ASSESSMENT OF ATMOSPHERIC DEPOSITION OF POLLUTANTS IN SOUTHERN BULGARIA BASED ON NEUTRON ACTIVATION ANALYSIS OF MOSS BIOMONITORS

G. Hristozova[1,3], S. Marinova[1], V. Svozilik[2], M.V. Frontasyeva[3]

[1]*Faculty of Physics, 'Paisii Hilendarski' University, Plovdiv, Bulgaria*
[2]*Institute of Environmental Technology, VSB-Technical University of Ostrava, Czech Republic*
[3]*FLNP, Joint Institute for Nuclear Research, Dubna, Russia*

Abstract. For the fifth time Bulgaria participates in the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (the UNECE ICP Vegetation). In the summer of 2015, 115 moss samples (*Hypnum cupressiforme, Pleurozium schreberi* and *Pseudoscleropodium purum*) were collected in accordance with the sampling strategy. Concentrations of a total of 37 elements were determined in moss biomonitoring species using instrumental epithermal neutron activation analysis. The concentrations are comparable with those in other European countries.

INTRODUCTION

The use of mosses and lichens as biomonitors is well-established in monitoring atmospheric deposits of metals in Europe. Due to their rudimentary root system and lack of vascular tissues, these plants obtain nutrients primarily through wet and dry deposition. Their morphological and physiological properties, and wide geographical distribution make them suitable biomonitors [1]. Several moss species are used in air pollution monitoring programs in more than 25 European countries under auspices of United Nations Economic Commission for Europe (UNECE) - International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation) [2]. Since 1990, at five-year intervals, a moss biomonitoring survey is conducted in parallel, in all participating European counties. Bulgaria was involved in the program in 1995.

SAMPLES AND METHODS

Object of study

Bulgaria is located in southeastern Europe, on the Balkan Peninsula. Total area of the country is about 111,000 km^2, and the relief is mostly mountainous. The climate to the north of Balkan Mountains is continental, and to the south, it transitions to Mediterranean. Summers are hot and dry, therefore few moss species are able to thrive and remain vital.

Bulgaria is rich in coal deposits, metal and non-metal ores. Main sectors of the economy nowadays are coal production, agriculture, heavy industry, production of construction materials, textile manufacturing, pharmaceutical industry, food processing, and petroleum refinement. The country has undergone a significant transformation over the past decades. There was a shift from a highly centralized, planned economy to an open market-based economy, characterized by slow economic restructuring and growth. The resurgence of the industry is expected to influence the ecological situation of the country.

For the purpose of the study, 115 moss samples were collected. Sampling was performed in accordance with the requirements of the ICP Vegetation Programme [3]. A map

of the sample collection sites is presented in Fig. 1. Using GPS, longitude and latitude were noted for all sampling sites (Table 2). All collected samples were put into paper bags for storage and transportation.

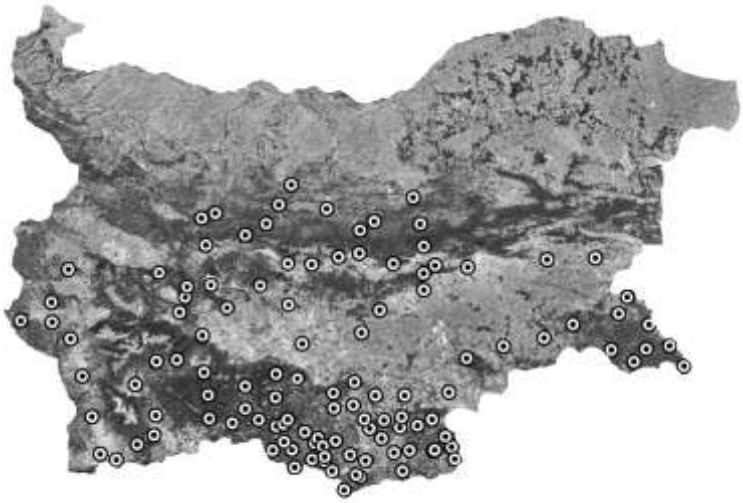

Fig. 1. Sampling sites.

Methodology and equipment

The samples were air-dried to constant weight at 40 ^{o}C for 48 h, and extraneous plant material was removed. Samples remained unwashed and were sorted, so that only the green living part of the moss, approximately corresponding to a three-year growth, was subjected to analysis. Moss samples of about 0.3 g were packed in polyethylene foil bags for short-term irradiation and in aluminum cups for long-term irradiation [4]. Neutron activation analysis was performed in the radioanalytical laboratory at the fast pulsed reactor IBR-2 of the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research (FLNP JINR), Dubna, Russia. Qualitative and quantitative analysis were conducted on the basis of certified reference materials.

