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BIOMONITORING OF ATMOSPHERIC METAL DEPOSITION IN THE REPUBLIC OF MACEDONIA

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Abstract

For the first time the moss biomonitoring technique was applied to air pollution studies over the entire territory of the Republic of Macedonia. Its mountainous and hilly relief, in spite of arid climate, was favorable for collecting terrestrial moss *Hypnum Cupressiforme*, *Campothecium lutescens*, and *Homolothecium Sericium*. Moss samples were collected in September-October 2002 in accordance with the sampling strategy of the European moss survey program. The sampling network included 73 sites evenly distributed over the territory of the country of 25713 km^2. A total of 44 elements Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Ga, As, Se, Br, Rb, Sr, Mo, Ag, Cd, In, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, Hf, Ta, W, Au, Hg, Th, and U were determined by two complementary analytical techniques – instrumental neutron activation analysis (INAA) using epithermal activation at pulsed fast reactor IBR-2, FLNP JINR, Dubna, Russia, and atomic absorption spectrometry (AAS) in Sts. Cyril and Methodius University, Skopje, Macedonia. The large concentration range – from 10 000 ppm for Al and K to 0.001 ppm for some rare earths – was covered. Principal component analysis distinguished among the nine factors some pointing toward natural crust, marine, and vegetation components. The other 6 factors reflect anthropogenic origin of trace element deposition in the Macedonian moss samples: ferrous and non-ferrous industries, oil refinery, and fertilizer production and central heating stations. Four areas are experiencing environmental stress: Veles, Skopje, Tetovo and Kavadarci-Negotino, whereas agricultural 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 elemental hypothesis for the spatial distribution of Balkan endemic diseases is explored.

Keywords: Biomonitoring, moss, heavy metals, INAA, AAS

INTRODUCTION

The use of mosses as biomonitors was introduced in Scandinavian countries more than three decades ago and it is widely accepted as a method to assess the atmospheric deposition of metals [1, 2]. Mosses have 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. The data from the existing surveys for heavy metal concentrations in mosses are an invaluable resource for international negotiations on heavy metal pollution. 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 in mosses project is coordinated by the Coordination Centre of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation). The data from the moss surveys allow both spatial and temporal trends in heavy metal concentration/deposition to be examined, and the areas where there is high deposition of heavy metals from long-range transport to be identified.

The presence of heavy metals in the air within the Macedonian territory has been studied only for some particular locations such as the towns of Veles and Skopje using atomic absorption spectrometry (AAS) [3-7]. The aim of the present study was to cover the entire territory of Macedonia and to include other metals that are not accessible with AAS. It will also provide a basis for comparisons with future studies. Although the most obvious reason for this kind of study is concerns about health effects from air pollution, another important issue is the economic impact of polluting factors, having in mind that Macedonia is an exporter of food products to EU and other countries.

The Republic of Macedonia is located in the central part of the Balkan Peninsula. It is a landlocked country having an area of 25,713 km^2 with approximately 80% of the territory in mountainous regions. The country is under the influence of continental climate 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 largest industries (by value of annual output) are coal production, metal (lead, zinc, steel and ferro-alloys) production, and textiles.

The primary task of the present study is to reveal unknown pollution sources and depict the deposition patterns in areas affected by anthropogenic impact of heavy metals. Epithermal neutron activation analysis, previously used in similar studies of atmospheric deposition in Bulgaria [8], Romania [9, 10], Northern Serbia and Bosnia [11], in the South Ural Mountains [12] and Central Russia [13, 14], was employed also in the present study.

EXPERIMENTAL

Sampling

Samples of the three moss species *Hypnum cupressiforme, Campothecium lutescens* and *Homolothecium sericium* were collected at 73 localities (Fig. 1) 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, 2]. 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 x 50 m. Collected material were stored in paper bags. A separate set of disposable polyethylene gloves was used for collection of each sample.

Sample preparation

NAA. In the laboratory the samples were cleaned from extraneous plant material air-dried to constant weight at 30–40 °C for 48 hours. The samples were not washed and not homogenised. Green-brown moss shoots representing 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 [15]. 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 same weight (about 0.3 g) were packed in aluminium cups.

