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Atmospheric Deposition Studies Based on a 20-year Period of Moss Biomonitoring in the Vicinity of a Lead-zinc Plant in Kardzhali, Bulgaria (1995/6-2015/16)

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Abstract. In 2015, for the fifth consecutive time, Bulgaria participated in the moss survey carried out in the framework of the UNECE ICP Vegetation (United Nations Economic Commission for Europe, International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops). Over the years, the areas studied included several 'environmental hotspots', one of which was a hazardous industrial enterprise – the Kardzhali lead-zinc smelter. It was known to be the main source of lead, cadmium, zinc, and sulfur oxide contamination in the country. An overview of the available data from all moss surveys was made to reveal temporal and spatial deposition trends for the investigated metals and metalloids during the 20-year period of participation. Throughout the surveys, three analytical techniques were used: neutron activation analysis, atomic absorption spectrometry, and atomic emission spectrometry with inductively coupled plasma. Up to 47 elements were determined in 2005/6, 2010/11 and in 2015/16 (Ag, Al, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Fe, Hf, Hg, I, In, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, Tm, U, V, W, Yb, and Zn). The results were anticipated to be an extension to the available data on a small number of elements investigated by the State regulatory bodies and those reported to the ICP Vegetation programme. Due to violation of state environmental policy, a temporary shutting down of the production processes took place during the 2010/11 moss survey. It follows that biomonitoring took place around the time when the deposition rates were the highest, and then continued through 2015/16, while there was no industrial output. The smelter in Kardzhali is going to be reinstated in the near future after a major renovation. The moss survey data could be used to assess the new pollution-control equipment efficacy, and for estimation of health and environmental risks, and aid risk-management decisions.

INTRODUCTION

The Kardzhali region, Southeastern Bulgaria, is an area at environmental risk associated with the local non-ferrous manufacturing and mining industry, and poor management of production and domestic waste disposal [1]. In the past, the main industrial production processes were related mainly to the operation of the Lead-Zinc Complex Plc smelter and Gorubso-Kardzhali tailings, and also Bentonite Plc., Monek Yug Plc., and S&B Industrial Minerals Plc. The lead-zinc smelter, located in the industrial part of town, was found in 1955 and the main activities were production of zinc, lead, bismuth, cadmium, and their alloys; sulfuric acid, and processing of exhausted batteries. The smelter was known to be the main source of lead, cadmium, zinc, and sulfur oxide contamination in the country. Surveys in the area of Kardzhali, particularly in the last decade, show increased trace metal content in soils and plants, including mosses, as a consequence of mining of polymetallic ores, flotation, and heavy metal production [2]. According to the Ministry of

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Environment and Water, Kardzhali used to be one of the ecological “hot spots” in Bulgaria. A temporary shutting down of the production processes took place in the summer of 2011, as a penalty for failure to meet the requirements of the state environmental policy. Over the past three decades, the largest industrial enterprises in Bulgaria have been closed, which has greatly reduced local pollution emissions. Still, data from state air quality monitoring stations show continuous and systematic exceeding of daily and annual limit values for particulate matter concentrations (PM10) in over 20 towns. This is attributed to domestic heating, especially burning wood and coal, vehicle emissions, mainly due to obsolete fleets lacking catalytic converters, and to a lesser extent, electricity production and industrial activities.

Beside state air quality monitoring programmes focusing on few indices, moss biomonitoring techniques could be used as an alternative and complementary method to investigate atmospheric depositions of metals. Passive moss biomonitoring is well-established and applied by the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation). The focus of this programme is to study long-range transboundary air pollution under the auspices of The United Nations European Cooperative Programme „Atmospheric Heavy Metal Deposition in Europe” [3]. 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 studying atmospheric depositions of metals [4]. Their wide geographical distribution facilitates large-scale monitoring. Data on a relatively large number of elements, namely Al, As, Cd, Cr, Cu, Fe, Ni, Pb, Sb, V, and Zn, are determined in mosses collected in parallel in all participating countries; and is used to validate air pollution models by the International Cooperative Programme on Modelling and Mapping of Critical Levels and Loads and Air Pollution Effects, Risks and Trends (ICP Modelling and Mapping). The ICP Vegetation programme has been initiating moss surveys at five-year intervals since 1990.