RESULTS AND DISCUSSION

Summarized results of the determined elemental contents are presented in Table 1. A comparison with data from the 2005 ICP Vegetation survey for Bulgaria shows a decrease in the concentration of element pollutants. This could be explained by the shutdown of several major industrial facilities and the implementation of better filtering technologies and emission control introduced by the functional operational factories. A comparison with background values from parts of Norway [5], where the influence of air pollution is considered minor, shows that As, Cr, Fe, and V contents are still high. Generally, levels of air pollution on the Balkans, as well as in several eastern and central European countries, are high (Fig. 2). In contrast, the environmental situation in Scandinavian countries is characterized by transboundary pollution and the influence of local emitters of pollution is low. In Bulgaria, major sources of anthropological contamination are road transportation, smelting and mining, the textile industry, glass production, phosphate fertilisers in agricultural areas and coal burning (Fig. 3).

Table 1. Results and comparison. Descriptive statistics.

	Bulgaria, 2015 N=115 [mg/kg]		Bulgaria, 2005 [5] N=99 [mg/kg]		Bulgaria, 2000 [5] N=103 [mg/kg]		Norway [6] [mg/kg]	
	median	range	median	range	median	range	median	range
Na	225	79-1560	725	189-8210	523	155-5580	-	-
Mg	2080	514-8550	-	-	-	-	1730	940-2370
AI	2310	569-10900	6930	1532-43600	3843	1111-46400	200	67-820
CI	78.8	16.6-861	232	84-1330	161	59-1180	-	-
K	5670	3250-14200	6020	2750-13800	5760	3270-20500	-	-
Ca	6630	606-14200	8960	4530-32200	7280	2270-19700	2820	1680-5490
Sc	0.408	0.104-3.13	0.92	0.21-7.20	0.65	0.2-6.4	0.052	0.009-0.220
Ti	143	46.4-764	340	94-2590	-			12.4-66.4
V	3.89	1.3-22.7	8.7	2.23-64	8.4	2.2-113	0.92	0.39-5.1
Cr	2.73	0.219-25	3.8	1.18-55	3.2	0.5-26.9	- -	0.10-4.2
Mn	180	39-551	243	45-1270	251	32-986	256	22-750
Fe	1190	376-7240	3000	689-19400	2310	692-147	209	77-1370
Co	0.585	0.197-3.29	1.49	0.35-28	1.08	0.23-10.6	0.202	0.065-0.654
Ni	2.11	0.451-13.5	5	1.08-29	4.1	0.5-18.6		0.12-6.6
Cu	7.36*	3.2-46.88*	6.84**	0.1-63.9**	14.5**	5.34-1860**		-
Zn	27.8	9.52-101	45	23-774	41	19-379		7.9-173
As	0.447	0.201-3.57	0.97	0.27-8.76	1	0.35-59	0.093	0.020-0.505
Se	0.2	0.00753-0.671		0.09-4.71	0.24	0.01-1.18	0.33	0.05-1.30
Br	2.76	1.21-9.39		1.33-18				-
Rb	7.38	2.24-50.7	15	5.16-68	12	3-69	7.7	1.3-51.5
Sr	25	11.3-122	36	14-170	25	7-106	15.8	3.6-43.3
Cd	0.1*	0.02-1.56*	0.23**	0.1-5.56**	-	-	-	-
Sb	0.113	0.0397-0.511	0.29	0.07-8.7	0.23	0.07-20.2	0.033	0.004-0.240
I	1.28	0.48-2.99	2.6	0.85-6.31	1.4	0.6-4.4	2.5	0.6-41.7
Cs	0.207	0.0716-1.8	0.52	0.18-5.71	0.4	0.10-2.96	0.072	0.016-0.88
Ba	46	14.2-309	79	21-294	68	17-517	17.1	5.6-50.5
La	1.35	0.399-22.6	3.3	1-61.79	2.9	0.8-23.7	0.189	0.045-2.56
Ce	2.41	0.49-29.2	6.8	1.75-143	-	-	0.342	0.095-4.61
Nd	1.33	0.22-24.1	3.15	0.01-47	-	-	-	-
Eu	0.0701	0.00972-0.918	-	-	-	-	-	-
Tb	0.0258	0.00531-0.422	0.076	0.02-0.98	0.068	0.016-0.610	0.003	<0.002-0.030
Tm	0.0137	0.00147-0.214	0.057	0.02-0.67	-	-	-	-
Yb	0.094	0.0248-1.08	0.22	0.05-3.32	-	-	-	-
Lu	0.0198	0.0003-1.45	-	-	-	-	-	-
Hf	0.158	0.0404-1.44	0.45	0.11-12.1	0.46	0.11-4.78	-	-
Ta	0.0355	0.00921-0.284	0.127	0.03-1.52	0.076	0.018-0.563	0.01	<0.01-0.07
W	0.0994	0.0244-1.44	1.22	0.25-13	0.193	0.03-1.39	0.127	0.009-1.23
Pb	10.72*	3.72-102.8*	11.7**	0.5-368**	18.9**	4.55-887**	-	-
Th	0.39	0.091-2.8	0.86	0.27-23	0.56	0.11-4.53	0.033	0.004-0.240
U	0.124	0.0327-3.2	0.3	0.09-6.28	0.2	0.03-1.87	0.015	0.001-0.138