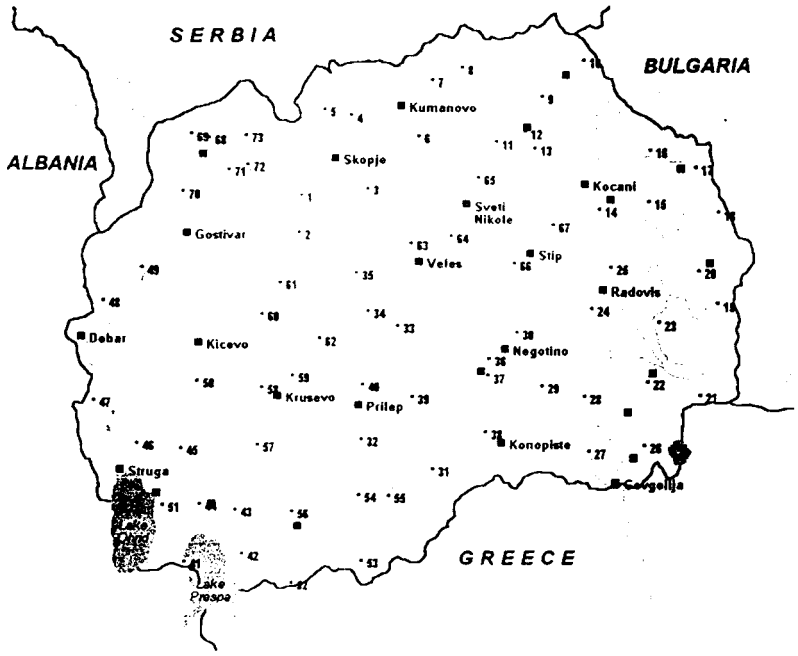

Fig. 1. Sampling network in Macedonia

AAS. The environmentally important element lead cannot be determined by INAA, and Cu and Hg are difficult at the relevant concentration levels. These elements were therefore determined by AAS. Moss samples (0.5 g) were placed in a Teflon digestion vessels, 5 ml of HNO_3 and 2 ml H_2O_2 (30 %, *m/V*) were added, the vessels are capped closed, tightened and placed in the rotor of the microwave digestion system Milestone, Ethos Touch Control. The digestion was carried out with the digestion programs: (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 quantitatively transferred in 10 mL calibrated flasks.

Analysis

NAA. The NAA was performed at the pulsed fast reactor IBR-2 at the Frank Laboratory of Neutron Physics, Dubna, Russia. Two different irradiation times were used: 60 s (Ch2 conventional NAA) and 100 hours (Ch1 – epithermal NAA). Characteristics of neutron flux density in the channels equipped with the pneumatic system are given in Table 1 [16].

Table 1. Flux parameters of irradiation positions [16]

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

To determine short-lived isotopes 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 for 20 min after 9–10 min decay. Long-lived isotopes were determined

after irradiation for 100 hours in the cadmium-screened channel 1. After irradiation samples were re-packed into clean containers and measured after 4–5 and 20–23 days for 45 min and for 3 h, respectively. Gamma spectra were registered as described elsewhere [17].

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 Frank Laboratory of Neutron Physics [18].

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
Zr	^{95}Zr	64.0 d	756.7	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
Sm	^{153}Sm	46.7 h	103.2	3
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 days of decay;
Method 4: epithermal NAA, measured after 20–23 days of decay.

The QC of NAA results was ensured by simultaneous analysis of the reference materials (RM) Lichen 336 IAEA (International Atomic Energy Agency) and standard reference materials SRM-1575 (pine needles) from the US NIST (National Institute of Standards and Technology). NORD DK-1 (moss reference sample) prepared for doing the calibration in the laboratories participating in the corresponding 1990 Nordic survey was also used [19].

AAS. Lead was determined by Zeeman electrothermal atomic absorption spectrometer (ZETAAS) Varian SpectrAA 640 Z, copper with flame atomic absorption spectrometer (FAAS) Thermo Solaar S4 and mercury by cold vapour atomic absorption spectrometry (CV-AAS) using continuous flow vapour generation accessory (VGA-76, Varian) connected to an atomic absorption spectrometer (SpectrAA 55B, Varian).

The QC of AAS determinations was performed by standard addition method and it was found that the recovery for the investigated elements ranges between 98.5 to 101.2 %.

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 3, along with corresponding data from similar studies in neighbouring Balkan countries. For comparison with a pristine territory corresponding data for northern Norway are shown in the right-hand column of Table 3.