In 1995, Bulgaria was involved in the program. Sampling has been performed regularly, and the predominant biomonitoring species is *Hypnum cupressiforme*. The sampling networks have been non-uniform through the years due to the typically hot and dry summers, mountainous terrains, and different groups partaking in sampling campaigns. Generally, the reported median values for all investigated elements are relatively high in Eastern and Central European countries as compared to data from Scandinavian and western European participants. In 1995/6, the highest maximal Pb concentration determined in moss tissues was reported in Bulgaria. During the 2000/1 survey, the Bulgarian median As value was the highest reported, as well.

The objective of this study was to investigate the trends for contents of metals reported to ICP Vegetation programme since 1995, specifically for the area affected by the Kardzhali lead-zinc smelter – one of the most hazardous industrial enterprises in Bulgaria. An overview of all data submitted to the programme was made in order to select the relevant sampling points.

STUDY AREA. MATERIALS AND METHODS

For the 1995/6, 2000/1, 2005/6, 2010/11, and 2015/16 moss surveys, all sampling sites on the territory of the Kardzhali municipality and within a distance of 30 km from its borders (in the municipalities of Haskovo and Smolyan) were considered. In 2010/11, a parallel passive moss biomonitoring study was performed in the town of Kardzhali and its vicinity, at a higher sampling density than recommended by ICP Vegetation protocols, therefore the results were not discussed in this review [5]. Only non-urban sampling sites from the data submitted to the ICP Vegetation programme were selected.

The climate in this particular region of Bulgaria is subtropical and transitions to Mediterranean to the south, near the border with Greece. Few overlapping sampling sites between the surveys were found due to the hot and dry summers when mosses cannot thrive. Former extensive mining activities are related to the abundance of metal and non-metal ores typical for the Rhodope mountains [6], and historic and active mining sites are present in the region. Relative to the location of the smelter chimneys, the resulting area covered about 30 km to the North and South and 60 km to the East and West (Fig. 1). The region is characterized by a bidirectional wind rose, and the predominant wind directions are north and south. Dispersion of local pollutants is known to be poor due to geographic particularities, and the number of days with calm weather and fog.

During all moss surveys, sampling was performed in accordance with the ICP Vegetation protocols. All collected *Hypnum cupressiforme* samples were put into paper bags for storage and transportation.

Between 1995/6 and 2010/11, the main analytical technique inductively coupled plasma atomic spectroscopy [7-9]. For the ICP Vegetation 2015/16 moss survey, 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. Inductively coupled plasma atomic emission spectroscopy was carried out in the Agricultural University, Plovdiv, Bulgaria, as a supplementary technique for the determination of Cd, Cu, and Pb. Quality control was carried out using the certified moss reference materials M2 and M3 (Finnish Forest Research Institute).

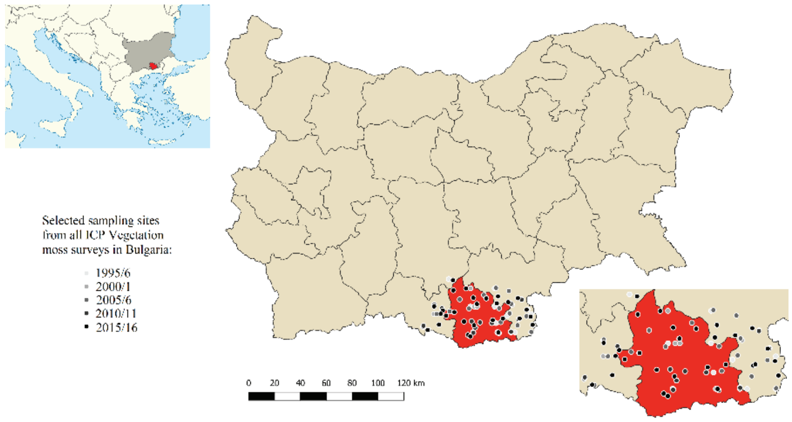

FIGURE 1. Location of Bulgaria and the Kardzhali municipality. Sampling sites from all moss surveys.