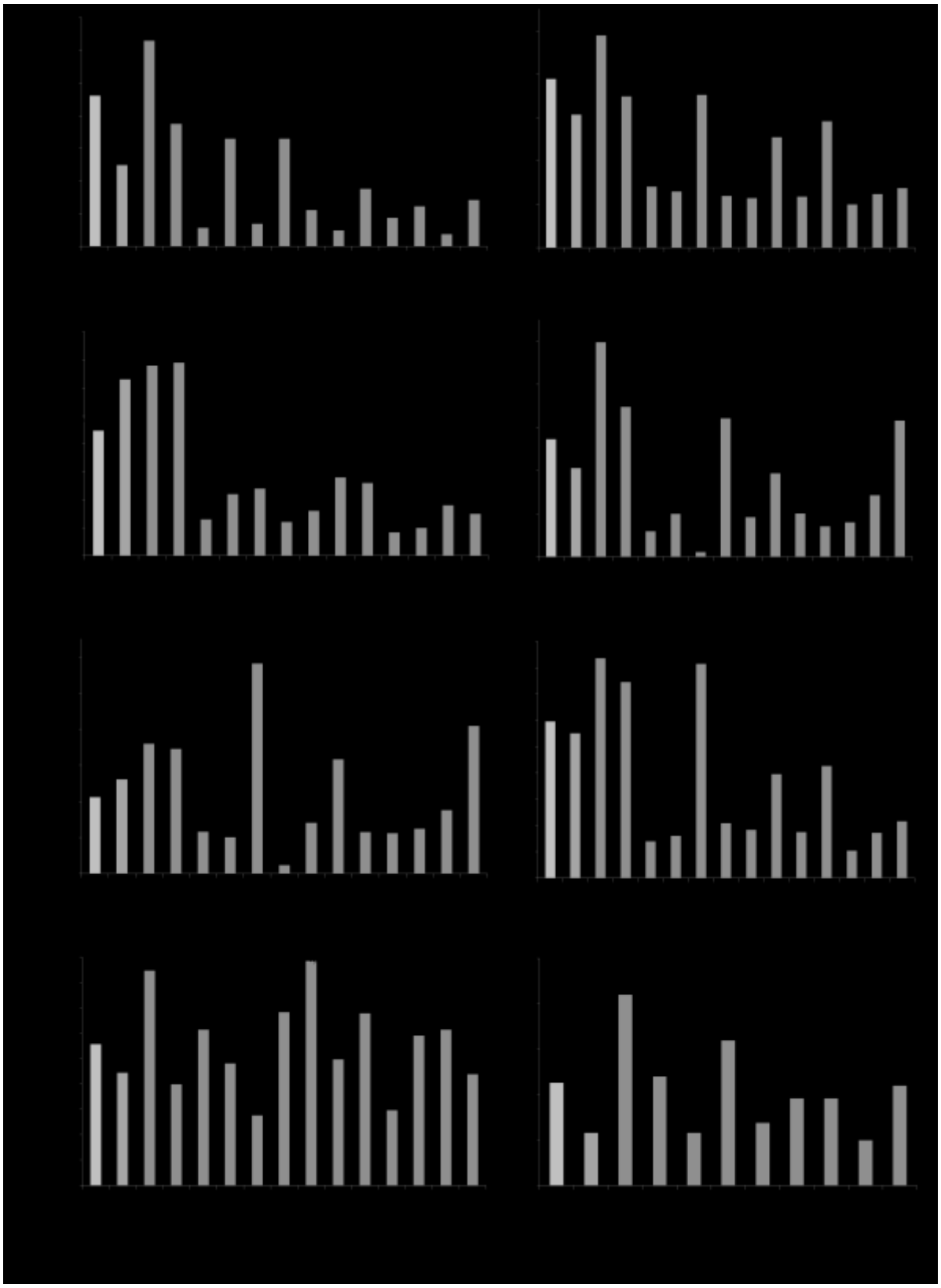

Fig. 2. Comparison of median values for Bulgaria (2015) and several participating countries in the 2010 ICP Vegetation survey.