Principal component analysis (factor analysis) was used to identify and characterise different pollution sources and to point out the most polluted areas (Table 4).

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 due to soil particles adhered to the moss samples. Probably some increasing of the content of U and Th is due to air pollution from coal ash from thermo-electrical power plant in Bitola using lignite as a fuel [21]. Geographical distribution of U, Th, Hf and Sm are shown in Fig. 2.

Factor 2 (Ni, Zn, Se, Ag, Cd, In, Sb, Pb). This factor contains elements normally associated with air pollution. It appears to be connected in particular with a lead-zinc smelter in Veles and ferro-nickel smelting plant in Kavadarci, but is also dominant further along the Vardar River valley. The geographical distributions of some elements in Factor 2 are shown in Fig. 3. Here Se is also present with a lower loading (0.35) and that may evidence for copper flotation plant near Radoviš and lead and zinc smelter in Veles and coal combustion (near Bitola).

Factor 3 (Cl, Mn, Mo, W, Au) is most probably associated with the interaction of the moss with high vegetation [22].

Factor 4 (Mg, Al, Sc, Ti, V, Cu). From the elemental composition it appears to be a soil factor associated with basic rocks. The dominant area for this factor is in the south-east part of the country next to the Greek border. Its element composition also indicates anthropogenic origin, but the source is not clear. There are no anthropogenic activities with Mo, W and Au emission, except for 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 is due to open iron mine of magnetite ore [23] which is not in operation any more. The appearance of Au in mosses in the eastern part of the country appears to be related to the copper flotation plant near Radoviš.

Table 3. Comparison of the results obtained in present study with other Balkan countries and Norway, mg/kg

	Macedonia (Present work)		Northern Serbia [11]		Bosnia-Herzegovina [11]		Romania (Transylvania) [10]		Bulgaria (West and South) [18]		Norway [20]	
No of samples	73		92		23		70		103		464	
Element	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
Na	419	118-8673	694	178-2440	360	91-1100	902	192-4330	523	155-5573		
Mg	2377	674-7421	2780	1100-8130	2670	1040-9520	2850	480-6840	2026	748-12500	1543	645-3678
Al	3736	825-17600	6800	1280-22090	6270	2305-20740	5545	830-23000	3843	1111-46350	350	97-10970
Cl	149	43-693	256	105-1030	344	156-715	370	160-1300	161	59-1180		
K	8615	2861-18190	5090	2710-11750	4820	1950-6820	7770	4770-19980	5764	3274-20490		
Ca	5593	1207-23640	7720	2890-18120	10310	5323-34330	5770	1250-23500	7283	2266-19650	3120	1379-22512
Sc	0.81	0.12-6.79	1.31	0.27-4.13	0.47	0.13-1.37	0.94	0.21-6.13	0.65	0.2-6.4		
Ti	163	12-1365	71	11-297	57	14-222					31	10-414
V	6.9	1.79-43	11	2.85-39	11	2.89-34	8.7		8.4	2.2-112.6	1.35	0.28-22.6
Cr	7.47	2.33-122	6.51	1.14-22	5.09	0.94-19	13.8		3.2	0.5-26.9	0.69	0.058-259
Mn	186	37-1475	217	30-2340	503	38-1770	265	27-1470	251	32-986	333	28-5415
Fe	2458	424-17380	3110	720-9230	1600	439-4750	3290	815-21340	2314	692-14700	362	99-11216
Co	1.09	0.24-13.6	8.24	1.42-39	1.09	0.18-7	1.41	0.32-7.0	1.08	0.23-10.6	0.17	0.014-2.6
Ni	2.4	0.09-24	6.73	1.96-26	7.14	0.92-25	5.4	0.6-32	4.1	0.5-18.6	1.1	0.057-72.1
Cu	27.29	2.97-83.33	16.9	6.31-3140	67.1	10-80	21.5	2.21-2420	14.5	5.34-1860	4.26	1.74-206
Zn	39	14-203	44	14-415	25	10-57	135	39-2950	41	19-379	32	9.7-661
As	0.80	0.12-8.0	3.35	0.46-61	1.12	0.31-3.7	2.2	0.59-45.1	1	0.3-59.0	0.135	0.0023-2.63
Se	0.18	0.013-0.61	0.39	0.046-10	0.09	0.035-0.18	0.36	0.08-5.01	0.24	0.01-1.18		
Br	2.16	0.06-7.7	5.75	1.83-18	4.31	1.99-8.1	8.6	2.03-20.9	3.6	1.1-11.6		
Rb	10.9	5-47	13	3-47	9	3-19	15.0	5.8-135	12	3.0-69	9.9	1.2-50.7
Sr	31	11.8-136	22	6.8-95	14	5.8-32	37.4	1.8-290	25	7-106	11.5	2-74.2
Mo	0.19	0.03-1.12	0.85	0.12-23	0.97	0.26-3	0.65	0.13-10	0.99	0.16-3.36	0.108	0.0087-2.42
Ag	0.040	0.007-0.20	0.078	0.012-1.5	0.052	0.015-0.076	0.13	0.03-4.54			0.021	0.0017-0.27
Cd	0.16	0.016-2.95	<0.4	<0.4-6.5							0.087	0.001-2.65

