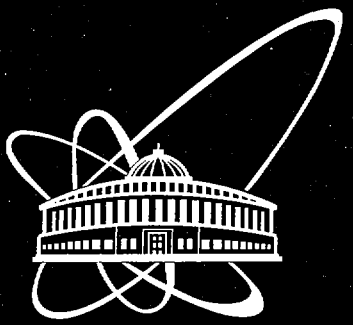

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ATMOSPHERIC DEPOSITION OF HEAVY METALS IN SERBIA STUDIED BY MOSS BIOMONITORING, NEUTRON ACTIVATION ANALYSIS AND **GIS** TECHNOLOGY

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Introduction

The use of terrestrial mosses as biomonitors in large-scale multi-element studies of heavy metal atmospheric deposition is a long established technique. The moss technique (Rühling and Tyler, 1968), first introduced in Scandinavia, has shown to be very suitable for studying the deposition of heavy metals as well as other trace elements. It is now being used as part of monitoring programs for air pollutants in most European countries (Rühling and Steinnes, 1998).

In the present paper the results of a systematic study of air pollution with heavy metals and other trace elements in the northern part of Serbia is presented. The moss technique was applied in Serbia in 2000 for the first time. This was done to cover one more "white spot" on the heavy metal atmospheric deposition map of Europe. Part of Bosnia was also covered by this survey. The most important results to be expected from this study were as follows:

- identification of areas with high contamination levels to be considered for the evaluation of environmental risk;
- establishment of possible consequences of the NATO military action during the spring of 1999 on the environmental situation;
- creation of a database for continued studies at regular intervals;
- establishment of a regional sampling network for future monitoring programs;
- comparison of the environmental contamination levels in parts of Serbia with other strongly polluted areas in Europe.

The northern part of Serbia is predominantly an agricultural region with a couple of oil refineries, some chemical industries, and several coal-fired power plants. The richest mineral resources and the most highly industrialized region are located in the mountain part of Serbia, and are already known as a dominant pollution source. A high concentration of industrial activity is clustered within a limited geographical region in east Serbia, near the Romanian and Bulgarian borders. The most important metal in this region is copper with associated elements such as arsenic, zinc, selenium, indium etc.

During the NATO military action in the spring of 1999 the two largest refineries and several chemical plants were damaged.[1] As a consequence of this large amounts of pollutants were emitted to the atmosphere. The general influence of these events on the environmental situation in the region, and possible consequences of the associated emissions, have not yet been carefully investigated. This paper is one of the first attempts to establish scientific facts relevant to the regional environmental situation.

It is important to note that as consequence of the political situation in Yugoslavia during the last ten years and the economic embargo forced on the country, most of the Serbian industry either works at reduced capacity or does not work at all. It now seems reasonable to expect considerable increase in industrial activities in the years to come, and consequently increased negative influence on the environment. The data presented in this paper may be used as a reference level for comparison with future measurements of heavy metal pollution in the areas considered.

Methodology

Study area and sampling

Samples of the moss *Hypnum cupressiforme* were collected during the summer of 2000 according to guidelines described in detail elsewhere.[2] Epigeic moss (growing on the ground) was sampled. The sampling sites were located at least 300 m from main roads and populated areas and at least 100 m from smaller roads or single houses. From each sampling site, 5 to 10 sub-samples were taken within a 50 x 50m area and mixed in the field. The samples were collected with plastic gloves and stored in clean plastic bags. Unwashed green parts of moss plants, cleaned and dried at 40 °C, were taken for analysis. No further homogenization of the samples was performed.

The location of the sampling sites are shown on the map in Fig.1. Marked on this map are also some locations where oil refineries and other chemical industries were bombed during the 1999 NATO military action.

