0.01	-0.16	-0.11
Ti	0.64	0.03	-0.02	0.69	0.05	0.02	0.00	0.10	0.08
V	0.41	0.13	0.08	0.80	0.24	0.03	0.06	-0.10	0.00
Cr	0.16	0.31	0.14	0.15	0.72	-0.04	0.15	0.13	0.15
Mn	0.19	-0.03	0.32	0.36	-0.18	0.63	-0.11	0.12	-0.04
Fe	0.69	0.19	0.08	0.43	0.47	0.04	0.00	-0.05	-0.06
Co	0.53	0.16	-0.03	0.37	0.42	0.34	0.09	0.14	-0.10
Ni	0.15	0.57	-0.08	0.29	0.43	0.05	0.27	0.31	0.00
Cu	0.41	0.02	0.25	0.56	-0.18	0.19	-0.08	0.16	0.22
Zn	0.17	0.88	0.02	0.13	0.24	0.09	0.00	0.18	0.07
As	0.55	0.21	0.58	0.03	0.29	-0.03	0.11	-0.08	0.08
Se	0.22	0.52	0.34	0.06	0.33	0.09	0.02	-0.07	0.15
Br	0.36	0.01	0.42	0.22	0.10	0.34	0.23	-0.20	0.32
Rb	0.87	0.07	0.08	0.15	0.02	0.20	-0.04	0.25	0.04
Sr	0.34	0.19	0.03	0.28	0.05	-0.29	0.27	0.56	-0.05
Zr	0.90	0.13	0.28	0.08	0.09	0.00	-0.05	-0.10	-0.07
Mo	0.31	-0.05	0.65	0.19	0.08	0.06	0.07	0.27	0.11
Ag	-0.01	0.44	-0.01	0.31	-0.03	-0.25	-0.05	0.16	0.45
Cd	0.03	0.94	-0.09	-0.10	0.02	-0.01	-0.04	0.06	0.03
In	-0.07	0.69	0.15	0.16	-0.22	0.18	-0.06	-0.08	-0.07
Sb	0.21	0.89	0.11	0.08	0.16	-0.06	0.10	-0.04	0.09
I	0.24	0.01	0.21	0.24	0.03	0.52	0.49	-0.09	0.28
Cs	0.69	0.16	0.37	0.24	0.22	-0.05	0.23	0.05	-0.01
Ba	0.67	0.00	0.17	0.21	-0.10	0.00	-0.05	0.35	0.24
La	0.95	0.05	0.00	0.16	-0.01	0.04	0.05	0.14	0.09
Ce	0.94	0.08	-0.04	0.15	0.03	0.03	0.10	0.15	0.08
Sm	0.95	0.06	0.08	0.17	0.05	0.05	0.07	0.04	0.01
Eu	0.76	0.07	-0.03	0.38	0.28	-0.03	0.01	-0.09	-0.16
Tb	0.94	0.08	-0.05	0.21	0.06	0.03	0.07	0.08	0.02
Hf	0.93	0.10	0.18	0.01	0.09	-0.02	-0.07	-0.11	-0.07
Ta	0.92	0.09	0.24	0.05	0.10	0.07	-0.01	-0.05	-0.07
W	0.31	0.10	0.63	0.05	0.05	0.23	-0.02	-0.07	-0.20
Au	0.06	0.18	0.48	-0.01	-0.26	-0.30	-0.06	-0.02	-0.18
Hg (AAS)	-0.04	0.33	-0.03	0.01	0.07	0.03	0.02	-0.06	0.79
Pb (AAS)	0.12	0.92	0.06	0.09	-0.06	-0.02	0.08	-0.06	0.08
Th	0.92	0.08	0.03	0.17	-0.09	-0.02	0.09	0.18	0.08
U	0.94	0.04	0.17	0.14	-0.03	0.03	0.06	0.11	0.05

Rotation Method: VARIMAX with Kaiser Normalization.