	Macedonia (Present work)		Northern Serbia [11]		Bosnia-Herzegovina [11]		Romania (Transylvania) [10]		Bulgaria (West and South) [18]		Norway [20]	
No of samples	73		92		23		70		103		464	
Element	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
In	0.043	0.0032-0.16	0.025	0.0036-0.34	0.019	0.0057-0.048						
Sb	0.2	0.039-1.4	0.52	0.13-7	0.25	0.068-1.5	0.88	0.16-51	0.23	0.07-20.2	0.056	0.001-0.46
I	1.18	0.36-2.8	2.09	0.87-4	1.80	0.60-3	2.17	0.76-5.55	1.4	0.6-4.4		
Cs	0.39	0.097-1.7	0.76	0.11-18.2	0.39	0.079-2.5	0.51	0.12-3.4	0.40	0.10-2.96	0.129	0.01-2.06
Ba	54	14-256	39	13-130	41	8-90	101	20-658	68	17-517	19.2	4.3-217
La	2.32	0.50-22	4.66	1.09-13	3.11	0.82-8	2.4	0.4-15.2	2.9	0.8-23.7	0.28	0.049-9
Ce	5.60	0.83-42	9.2	1.84-28	3.31	0.87-12	6.1	0.9-42.5	-	-	0.54	0.098-17.6
Eu	0.110	0.03-0.48	0.08	0.02-0.48	0.17	0.019-0.48	-	-	-	-	0.010	<0.0003-0.24
Tb	0.06	0.01-0.56	0.11	0.02-0.36	0.13	0.041-0.31	0.07	0.01-0.42	0.068	0.016-0.610	0.005	≤0.0001-0.16
Hf	0.26	0.05-3.8	0.78	0.15-2.6	1.06	0.29-3.8	0.56	0.12-4.66	0.46	0.11-4.78	0.006	0.001-0.16
Ta	0.09	0.013-0.79	0.11	0.024-0.29	0.13	0.04-0.36	0.10	0.01-0.66	0.076	0.018-0.563	<0.0005	<0.0005-0.14
W	1.21	0.25-3.9	1.34	0.19-3.3	0.21	0.03-0.52	1.02	0.12-8.74	0.193	0.03-1.39	0.04	0.002-0.89
Au	0.0061	0.001-0.034	0.0041	0.00029-0.087	0.0057	0.0017-0.017	0.025	0.003-0.114	0.0042	0.0009-0.0465		
Hg	0.056	0.018-0.264	0.386	0.01-2.69	0.173	0.4-4.85	-	-	-	-	0.052	0.022-0.208
Pb	6.0	1.5-37.2	-	-	-	-	14.3	6.45-31.5	18.9	4.55-887	2.70	0.5-27.7
Th	0.67	0.12-7.6	0.82	0.18-2.4	0.38	0.11-1.5	0.81	0.21-4.16	0.56	0.11-4.53	0.054	<0.0002-1.7
U	0.21	0.03-1.45	0.32	0.08-1.03	0.21	0.05-0.61	0.28	0.04-1.36	0.20	0.03-1.87	0.017	<0.0004-0.37

Table 4. Factor analysis of NAA and AAS data on moss samples from Macedonia

Rotated Matrix Component									
Factor	1	2	3	4	5	6	7	8	9
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
% Total	*43.1*	*11.4*	*5.6*	*4.8*	*4.3*	*3.7*	*3.1*	*2.7*	*2.4*
Eigenvalue	18.5	4.9	2.4	2.1	1.8	1.6	1.3	1.1	1.0
Rotation Method: VARIMAX with Kaiser Normalization									