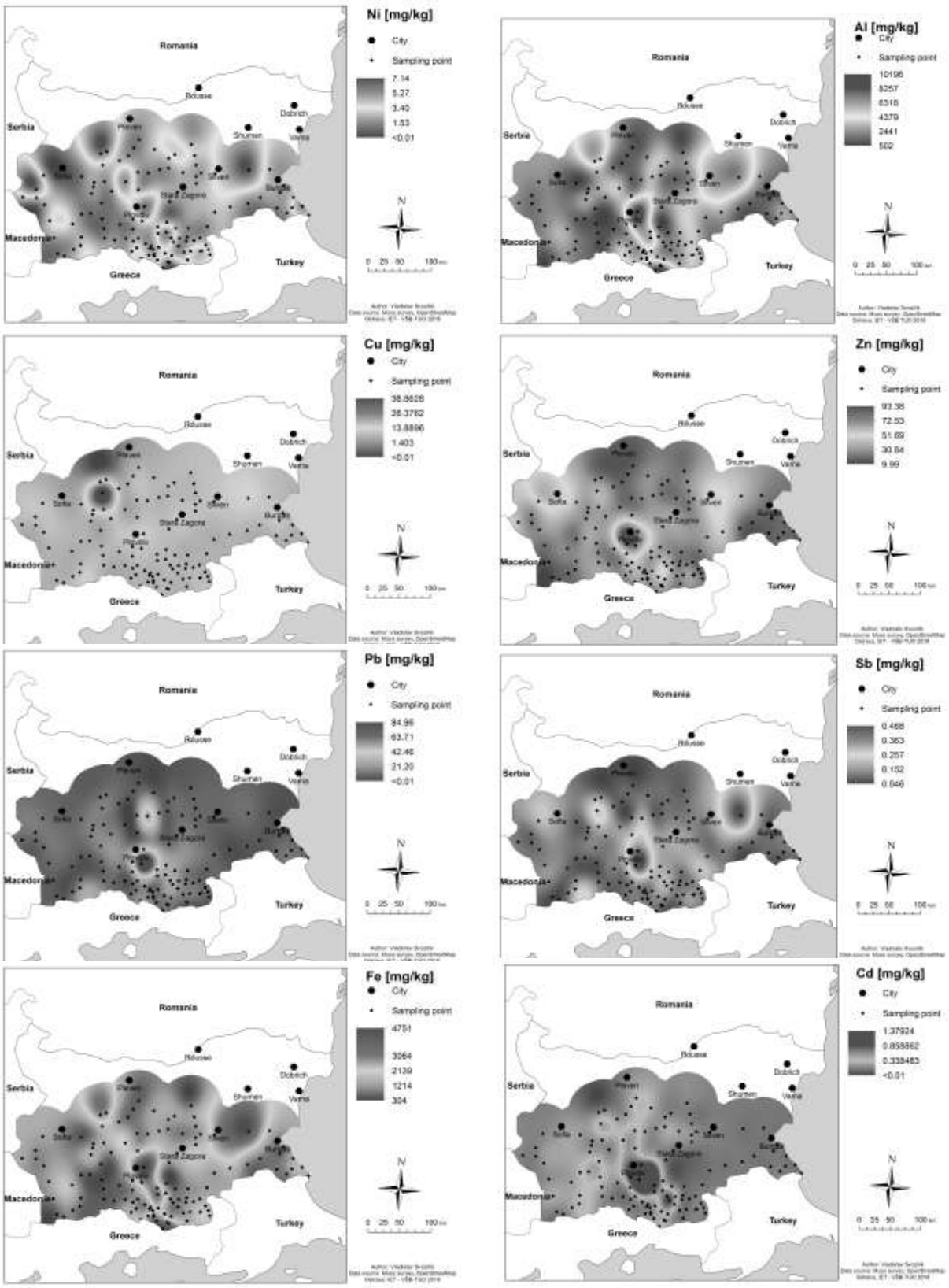

Fig. 3. Atmospheric deposition patterns for Ni, Cu, Pb, Fe, Al, Zn, Sb, and Cd.

CONCLUSIONS

The moss technique is an effective means of studying spatial and temporal trends of atmospheric deposition. Concentrations of a total of 37 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Zn, As, Se, Br, Rb, Sr, Sb, I, Ba, Cs, La, Ce, Nd, Eu, Tb, Tm, Yb, Lu, Hf, Ta, W, Th, U) were determined in moss biomonitoring species using instrumental epithermal neutron activation analysis. The concentrations are comparable with those in other European countries. Comparison with data from previous moss surveys shows a decrease in the concentrations of element pollutants, investigated by the ICP Vegetation programme. The results obtained supplement state monitoring air quality data, which is limited to a small number of sites and pollutants. They could provide for a better estimation of health and environmental risks, and aid risk-management decisions.

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