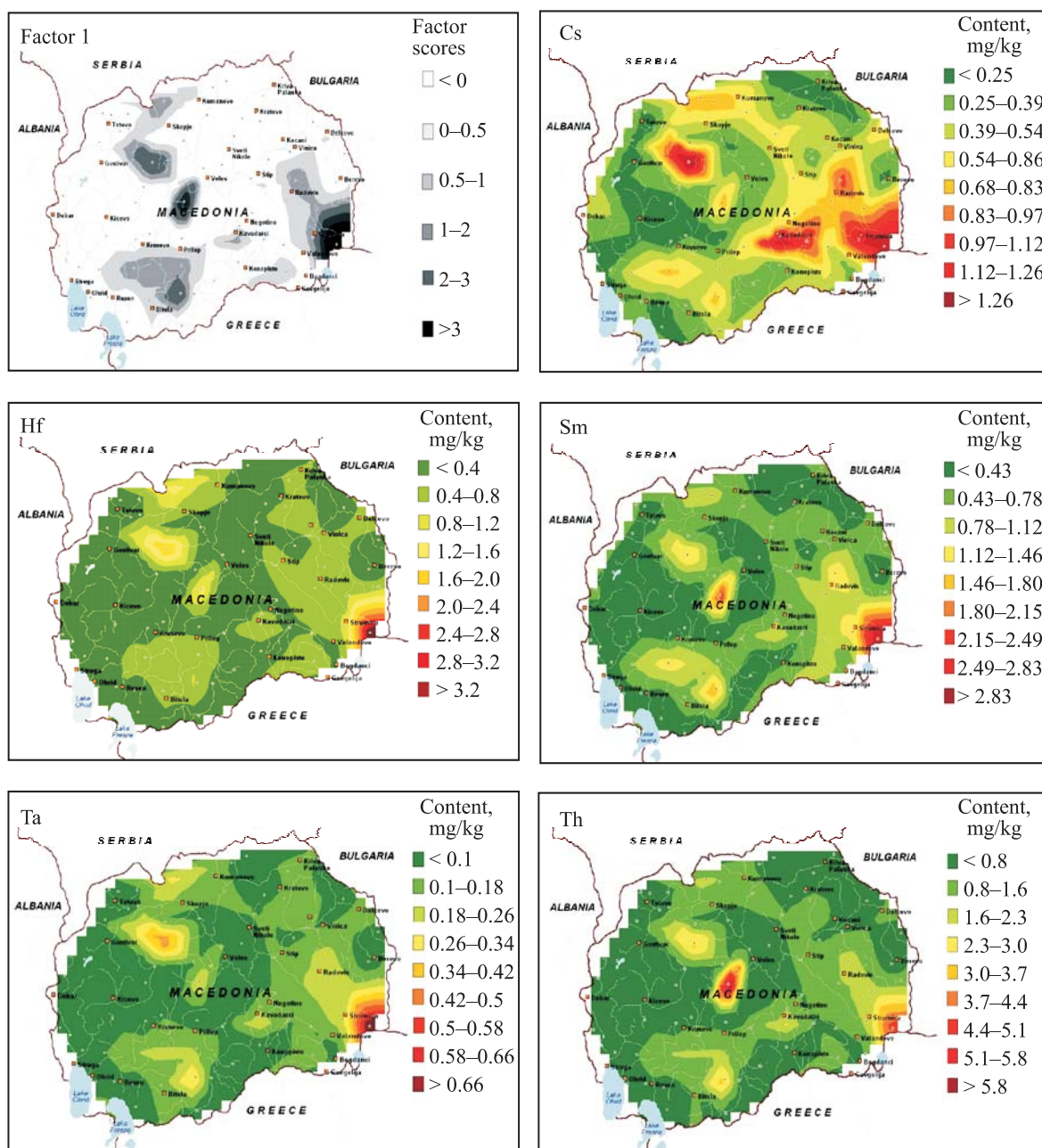


Fig. 6. Geographical distribution of some selected elements relevant to Factor 1. Black-and-white map (Factor 1) is built on its factor scores

Nine identified factors are interpreted as follows:

Factor 1 (Na, Mg, Al, Sc, Ti, Fe, Co, As, Rb, Zr, Cs, Ba, La, Ce, Sm, Eu, Tb, Hf, Ta, Th, U). This factor has a typical crustal composition and is probably significantly influenced by soil particles adhered to the moss samples. The association of As with this factor however indicates some contribution from coal fly ash as well. Geographical distribution of factor scores of Factor 1 and selected distributions of some characteristic elements are shown in Fig. 6. Probably, somewhat higher content of U, Th, and Sm in the South around Bitola (the hot-spot), close to sampling site 56, is due to air pollution from coal ash

from thermo-electrical power plant in Bitola using lignite as a fuel [27].

Factor 2 (Ni, Zn, Se, Ag, Cd, In, Sb, Pb). This factor contains elements normally associated with air pollution. It appears to be connected mainly with the lead-zinc smelter (Pb, Zn, Cd, and Sb) in Veles and a ferronickel smelter plant (Ni and Ag) in Kavadarci. This factor is also dominant further along this valley of the river Vardar extending from Skopje to Veles and continuing south-eastwards toward Greece. It is well known that along the valley there is frequent flow of air masses in both directions in winter and in summer, contributing to dispersion of emissions the distribution of polluting gases