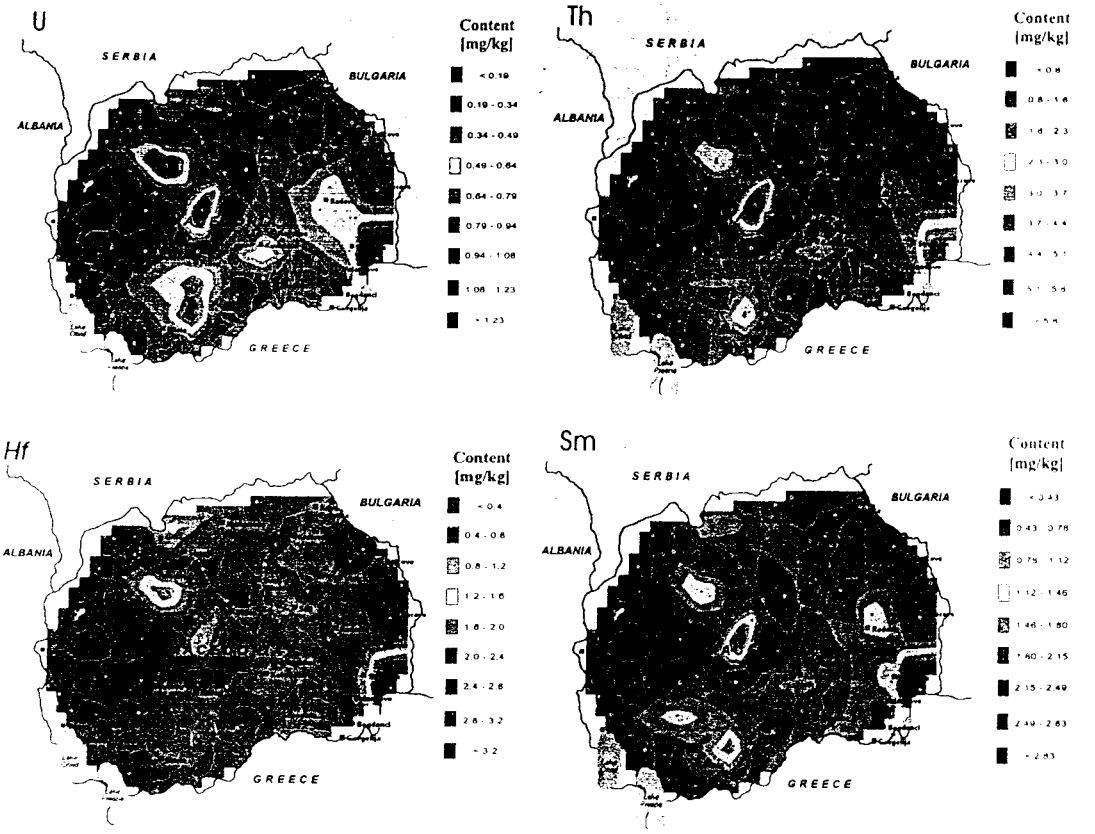

Fig. 2. Distribution by concentration of U, Th, Hf, Sm

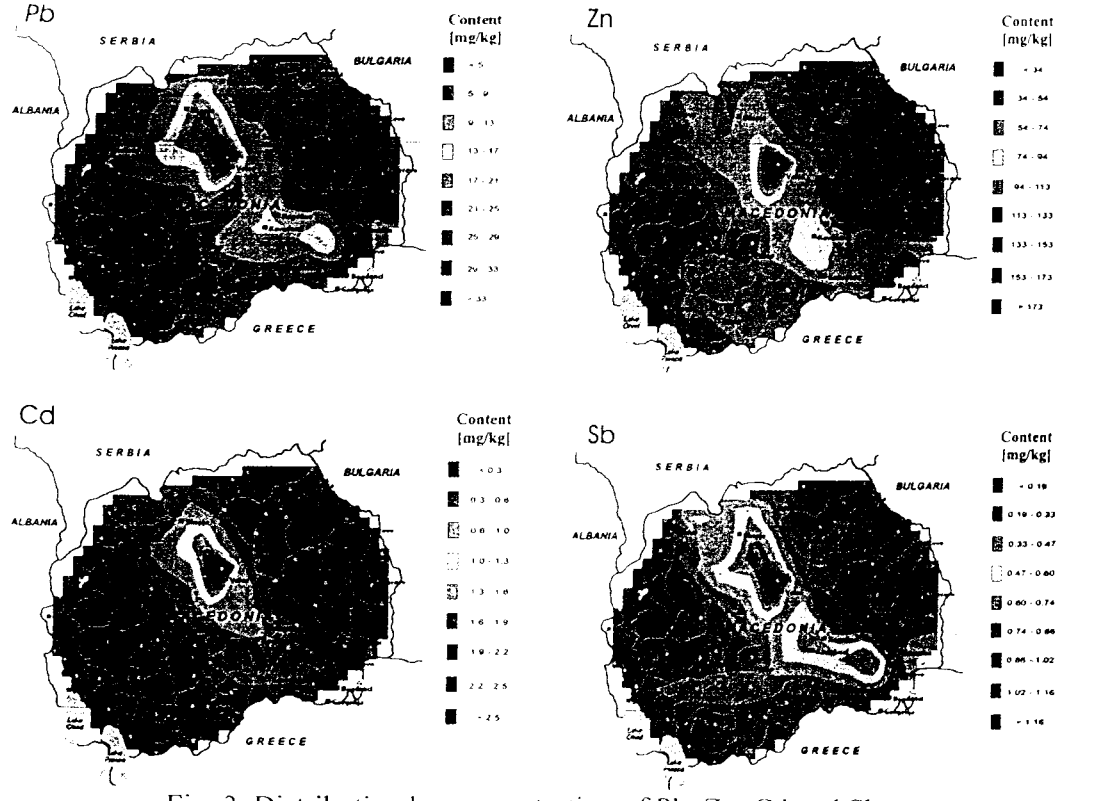

Fig. 3. Distribution by concentration of Pb, Zn, Cd and Sb

Factor 5 (Sc, Cr, Fe, Co, Ni) most probably is connected with some industrial activities in the towns of Tetovo (ferrochromium smelter plant) and Kavadarci (ferronickel smelter plant). Higher values of Ni, Fe and Co in this region could be explained by air pollution from ferro-nickel smelting plant in Kavadarci (see Fig. 4).

