ATMOSPHERIC DEPOSITION STUDY IN SOUTHERN BULGARIA BASED ON MOSS BIOMONITORS, NEUTRON ACTIVATION ANALYSIS AND INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY

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Abstract. For the fifth time Bulgaria participates in the moss survey carried out in the framework of 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 (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). Three additional environmentally important elements were analysed using inductively coupled plasma atomic emission spectroscopy (Cd, Cu, Pb). The determined concentrations were compared with data from previous moss surveys conducted in Bulgaria, as well as with data from other European countries participating in the ICP Vegetation programme.

INTRODUCTION

Mosses obtain nutrients primarily through wet and dry deposition, and possess a certain set of morphological and physiological properties (such as rudimentary root system and lack of vascular tissues), which make them suitable for biomonitoring of atmospheric depositions of metals [1]. Their wide geographical distribution facilitates large scale monitoring. The moss technique is a well-established method for monitoring in Europe. Several moss species have been thoroughly studied and accepted as biomonitors in air pollution monitoring programs conducted in more than 25 countries under the 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]. Surveys have been conducted in parallel at five-year intervals in all participating counties since 1990.

Bulgaria was involved in the program in 1995. Sampling was performed regularly, and the predominant biomonitoring species was *Hypnum cupressiforme*. The sampling networks were non-uniform throughout the years because of the climate conditions (hot and dry summers unfavourable for moss growth), mountainous terrains, and different member groups partaking in the sampling.

In previous moss surveys, it was ascertained that there were several persistent local hotspots corresponding to contemporary and historical non-ferrous and ferrous facilities, mining and smelting activities. Over the past three decades, the country has undergone a shift from a highly centralized, planned economy to an open market-based economy, characterized by slow economic restructuring and growth. The largest industrial enterprises have been closed down, which has lead to a reduction in local pollution emissions. Still, continuous and systematic exceeding of limit values for daily and annual particulate matter concentrations (PM10) is being reported via state air quality monitoring stations in over 20 towns. This is attributed to domestic heating (especially burning wood and coal), vehicle emissions (obsolete fleets lacking catalytic converters), and to a lesser extent, electricity production and industrial activities.

SAMPLES AND METHODS

Object of study

For the purpose of the study, 115 moss samples were collected in Bulgaria the summer and autumn of 2015. The predominant species was *Hypnum cupressiforme.* In its absence *Pleurozium schreberi* and *Pseudoscleropodium purum* were collected instead. Sampling was performed in accordance with the requirements of the ICP Vegetation Programme [3]. A map of the sampled sites is presented in Fig. 1. All collected samples were put into paper bags for storage and transportation.

Fig. 1. Sampling sites

Methodology and equipment

After removal of extraneous plant material, the unwashed samples were sorted, so that only the green living part of the moss was subjected to analysis. The samples were air-dried to constant weight at 40 ^{o}C for 48 h.

Instrumental epithermal neutron activation analysis was performed in the radioanalytical laboratory REGATA at the reactor IBR-2 of FLNP, JINR. 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.

Inductively coupled plasma atomic emission spectroscopy was carried out in Plovdiv, Bulgaria. 0.5 g of moss were treated with 7ml concentrated NHO_3 and 2 ml H_2O_2 overnight. Microwave digestion was performed. Digests were filtered and transferred quantitavely to 25 ml flasks.

RESULTS AND DISCUSSION

Concentrations of 34 elements in total were determined using instrumental epithermal neutron activation analysis (NAA) (Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Eu, Fe, Hf, I, K, La, Lu, Mg, Mn, Na, Nd, Ni, Rb, Sb, Sc, Se, Sr, Ta, Tb, Th, Ti, Tm, U, V, W, Yb, and Zn). Three additional elements (Cd, Cu, and Pb) were analysed by means of inductively coupled plasma atomic emission spectroscopy (ICP-ES).

Summarized results of the determined elemental contents are presented in Table 1. A comparison with NAA and AAS data of 2005 and 2000 for Bulgaria shows a decrease in the concentration of element pollutants. This could be explained by the shutdown of several major industrial facilities, the implementation of better filtering technologies, and emission control introduced in the functional operational factories. A comparison with background values for regions of Norway where the influence of air pollution is considered minor [5] shows that As, Cr, Fe, and V contents are still high.

Multivariate statistics (factor analysis) was applied to identify associations between the determined elements. Four factors were determined, of which one was interpreted as anthropogenic. Factor 1 is mixed, characterized by earth crust elements (Na (0.66), Mg (0.81), Al (0.74), Sc (0.80), Ti (0.65), V (0.84,) and Fe (0.82)) and marine aerosols (Cl (0.53), Br (0.53), and I (0.61)). Factor 2 contains REEs, U (0.61), and Th (0.84) – typical crust components, indicating presence of soil particles in the samples. Factor 3 has high loadings for As (0.75), Se (0.73), Sb (0.72), and Cu (0.74), which are found in ores. The highest loadings for this factor were for sites located near Cu-Ag mines. Factor 4 has high values for K (0.67) and Ca (0.65), characterizing wet deposition by higher vegetation.