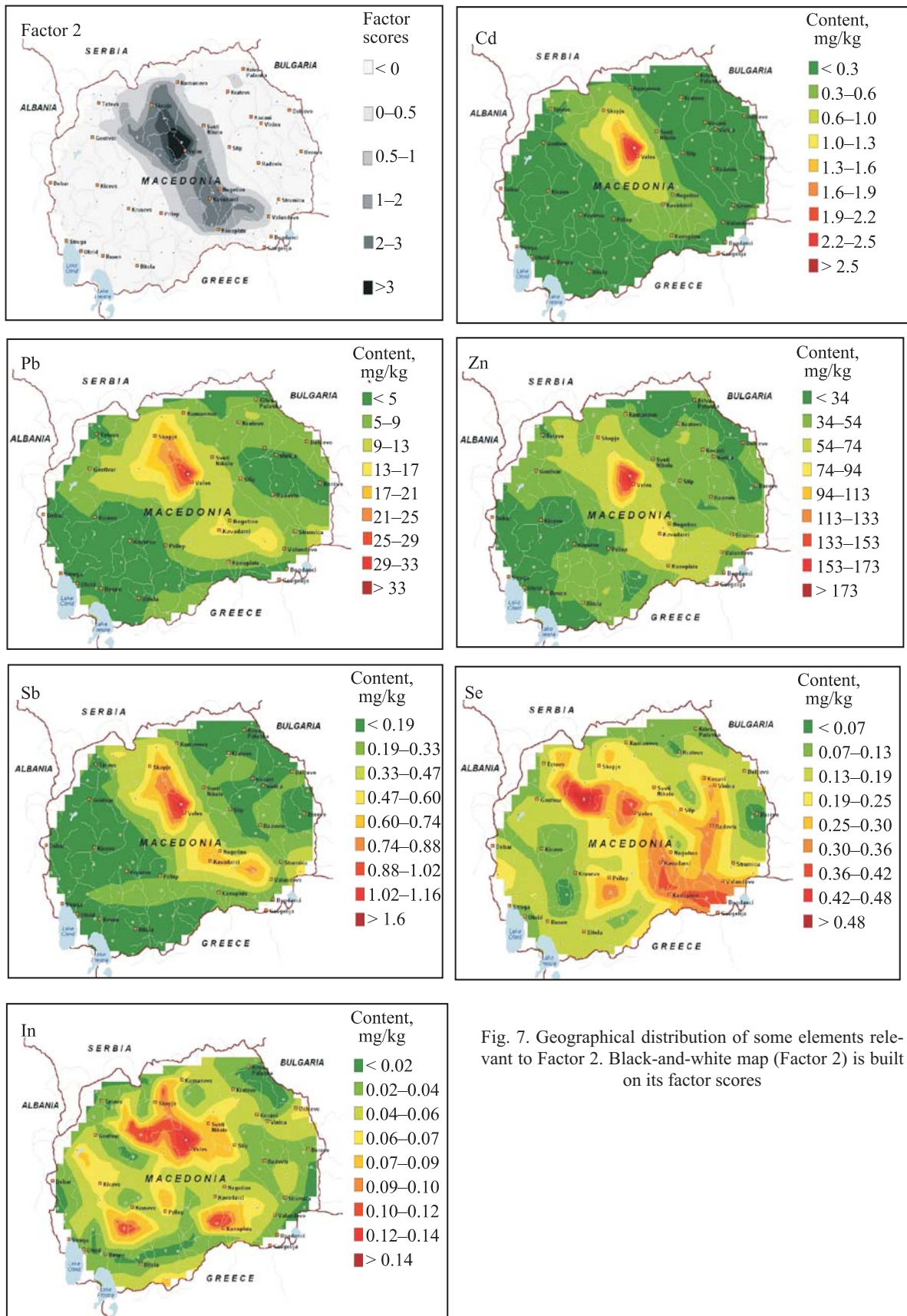


Fig. 7. Geographical distribution of some elements relevant to Factor 2. Black-and-white map (Factor 2) is built on its factor scores

from industry. Along the Vardar River there is a highway connecting Serbia in the North with Greece in the South. Influence of the exhaust gases from cars is more present

in the cities, in Skopje in particular, where the concentration of cars is the greatest. Considerable percentage of transport vehicles in use is older than 10 years, so most of