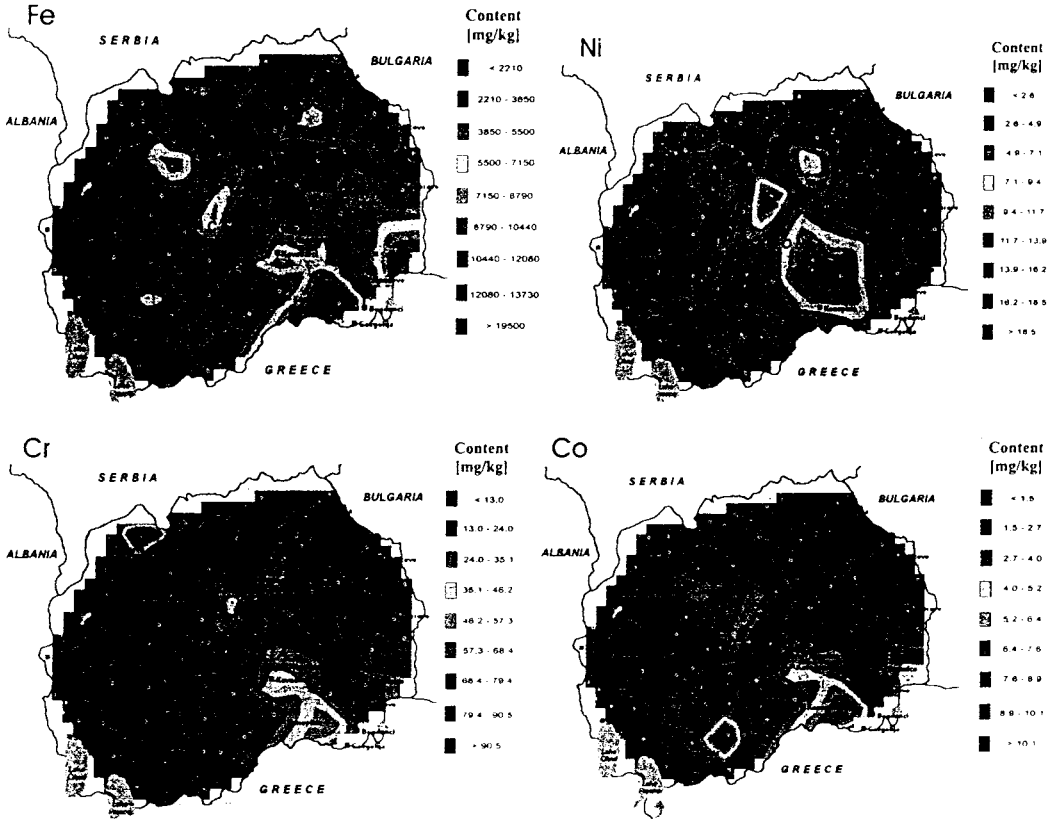

Fig. 4. Distribution by concentration of Fe, Ni, Cr, As

Factor 6 (Cl, Mn, Br, I) and **Factor 7** (Ca, I). This factors of the three halogens and Ca is located to the south-west and south of the country, and may reflect marine influence.

Factor 8 (K, Sr). As in the case of factor 3, factor 8 is most probably associated with higher vegetation. Fig. 10 shows the distribution of Factor 8 and the associated elements K and Sr. This factor corresponds relatively well to the forested areas of the country.

Factor 9 (Ag, Hg). This factor may be connected with local metals workshops in the vicinities of large and small settlements.

The most striking examples of metal pollution in Macedonia appear to be the lead-zinc smelter in Veles, the chromium smelter in Tetovo, north-west of Skopje and ferronickel smelter in Kavadarci.

The new results on Macedonia covered one more "white spot" in the map of heavy metal atmospheric deposition Europe. The results on As, Cd, Cr, Fe, Ni, V, and Zn were reported to the Atlas on Heavy Metals in European Mosses: 2000-/2001 Survey [24]. Scientists and graduate students from the University of Skopje, Macedonia, and

JINR, Dubna, Russia, intend also to contribute to the next European moss survey in 2005/2006.

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References

1. Å. Rühling, E. Steinnes, Atmospheric heavy metal deposition in Europe 1995-1996, NORD Environment, NORD 1998:15 (1998).
2. B. Smodis, M. L. Pignata, M. Saiki, E. Cortes Toro, B. Ni, B. Markert, B. J. B. Nyarko, J. Arunachalam, J. Garty, M. K. Voutchkov, H. Th. Wolterbeek, E. Steinnes, M. C. M. Freitas, A. Lucaciu, M. V. Frontasyeva, Validation and application of plants as biomonitors of trace element atmospheric pollution – a co-ordinated effort in 14 countries, *J. Atmos. Chem.*, **49**, 3-13 (2004).
3. M. Mulev, M. Melovski, Lj. Derlieva, The content of lead, zinc and copper in soil, leaves and bark of lime (Tilia plathyphyllos) in the city of Skopje, *Ann. Biol. Fac. Sci. Skopje*, **45**, 187-190 (1992).