RESULTS

For the 1995/6, 2005/06, and 2015/16 moss surveys, summarized results of the determined elemental contents in the selected sampling sites are presented in Table I . All elements determined using neutron activation analysis are shown, even though they are not included in the thematic report of the ICP Vegetation programme. Norwegian moss data for territories with a minor influence from local anthropogenic sources of air pollution were also included, since they have been used as background values in several studies in other countries, including Bulgaria [10]. For the elements, Al, As, Cu, Fe, Pb, V, and Zn, the median values were usually higher than those determined in Norway. The median content of Ni decreased in 2015, whereas the median Cr values exceeded the Norwegian one by a factor of 6 for the first time, so these two elements could be associated with anthropogenic contamination.

As sampling areas cover both impacted and non-impacted sites, distributions of the determined elements are rarely normal. Therefore, median values are preferred over mean values to describe central tendencies.

Figure 2 illustrates the temporal trends for the Kardzhali region using the median values of the selected sites sampled during all ICP Vegetation moss surveys. To avoid using logarithmic scale but fit the information for all elements, relative differences in percent were chosen.

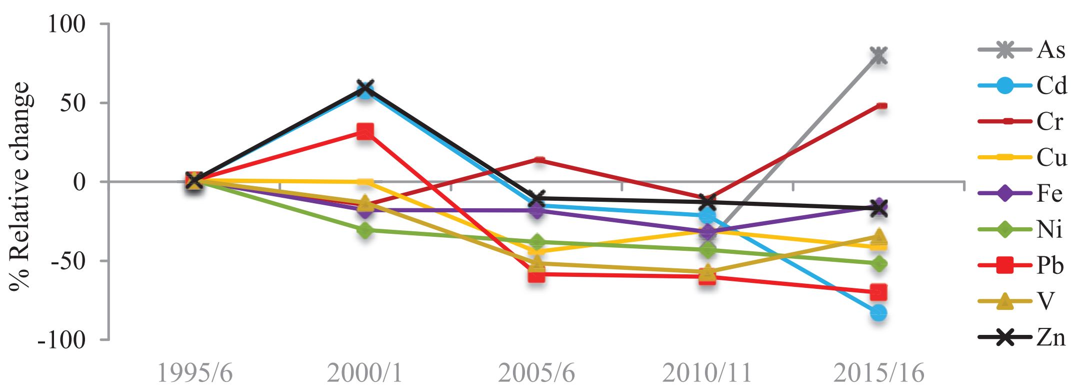

FIGURE 2. Temporal trends: median values, relative change (%): 1995/6 median values used as denominator. Data from ICP Vegetation moss surveys, selected sites in the region of Kardzhali (non-urban areas). Number of sampling sites in the studied region in each survey: 1995/6: N=17, 2000/1: N=14, 2005/6: N=28, 2010/11: N=13, 2015/16: N=29.

Median values relative to their corresponding 1995/6 medians were used to plot the trends. The elements As and Al were exceptions since As was determined in 2000/1, 2010/11, and 2015/16, and Al was requested to be reported to the programme for the first time in 2005/6. Cu, Pb, and Cd were the only three elements analyzed consistently with the same analytical technique.

TABLE I. Summarized results: element content (mg/kg) determined in mosses collected the studied area between 1995/6 and 2015/16. Data for an unimpacted region of Norway included for comparison.