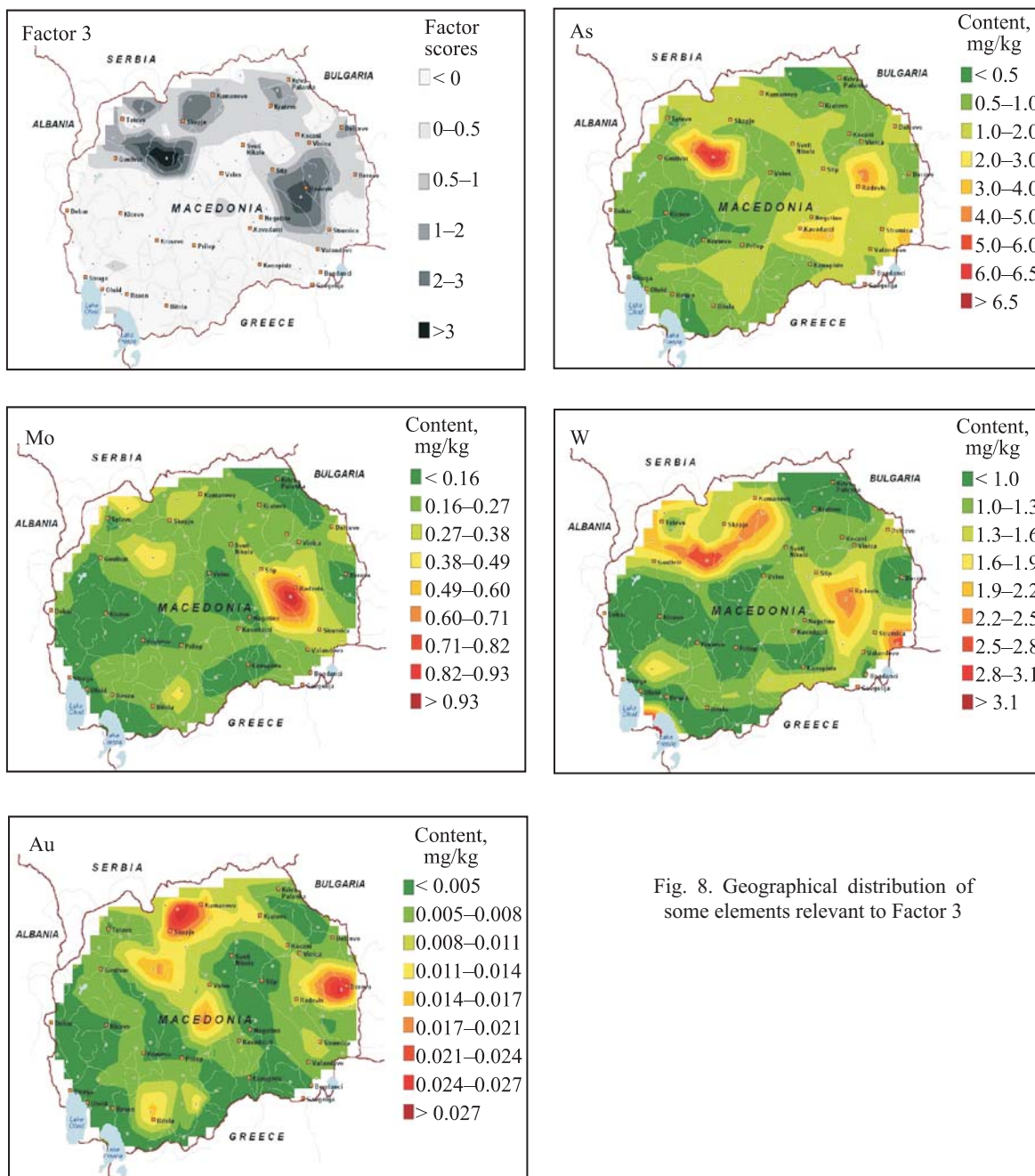


Fig. 8. Geographical distribution of some elements relevant to Factor 3

the petrol used is not of unleaded type. Indium and selenium appear to be more widely dispersed than the other elements associated with Factor 2. The geographical distribution of Factor 2 is shown in Fig. 7 together with those of some typical elements.

Factor 3 (As, Br, Mo, W, Au). The distribution maps of this factor and the associated elements are given in Fig. 8. Its element composition indicates anthropogenic origin, but the source is not clear. Most probably Mo, W and Au emissions are connected with the lead-and-zinc smelter in Veles where Au is present in the Pb–Zn concentrates, and Au production is present as a by-product. Higher content of Mo and W in the Radoviš region may

be due to dust from a magnetic ore mine, which is not in operation any more. The appearance of Au in mosses in the eastern part of the country may be related to a copper flotation plant near Radoviš. In case of arsenic it is known that its concentration in mineral waters in Kavadarci at Kožuf mine [28, 29] (sampling site 38) and Kočani [29] (sampling site 14) is within the range of 50–200 μL whereas the «normal» concentrations of arsenic in mineral waters from Macedonia range between 1–10 μL [29].

Factor 4 (Mg, Al, Sc, Ti, V, Fe, Cu). From the elemental composition it appears to be a soil dust factor associated with basic rocks and the copper flotation plant