4. M. Mulev, M. Melovski, Lj. Derlieva, The content of some heavy metals in leaves and bark of black pine (Pinus nigra) and in the top soil in the city of Skopje, *Ann. Biol. Fac. Sci. Skopje*, **46**, 119-132 (1993).
5. T. Stafilov, V. Jordanovska, Determination of cadmium in some vegetables produced in the area near the lead and zinc smelting plant in Veles, Macedonia, *Ekol. zašt. život. sred.*, **4**, 35-38 (1997).
6. S. Kulevanova, T. Kadifkova Panovska, T. Stafilov, A. Lazaru, Heavy metals content in lime flowers from urban environment, *Pharmacia (Sofia)*, **45**, 13-16 (1998).
7. T. Stafilov, R. Bojkovska, M. Hirao, Air pollution monitoring system in the Republic of Macedonia, *J. Environ. Protect. Ecol.*, **4**, 518-524 (2003).
8. J. Stamenov, M. Iovchev, B. Vachev, E. Gueleva, L. Yurukova, A. Ganeva, M. Mitrikov, A. Antonov, A. Strentz, Z. Vrbanov, I. Batov, K. Damov, E. Marinova, M. V. Frontasyeva, S. S. Pavlov, L. P. Strelkova, New results from air pollution studies in Bulgaria (Moss Survey 2000-2001). Preprint JINR, E14-2002-204, Dubna, 2002.
9. O. A. Culicov, M. V. Frontasyeva, E. Steinnes, O. S. Okina, Zs. Santa, R. Todoran, Atmospheric deposition of heavy metals around the lead and copper-zinc smelters in Baia Mare, Romania, studied by the moss biomonitoring technique, neutron activation analysis and flame atomic absorption spectrometry, *J. Radioanal. Nucl. Chem.* **254**, 109-115 (2002).
10. S. Cucu-Man, R. Mocanu, O. Culicov, E. Steinnes, M. V. Frontasyeva, Atmospheric deposition of metals in Romania studied by biomonitoring using the epiphytic moss *Hypnum cupressiforme*, *Int. J. Environ. Anal. Chem.*, **84**, 845-854 (2004).
11. M. V. Frontasyeva, T. Ye. Galinskaya, M. Krmar, M. Matavulj, S. S. Pavlov, D. Radnović, E. Steinnes, Atmospheric deposition of heavy metals in northern Serbia and Bosnia-Herzegovina studied by moss biomonitoring, neutron activation analysis and GIS technology, *J. Radioanal. Nucl. Chem.*, **259**, 141-147 (2004).