Fig. 1 shows the temporal trends for metals reported in the moss surveys, with the exception of Sb. Data for this element determined in mosses using INAA in 2000/2001 is available elsewhere [6], and in the thematic report in 2005/2006 as additional data. Median values for Sb decreased by 52% (from 0.23 mg/kg in 2000, 0.29 mg/kg in 2005, to 0.11 mg/kg in 2015).

A comparison between the median values submitted in the ICP Vegetation reports for Bulgaria shows that with the exception of As, all reported metals have decreased atmospheric depositions between 1995 and 2010.

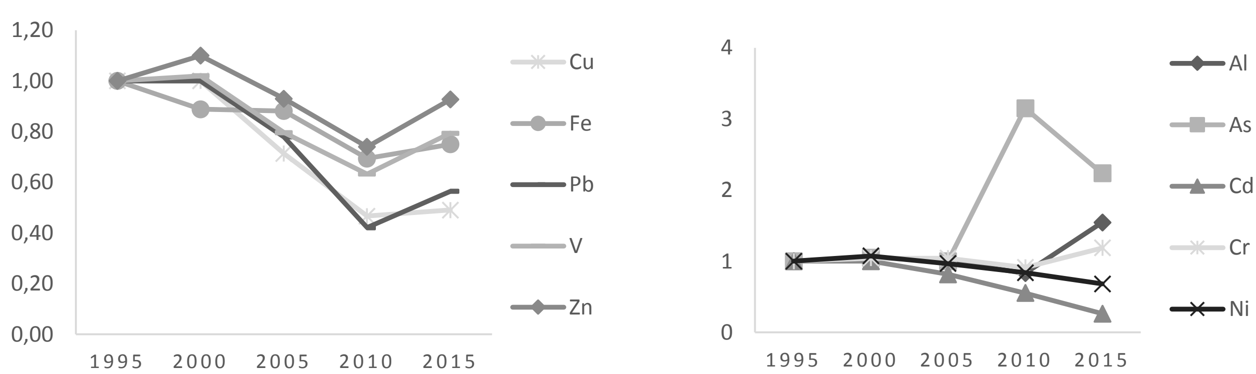

Fig. 1. Temporal trends – median values for concentrations of 10 metals, normalized to their values for 1995

The median value for As increased sharply in 2010 but has decreased again in 2015 (from 0.2 mg/kg in 1995, 0.21 mg/kg in 2000, 0.2 mg/kg in 2005, 0.63 mg/kg in 2010 and 0.44 mg/kg in 2015).

The maximal values for As in 2015 could be attributed to operation activities in cement plants and fossil fuel power stations.

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 [7] [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

It should be noted that due to the analytical methods applied (ICP-ES until 2010, NAA in 2015), some differences in the results are anticipated. They arise from the sample preparation and sensitivities, and in ICP-ES, refractory compounds in the samples may potentially be omitted. Still, the trends for decreasing in Ni and Cd atmospheric depositions are retained in 2015. Fe and Cu have a slightly higher median value in 2015 than in 2010.

Bulgarian mosses had the highest concentration of Pb (maximal values) in the European moss survey in 1995. Since then, leaded petrol has been phased out. Open quarries and tailings, and an explosion in an ordnance plant in Iganovo (VMZ Sopot) explain the observed maximal values for Pb in 2015.

In 2015, the highest concentrations for the elements Al, V, Ni and Fe were determined in three of the border crossing posts with Greece (Kulata, Ivaylovgrad, Zlatograd), along the nearest major roads, and in a site located relatively close to a fossil fuel power station.

CONCLUSIONS

Concentrations of a total of 37 elements were determined in 115 moss samples using instrumental epithermal neutron activation analysis (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, and U). Three additional environmentally important elements were analysed by means of inductively coupled plasma atomic emission spectroscopy (Cd, Cu, and Pb). The concentrations determined are comparable with data from other European countries, reported in the 2010 moss survey. In 2010 there was an observation that, in general, since the beginning of Bulgaria's participation in the ICP Vegetation programme in 1995, concentrations of metals deposited from the atmosphere have steadily decreased by about 30%. The most recent survey data does not show continuation of that trend for all elements reported. Following the shutdown of several major industrial facilities and the implementation of better filtering technologies, a vehicle fleet renewal and more strict environmental and safety regulations are required to improve air quality. 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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