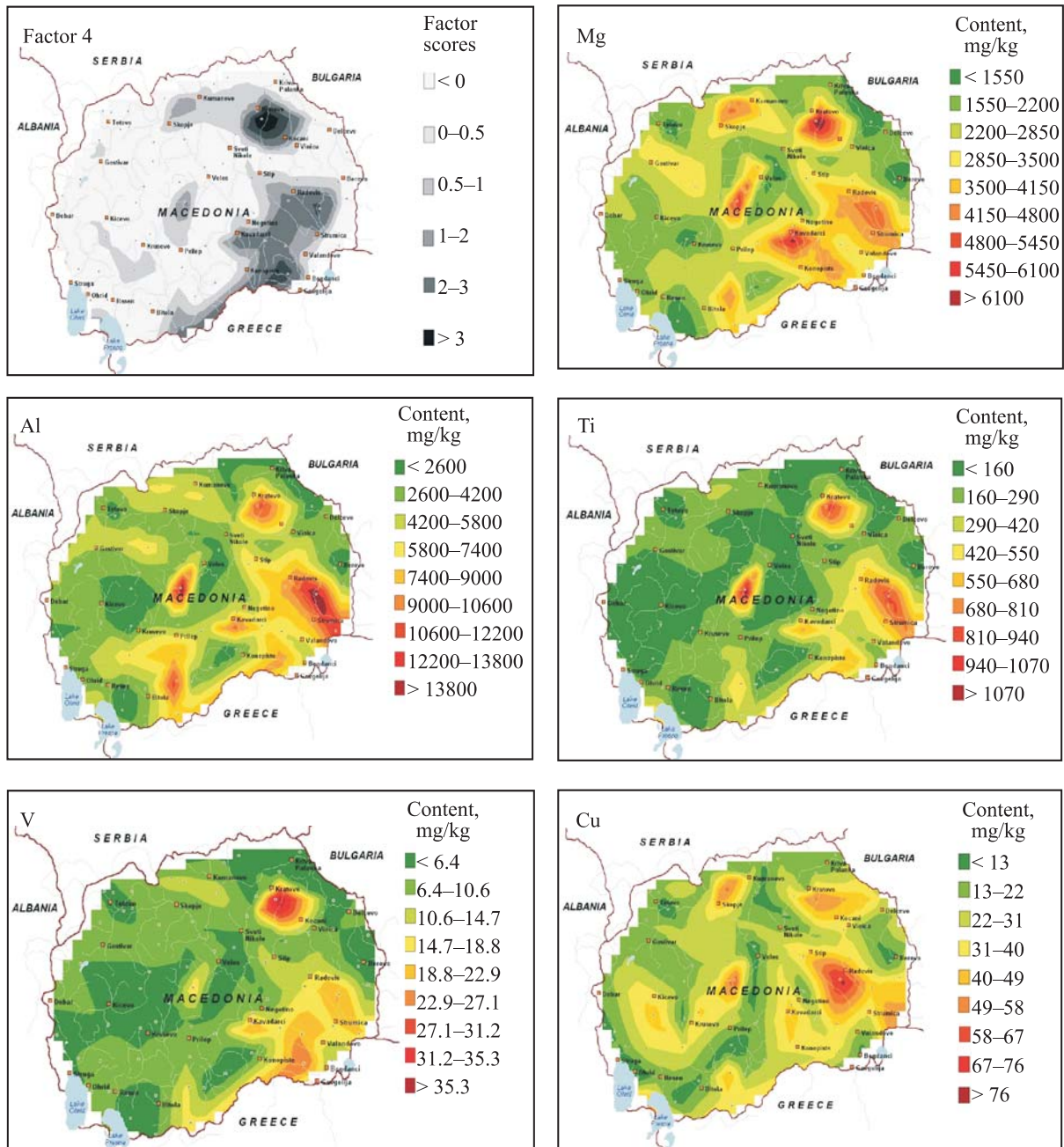


Fig. 9. Geographical distribution of some elements relevant to Factor 4

near Radoviš. The dominant area for this factor is in the south-east part of the country next to the Greek border. Distribution maps of Factor 4, Mg, Al, Ti, V, and Cu are shown in Fig. 9.

Factor 5 (Sc, Cr, Fe, Co, Ni) is most likely connected with past industrial activities near the town of Tetovo (a previously active ferrochrome smelter) and current activity near Kavadarci (ferronickel smelter). The corresponding distribution maps are given in Fig. 10.

Factor 6 (Cl, Mn, Br, I). The element Mn is most probably associated with the interaction of the moss with higher vegetation, and halogens may reflect their marine influence [30] (Fig. 11).

Factor 7 (Ca, I). Iodine is split into two factors — Factor 6 and Factor 7 with quite similar factor loadings: 0.52 and 0.49. Its combination with Ca may point out that limestone and dolomites of marine origin are enriched in iodine due to the fact that in the prehistoric times the territory of Macedonia was a bottom of a sea, and nowadays iodine is revealing itself through the weathering proces-

