CROSS BORDER RESPONCE OF MOSSES TO ATMOSPHERIC DEPOSITION OF 10 ELEMENTS IN SOUTHWESTERN BULGARIA AND EASTERN FYROM

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ABSTRACT

This study aims at first cross-border assessing of 10 heavy metals and toxic elements accumulation in the tissues of moss Hypnum cupressiforme reflecting wet and dry atmospheric deposition during 3-years period in Southwestern Bulgaria and Eastern FYROM. It is a part of the Bulgarian participation in the European moss survey 2005/2006 (United Nations Economic Commission for Europe International Co-operative Programme on Effects of Air Pollution on Natural Vegetation and Crops). Moss samples were collected at the same time in Bulgaria and FYROM, in March 2006, just before the beginning of the vascular plants growing season. Concentrations of Al, As, Cd, Cr, Cu, Fe, Ni, Pb, V, and Zn in 3-years parts of mosses were determined by ICP-AES method after wet digestion. Data obtained from 24 Bulgarian and 12 FYR Macedonian moss sites, covering in total almost 15 000 km^2, showed different atmospheric deposition patterns for the period 2003-2005 particularly for Cd, Cr, Cu and Fe. The determined concentrations revealed no serious pollution by airborne heavy metals and toxic elements contaminants. None with proved statistical significant difference element, between Bulgarian and FYR Macedonian part, appeared in this first study. Obtained results showed that high concentrations of metals were around ore-fields, old mines, local industry and serpentine spots. No transboundary atmospheric pollution in the studied part of southeastern Europe was statistically proved.

Keywords: Atmospheric deposition, *Hypnum cupressiforme*

Introduction

Monitoring of atmospheric pollution has become very important in the second part of the previous century due to the increasing use of coals, petrol and oils, rapid growth of ferrous and non-ferrous industry, etc. Because of the high costs associated with technical measurements of airborne contaminants, alternatives have been developed. Rühling and Tyler (13) first described the use of mosses for the assessment of atmospheric pollution in Sweden. For monitoring heavy metal airborne pollution, moss species are especially suitable due to their high cation-exchange capacity (3). Carpet-forming moss species have a number of advantages as biomonitors: vast geographical distribution; mineral supply obtained mainly by wet and dry precipitation; ability to accumulate elements in concentrations higher than the medium; fast uptake due to the lack of epidermis and cuticle, and the large surface-to-weight ratio, alive tissues of 3-4 years old and evergreen; easy and cheap technique (9, 12, 15). Bulgaria was included in the project Atmospheric Heavy Metal Deposition in Europe using Mosses in 1994 (12, 16, 17, 18). Recently more than 28 countries were involved in the UNECE ICP Vegetation (United Nations Economic Commission for Europe International Co-operative Programme on Effects of Air Pollution on Natural Vegetation and Crops) - Heavy Metals in European Mosses (5, 6, 7). Bulgaria is one of the main sources of heavy metals in Southeastern Europe; e.g. the official EMEP data (Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutant in Europe) for the total 2005 emissions (including anthropogenic, natural and historical) of Pb and Cd in Bulgaria were 115 and 12 t y^{-1} respectively (10, 11).

The aim of this study was to present atmospheric pollution during 3-years period (2003-2005), assessed by mosses, and following the European Moss Survey 2005/2006, in Bulgaria, especially its Southwestern part. Additionally, to compare the data with summarized results of European moss surveys, and to test temporal changes from previous periods. The first cross-border data for Eastern FYR of Macedonia are reported.

Materials and methods

The moss sampling programme followed the requirements of the European moss surveys (2, 12). The sampling net included 215 sites in the first Bulgarian moss survey (1995), 217 and 213 in second and third moss surveys (2000, 2005), respectively, where the recommended pleurocarpous moss species in needed quantities could be found: *Hylocomium splendens* (Hedw.) Schimp., *Hypnum cupressiforme* Hedw., *Pleurozium schreberi* (Willd. ex Brid.) Mitt., *Rhytidium rugosum* (Hedw.) Kindb., *Pseudoscleropodium purum* (Hedw.) M.Fleisch., *Abietinella abietina* (Hedw.) M.Fleisch. (nomenclature according to (8)). The prevailing part of the sampled mosses was growing on soil, followed by dead wood, and around 20% - on rocks. The moss sampling was done at the same time in the study area (Fig. 1) Southwestern Bulgaria and Eastern FYR of Macedonia, in March 2006, just before the beginning of the vascular plants growing season.

After the identification of the species, samples were air-dried, cleaned very carefully and age separated (3-years part). Moss samples were not washed, but homogenized by hands, using nylon gloves. They were stored deep-frozen until further analytical treatment. Before analysis the samples were dried at 40°C and then wet-ashed. About 1 g moss material was treated with 15 ml nitric acid (9.67 M) overnight. The wet-ashed procedure was continued with heating on a water bath, following by addition of 2 ml portions of hydrogen peroxide. This treatment was repeated till full digestion. The filtrate was diluted with double distilled water (0.06 µS cm^{-1}) to 25 ml. All solutions were stored in plastic flasks. Triplicates of each sample were prepared independently. Elements Al, As, Cd, Cr, Cu, Fe, Ni, Pb, V and Zn were determined by atomic emission spectrometry with inductively coupled plasma (ICP–AES) using VARIAN VISTA-PRO instrument. The detection limits were 0.004 mg L^{-1} for Cd, Cr, Cu, Ni and Zn, 0.02 mg L^{-1} for As, 0.03 mg L^{-1} for Pd and V, 0.04 mg L^{-1} for Al and Fe.