	1995/6		2005/2006		2015/16		Norwegian data [11]	
Elements	**median**	**range**	**median**	**range**	**median**	**range**	**median**	**range**
Al			1856	553-6832	2450	1170-10900	200	67-820
As					0.49	0.215-1.14	0.093	0.020-0.505
Ba					41.3	14.6-309	17.1	5.6-50.5
Br					2.37	1.25-5.19	4.5	1.4-20.3
Ca					6810	1120-9020	2820	1680-5490
Cd	0.47	0.36-4.51	0.74	0.15-5.23	0.08	0.02-1.56		
Ce					2.89	1.15-14.3	0.342	0.095-4.61
Cl					71.8	25.4-296		
Co					0.593	0.3-3.01	0.202	0.065-0.654
Cr	2.19	1.89-7.27	2.50	0.79-38.8	3.24	1.49-16.9	0.55	0.10-4.2
Cs					0.249	0.075-1.8	0.072	0.016-0.88
Cu	12.5	8.56-35.7	6.975	3.59-31.2	7.32	4.32-9.96		
Dy								
Fe	1592	1248-5238	1304	455-6587	1350	624-6370	209	77-1370
Hf					0.2	0.06-0.9		
I					1.42	0.64-2.99	2.5	0.6-41.7
In								
K					5130	3250-8880		
La					1.54	0.557-7.17	0.189	0.045-2.56
Mg					2230	550-8550	1730	940-2370
Mn					180	39-480	256	22-750
Mo							0.135	0.065-0.70
Na					225	121-1430		
Ni	4.73	2.13-45.9	2.93	1.635-90	2.29	0.95-13.5	1.14	0.12-6.6
Pb	47.1	11.4-443	19.58	5.45-217	14.08	3.72-46.12		
Rb					8.85	3.7-30.5	7.7	1.3-51.5
Sb					0.121	0.072-0.311	0.033	0.004-0.240
Sc					0.478	0.218-2.95	0.052	0.009-0.220
Se					0.224	0.008-0.467	0.33	0.05-1.30
Sm							0.33	0.05-1.34
Sr					26.1	12.7-122	15.8	3.6-43.3
Ta					0.0409	0.001-0.192	0.01	<0.01-0.07
Tb					0.0298	0.0121-0.123	0.003	<0.002-0.030
Th					0.497	0.141-2.8	0.033	0.004-0.240
Ti					150	73.3-764	23.5	12.4-66.4
U					0.148	0.0556-3.2	0.015	0.001-0.138
V	6.95	4.42-29.6	3.36	1.72-24.31	4.55	1.78-22.7	0.92	0.39-5.1
W					0.102	0.026-0.72	0.127	0.009-1.23
Zn	34.9	23.4-347	31.3	12.9-366	29	14.2-83.4	26.5	7.9-173

Between 1995/6 and 2010/11, the content of almost all element pollutants investigated for the moss surveys was characterized by a steady decline. Cd, Zn and Pb were exceptions since their content increased in 2000/1 by 57 %, 59 %, and 32 %, respectively, but decreased again in subsequent years. Median Cr content was also an exception, as it was greater in 2005/6 and 2015/16 relative to 1995/6. The 2015/16 results changed the overall trends, and only Cd was characterized by a sharp decline. Median values for Zn, Ni, and Pb continued their steady decline since 2005. After increasing in 2010/11, the median values for Cu declined again in 2015/16. Both As and Al contents were about 80 % higher in 2015/16 than in 2010/11. The content of Fe and V increased in 2015/16, which could be explained by the emergence of new quarries in the region and road construction. The content of As, Cr, Fe, and V determined in mosses increased in 2015/16, which could be explained by coal combustion for domestic heating, traffic pollution, machine production, and the agriculture industry. After the shutdown of the main industrial facility in town, the content of Cd sharply decreased, and Pb, Zn, and Cu remained stable.

CONCLUSIONS

Moss biomonitoring surveys provide a cost-effective means for a time-integrated evaluation of atmospheric deposition of pollutants. Principal advantages over conventional bulk collector analyses are the large geographic abundance of moss species suitable for biomonitoring and their inherent ability to retain elements deposited from the atmosphere.

The retrospective comparison of the moss survey data in the studied region showed a decrease in the content of almost all element pollutants investigated by the ICP Vegetation programme, with the exception of As, Al, and Cr. The results obtained supplement state monitoring air quality data, which is limited to a small number of sites and air quality indices.

Neutron activation analysis allowed for the determination of elements posing a risk to the human health like Se, Ti, Cr, Cu, Ni, Al, and As (first, second and third groups of toxicity) during the most recent moss survey in Bulgaria. As the smelter in Kardzhali is going to re-open after a major renovation, the 2015/16 results provide baseline values and could be used to assess the new pollution-control equipment efficacy. The open tailings, mines, quarries, coal combustion, road construction, and increased traffic in the region could potentially explain the lack of a distinct downward trend for all elements reported to the ICP Vegetation programme.

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