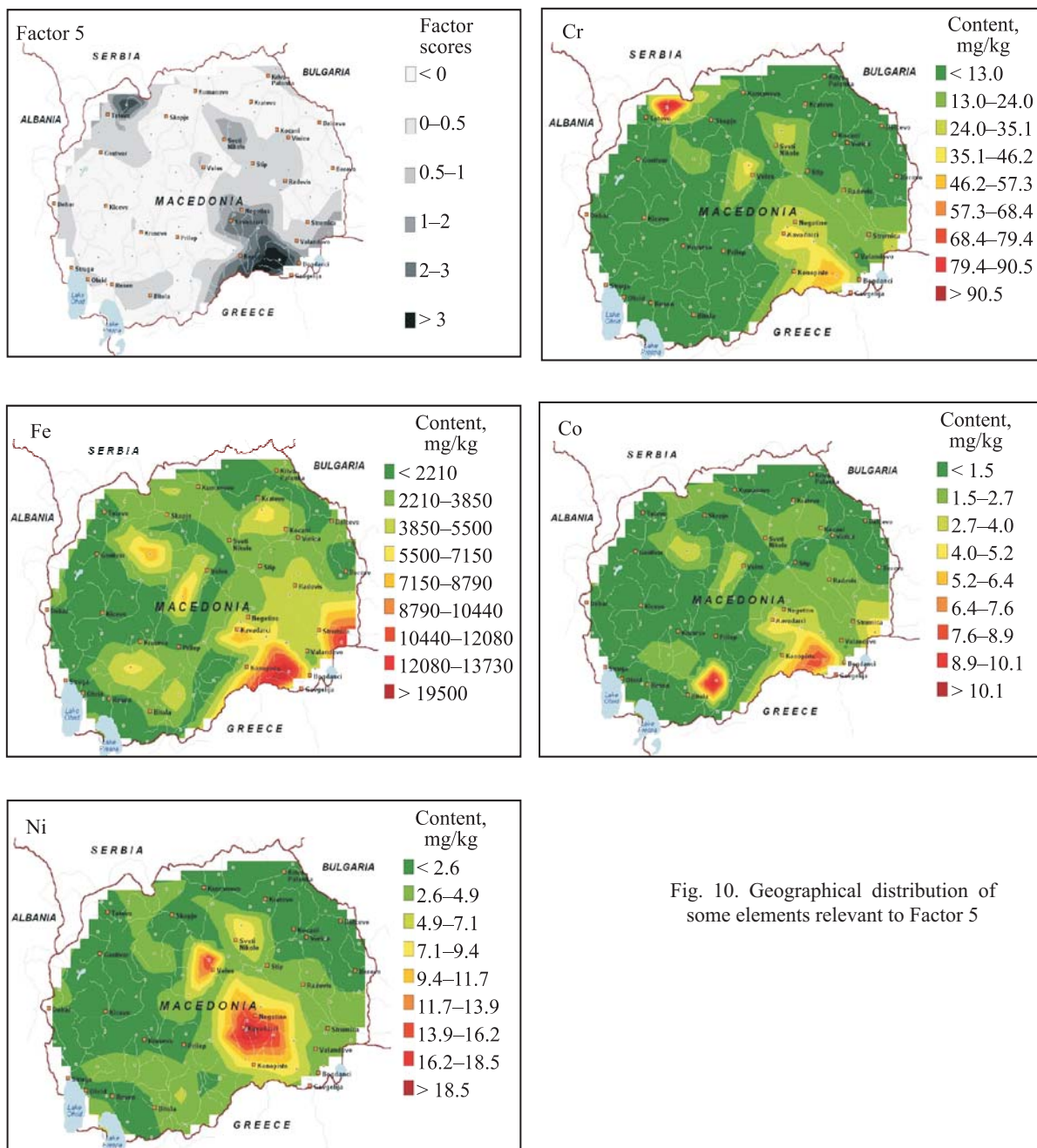


Fig. 10. Geographical distribution of some elements relevant to Factor 5

ses. The highest factor scores are observed in the south of the country (sites 30, 36–39, 45), which seems to confirm this hypothesis. High factor score for sampling site 4 in the north could be due to limestone quarries between Skopje and Kumanovo.

Factor 8 (K, Sr). As in the case of Factor 6, Factor 8 is most probably associated with higher vegetation. Figure 12 shows the distribution of Factor 8 and the associated elements K and Sr. This factor corresponds relatively well to forested areas of the country (sites 12, 24, 34, 55 in the relevant plot of factor scores in Fig. 5).

Factor 9 (Ag, Hg). This factor may be connected with small metal workshops in the vicinity of local settlements. The levels registered for mercury near Ohrid could be related to local industrial activity in production of mirrors for cars. Distribution maps of this factor are given in Fig. 13.

The most striking examples of metal pollution in Macedonia appear to be the lead–zinc smelter in Veles, the chromium smelter near the town of Tetovo, northwest of Skopje, and the ferronickel smelter in Kavadarci.