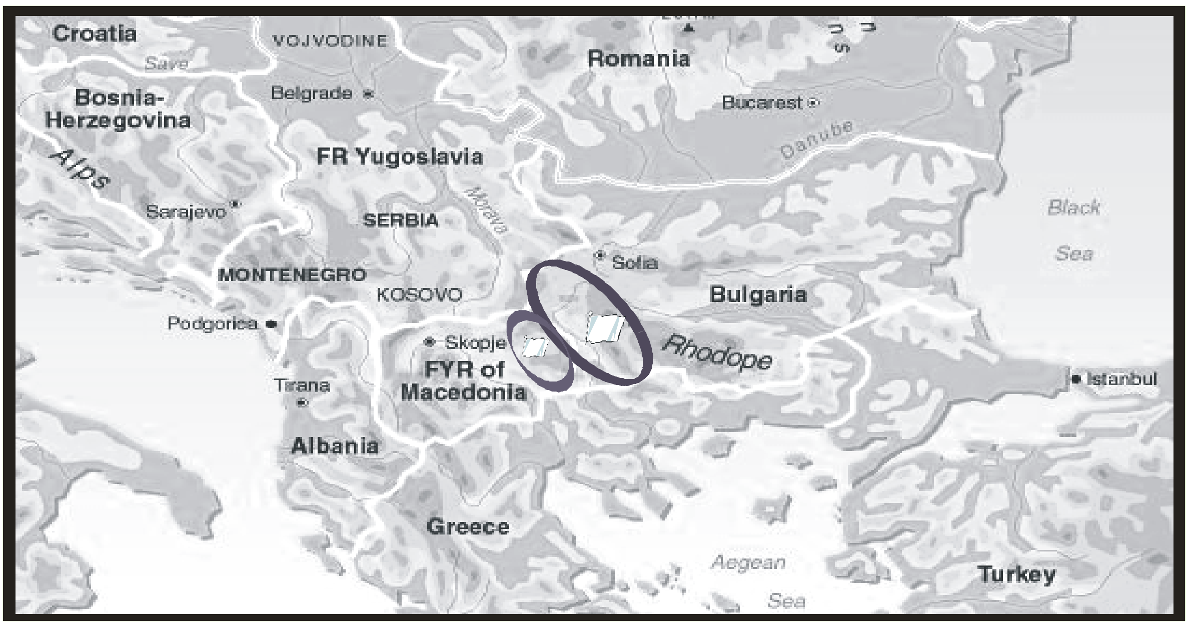

Fig. 1. Sampling area of the mosses in Southwestern Bulgaria and Eastern FYR of Macedonia.

The analytical precision was verified by replicating (deviation between the duplicates was below 5% in all cases) and by use of blanks and stock standard solutions (1000 µg L^{-1} Merck) for the preparation of working aqueous solutions. Quality control was ensured by standard moss reference materials M2 and M3 prepared in Finland for the European Moss Surveys. The measured concentrations were in good agreement with the recommended values (14). All concentrations are presented as mg kg^{-1} dry weight.

Results and Discussion

In this study are presented the results only of *Hypnum cupressiforme*, due to the fact that it is the main moss species proposed for moss surveys in Southeastern Europe (18), and is the only pleurocarpous species quantitative distributed in the whole study area.

The main results of 10 heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, V, Zn) and toxic elements (Al, As) of the Bulgarian moss survey 2005/2006 (5) and partly results for the first cross-border study in Southeastern Europe are presented in Table 1. Other cross-border moss data in this region from Southern Bulgaria and Northeastern Greece, and join moss network in Southeastern Bulgaria and European Turkey were already published (4, 20). Comparing the last published median values in European mosses (5) and the median concentrations of Bulgarian mosses, was found that the Pb, Fe, V, Ni and Cu values in *Hypnum cupressiforme* were higher (2-fold to 4-fold), than median values for European mosses. The Al, Cd, Cr and Zn median concentrations in Bulgaria were almost equal or close to the European median value. The obtained maximum values of all concerned elements were lower than the European maximum values: Ni (11 times), Al, V, Fe, Cu and Zn (2-3 times). The European maximum concentrations of Cd in mosses were observed in Bulgaria, "hot spots" in the region of Kardzhali, during the third and forth European moss surveys, 2000/2001 and 2005/2006 respectively (2, 5, 18).

TABLE 1.

Concentrations of heavy metals and toxic elements in mosses sampled in Bulgaria, Southwestern Bulgaria, Eastern FYROM and Europe during the moss survey 2005/2006 (mg kg^{-1} dry weight).