12. M. V. Frontasyeva, L. I. Smirnov, E. Steinnes, S. M. Lyapunov, V. D. Cherchintsev, Heavy metal atmospheric deposition study in the South Ural Mountains, *J. Radioanal. Nucl. Chem.*, **259**, 19-26 (2004).
13. E. V. Ermakova, M. V. Frontasyeva, E. Steinnes, Heavy metal and other trace elements deposition studied in Tula Region by means of moss-biomonitors, *Environmental Chemistry*, St.-Petersburg, **13**, No. 3, p. 167-180 (in Russian).
14. E. V. Ermakova, M. V. Frontasyeva, S. S. Pavlov, E. A. Povtoreyko, E. Steinnes and Ye. N. Cheremisina, Air pollution studies in Central Russia (Tver and Yaroslavl Regions) using the moss biomonitoring technique and neutron activation analysis. *J. Atmos. Chem.*, **49**, 549-561 (2004).
15. E. Steinnes, J. E. Hanssen, J. P. Rambæk, N. B. Vogt, Atmospheric deposition of trace elements in Norway: temporal and spatial trends studied by moss analysis, Water, Air, Soil Pollut. **74**, 121-140 (1994).
16. M. V. Frontasyeva, S. S. Pavlov, Analytical Investigations at the IBR-2 Reactor in Dubna, *JINR Preprint*, 2000, E14-2000-177, Dubna.
17. E. Steinnes, M. V. Frontasyeva, Epithermal Neutron activation analysis of mosses used to monitor heavy metal deposition around an iron smelter complex, *Analyst*, **120**, 1437-1440 (1995).
18. T. M. Ostrovnaya, L. S. Nefedyeva, V. M. Nazarov, S. B. Borzakov, L. P. Strelkova, in: Activation analysis in environment protection, D-14-93-325, Dubna, 1993, 319-326.
19. E. Steinnes, Å. Rühling, H. Lippo, A. Mäkinen, Reference materials for large-scale metal deposition surveys, *Accred. Qual. Assur.*, **2**, 243-249 (1997).
20. E. Steinnes, T. Berg, T.E. Sjøbakk, H. Uggerud, M. Vadset, Atmospheric deposition of heavy metals in Norway Nation-wide Survey 2000, Report, State Pollution Control Authority. Oslo, Norway, 2001, p. 28.
21. S. E. Manahan, Environmental Chemistry, Seventh Edition, Lewis Publishers, Boca Raton, Florida, 2000, p. 318.
22. E. Steinnes, A critical evaluation of the use of naturally growing moss to monitor the deposition of atmospheric metals, *Sci. Total Environ.*, **160**, 243-249 (1995).
23. T. Stafilov, Application of electrothermal atomic absorption spectrometry in analysis of samples from iron and steel production, *Metalurgija*, **30**, 75-80 (1991).
24. European Atlas: Heavy Metals in European Mosses: 2000/2001 Survey, UNECE ICP Vegetation. Editors: A. Buse, D. Norris, H. Harmens, P. Buker, T. Ashenden and G. Mills. Centre for Ecology & Hydrology, University of Wales Bangor, UK, March 2003, p. 45.