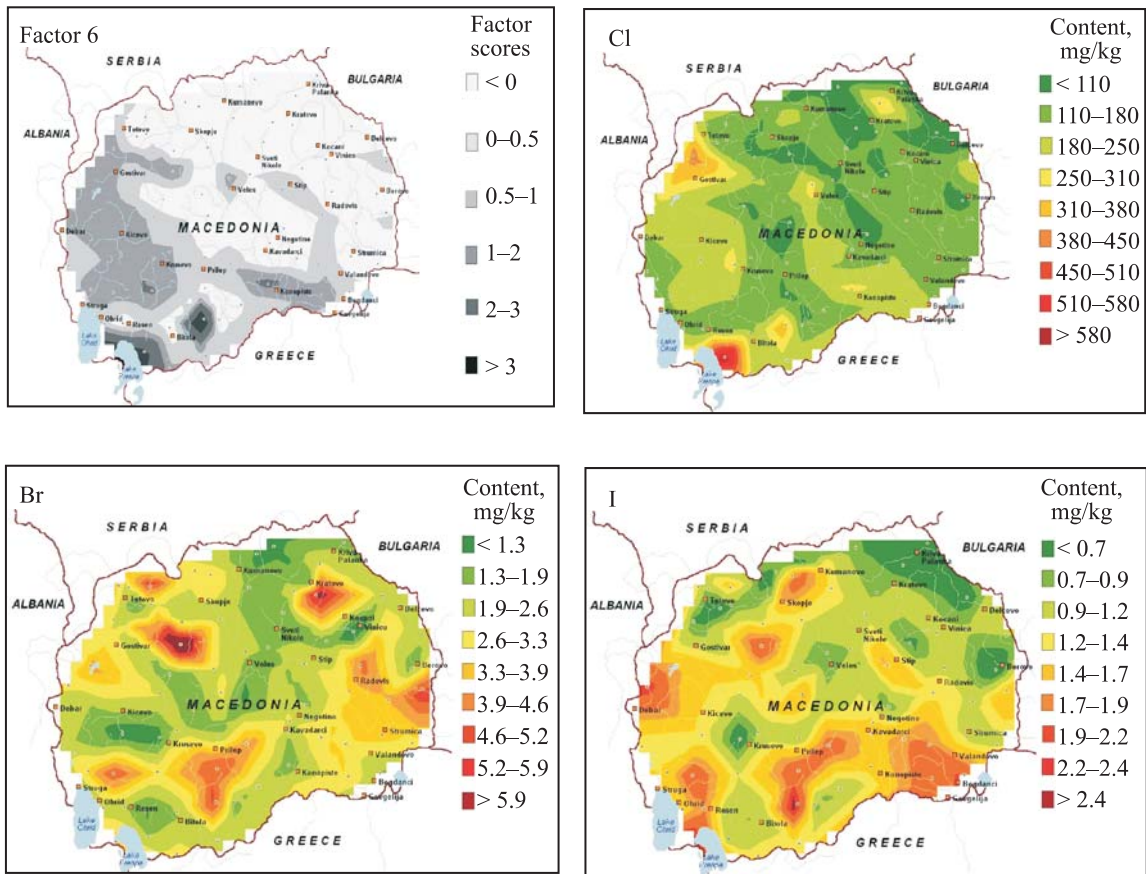


Fig. 11. Geographical distribution of some elements relevant to Factor 6

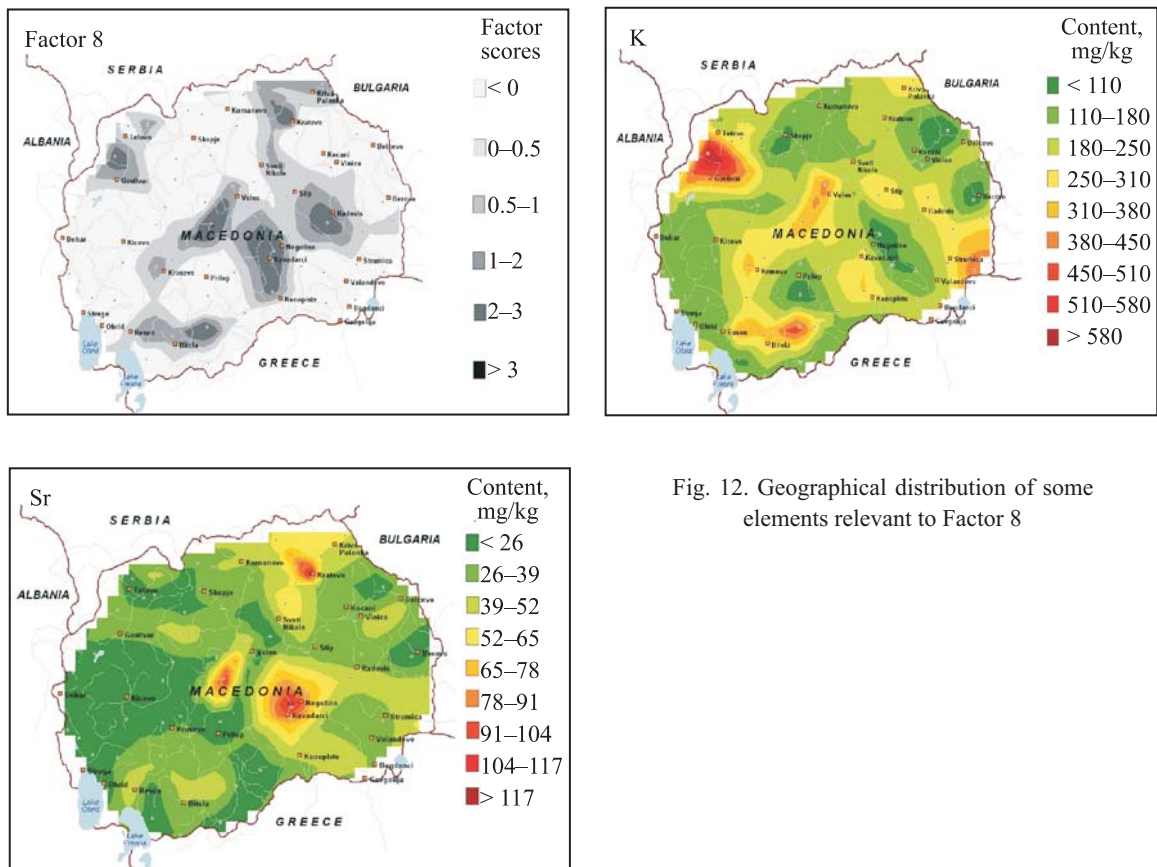


Fig. 12. Geographical distribution of some elements relevant to Factor 8

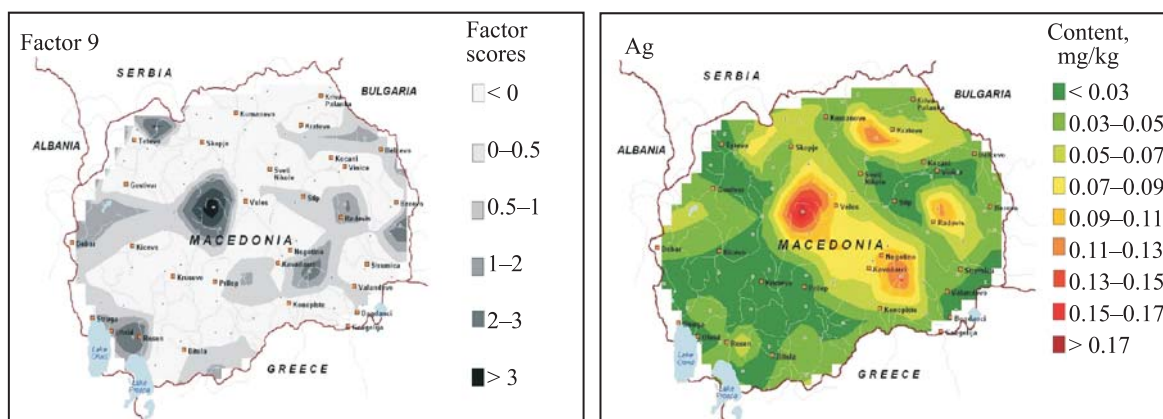


Fig. 13. Geographical distribution of some elements relevant to Factor 9

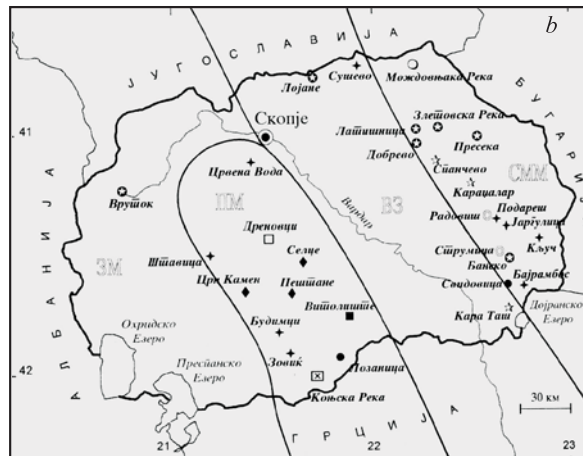
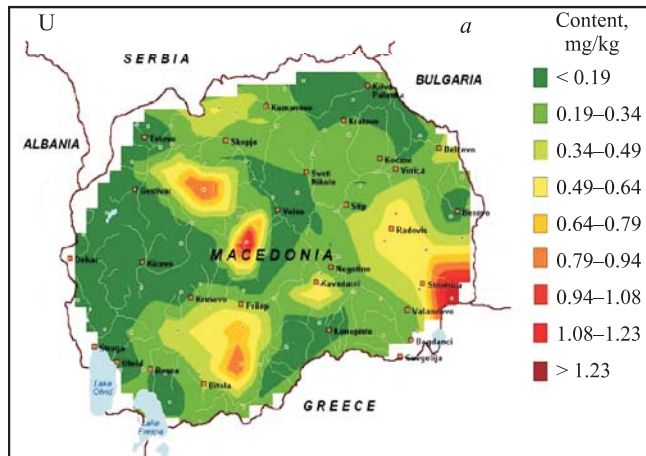
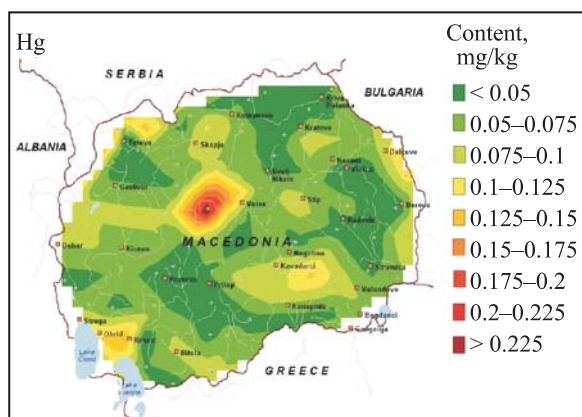


Fig. 14. Comparison of atmospheric deposition patterns determined by the moss technique and the location of uranium deposits in Macedonia [31]

URANIUM DEPOSITS AND MOSS URANIUM CONTENT

Particular interest is inherent with the data on atmospheric deposition patterns of uranium in moss in the vicinity of uranium deposits in the Republic of Macedonia (soil data) [31]. Distribution of uranium concentration in moss and soil over the sampled territory is shown

in Fig. 14. The observed geographical anomalies seem to correspond to the presence of the uranium minerals in some geochemical regions of Macedonia. The higher U abundance in the southwestern part of the country (near the town of Bitola) is probably due to fly-ash deposition

from the combustion of large amounts of lignite (about 6 million t per year) [32] (Macedonia's First National Communication, 2003) in the power plant near Bitola with air, and possibly also as a result of transboundary pollution from several power plants using lignite type of coal [27] in the northern part of Greece, just south of Bitola power plant. It should be mentioned that in the coal locality of Suvodol significant uranium minerals are present [31]. Minerals of uranium, especially plehblendita, are very soft and could be easily blown into the atmosphere with dust to be later accumulated from dry and

wet atmospheric depositions in moss growing in the surrounding area.

Similarly, the appearance of the uranium anomalies in the region of the city of Strumica (southeastern part of the country) could be explained by the presence of significant amount of uranium minerals in the granites deposit in the geological structure of this region [31]. It is important to notify that in this region the exploitation of albitic granites (with a relatively high content of U) is taking place. During exploitation of these granites the process of drilling and milling of the rock may release considerable amounts of dust particles into the environment.

CONCLUSION

This is the first study of the atmospheric environment within the Republic of Macedonia encompassing its entire territory, and it adds this country to the European moss network. The present study employed a higher-density sampling network than most similar studies, and supports the reliability of the study. In comparison with neighboring countries where similar studies have been made, the obtained results for Macedonia generally show a more favorable picture, but comparison with more pristine territories in Europe still shows that the country is considerably exposed to air pollution. The most important pollution sources appear to be smelters near the cities of Veles, Kavadarci and Tetovo. Fly ash from burning lignite coal in power plants near Bitola and

Kicevo is also an important polluting factor and it may explain some of the uranium deposition patterns. The significance of transboundary atmospheric transport in this region remains to be studied in the future.

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