Index	Al	As	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn
Bulgaria*										
Number of sites	213	213	213	213	213	213	213	212	213	213
Min	426	<0.4	0.10	0.79	2.64	186	0.92	1.87	0.77	9.38
Max	10394	12.60	5.23	57.8	281	9493	90	217	24.3	366
Median	1495		0.32	2.43	11.0	1399	2.99	14.8	3.88	27.9
Southwestern Bulgaria										
Number of sites	24	24	24	24	24	24	24	24	24	24
Max	6763	4.74	0.66	23.28	16.45	7777	11.9	30.2	20.2	50.3
Eastern FYROM										
Number of sites	12	12	12	12	12	12	12	12	12	12
Max	7035	5.88	3.33	9.55	56.1	2445	6.23	38.2	13.6	81.2
Europe										
Number **	4149	5021	5689	5581	5699	5566	5904	5621	5522	5930
Max **	31180	21.6	5.23	90.7	672	23490	1016	249	68.5	694
Median **	1226	0.45	0.20	2.0	6.30	409	1.7	4.1	2.1	31.4

* after (19)

** modified moss data from 28 European countries after (5)

Six elements – Al, As, Cd, Cu, Pb and Zn – were accumulated in higher concentrations in moss tissues collected in Eastern FYROM, while 4 elements – Cr, Fe, Ni and V - were found higher in the mosses sampled in Southwestern Bulgaria. The differences were 5-fold for Cd, and 3-fold for Fe. Two factors affected heavy metals concentration in moss samples of the study area: soil dust as dry deposition and respectively wet atmospheric pollution. In this study, the concentrations of heavy metals and toxic elements showed two different groups of element distribution patterns. In the first group are Pb, Cd, Cu and Zn, mainly originated from anthropogenic sources, whereas the second group consisted of Fe, V, Al, Cr, Ni and As. The Principle Component Analyses proved two components (F1 and F2) of heavy metals and toxic elements.

The color contour maps of Al, As, Cd, Cr, Cu, Fe, Ni, Pb, V, and Zn in moss samples of *Hypnum cupressiforme* from Bulgaria showed different deposition patterns (19). The high levels of metals Pb, Cd, Cr, Ni и V were located in Rhodopes Mountains, mainly due to Lead and Zinc Complex in town of Kardzhali, ore works and old mines, the Non-ferrous Metals Smelter near Asenovgrad, geochemical anomalies and small spots on serpentines. Copper and arsenic were accumulated mainly around copper smelter Union Miniere Pirdop Copper, open ore works Asarel - Medet Mining and Ore Dressing Plant, around Etropole as a centre of iron-, gold- and coppersmithing and mining, and along the border in Northwestern corner of Bulgaria.

No statistical significant temporal trends of airborne heavy metals and toxic elements were found in mosses by ANOVA, during the last 3 moss surveys, reflecting the dry and wet atmospheric 3-years deposition (1993-1995, 1998-2000, 2003-2005) for the Bulgarian territory. The significant decreasing trend of the element content of As, Cu, V, Zn, Cd and Pb, in most of the European countries involved in the last moss surveys (5), was not proved in the Bulgarian area due to still heavy local emissions, contaminated soils around non-ferrous and ferous industry, and site-specific characteristics as serpentine spots. However, all analyzed elements in *Hypnum cupressiforme* showed a small decline in time, the bigger decline between 2000 and 2005 (19).

Maximim value of Cd in Macedonian mosses in this study (3.33 mg kg^{-1}) was higher than the concentration of this heavy metal found in mosses (2.95 mg kg^{-1}) collected for the whole FYROM in 2002 (1).

The observed results of the accumulation in moss tissues of the Bulgarian area, during the 3-years period (2003 - 2005), should reflect the decrease of the important airborne pollutants Pb and Cd. The Pb and Cd decrease of the anthropogenic sources emissions during 2003 - 2005, to around 50% for Pb, and 40 % for Cd in the country was pointed out by EMEP/MSC-E Status Reports (10, 11). The significant decrease of accumulation in *Hypnum cupressiforme* was not expected due to heavily polluted soils and open ore mines in some sites as well as contamination by windblown dust and motorway construction.

In conclusion, during the period 2003 - 2005, the Southwestern Bulgarian territory and Eastern part of FYR of Macedonia of almost 15 000 km^2, was not seriously polluted by atmospheric heavy metal and toxic element contaminants, despite the fact that the area has more than 0.5 million inhabitants, almost 100 industry factories, 5 power plants, coal and polymetal works and old mines, and high motor traffic through 3 border points. No significant temporal trends of airborne heavy metals and toxic elements were proved in mosses, during the last 3 Bulgarian moss surveys, reflecting the dry and wet atmospheric deposition (1993 - 1995, 1998 - 2000, 2003 - 2005). Data obtained of the moss *Hypnum cupressiforme*, used for the assessment of atmospheric deposition in this part of Southeastern Europe, proved none transboundary pollution through Bulgarian – FYROM borders.

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