Analysis

Moss samples of about 0.3 g were packed in aluminum cups for long-term irradiation or heat-sealed in polyethylene foil bags for short-term irradiation in the IBR-2 reactor, Dubna, Russia. The irradiation facilities used are briefly described in Table 1. Elements yielding long-lived isotopes, 29 in all, were determined using the Cd–screened channel 1 (Ch1) (epithermal neutron activation analysis, ENAA). Samples were irradiated for 5 days, re–packed, and then measured twice after 4–5 and 20 days of decay, respectively. Measurement time varied from 1 to 5 hours. To determine the short–lived isotopes of Na, Mg, Al, Cl, K, Ca, Mn, Cu (^{66}Cu) I, and Br (^{80}Br), channel 2 (Ch2) was used (conventional NAA). Samples were irradiated for 5 min and measured twice after 3–5 min of decay for 5-8 and 20 min, respectively.

Table 1. Flux parameters of irradiation positions

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	3.31	4.23
Ch2	1.23	2.96	4.10

Data processing was carried out using software developed in FLNP JINR, and element concentrations were determined on the basis of certified reference materials and flux comparators.[3] For long-term irradiation in Ch1, single comparators of Au (1μg) and Zr (10 μg) were used. For short-term irradiation in Ch2 a comparator of Au (10 μg) was employed. Concentrations of elements yielding long–lived isotopes were also determined using certified reference materials: SDM sediment (International Atomic Energy Agency, Vienna), Montana Soil (NIST) and moss DK-1, prepared for calibration of laboratories participating in the corresponding 1990 survey in Northern Europe.[4]

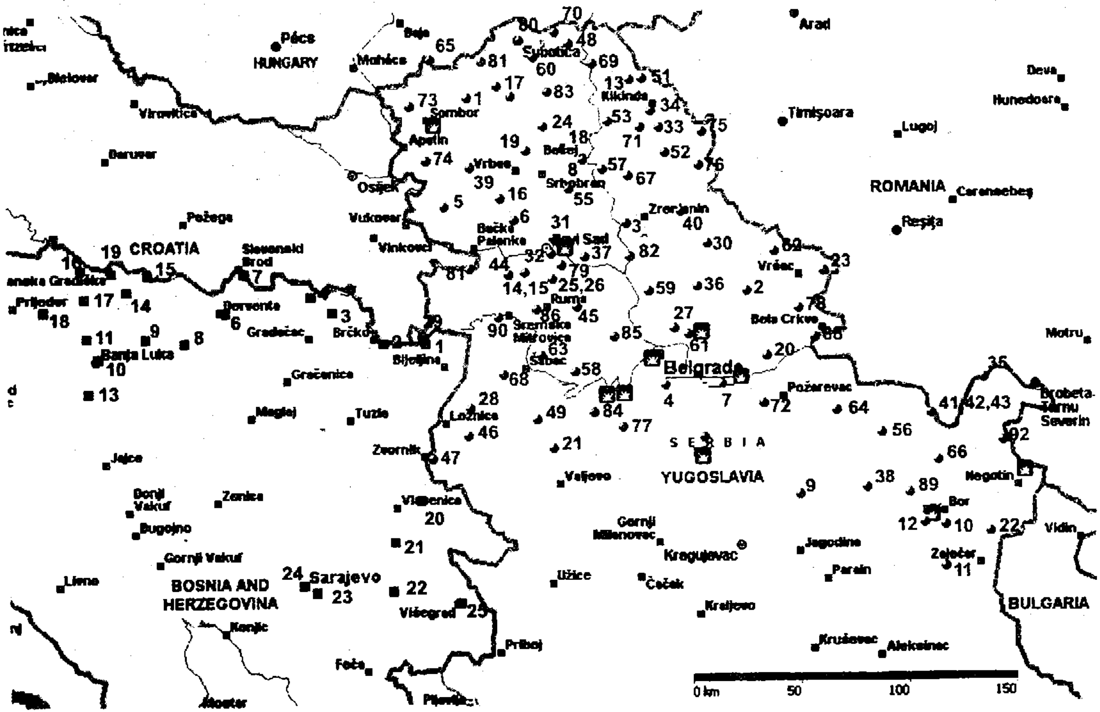

Figure 1. Sampling sites

Results and discussion

Mean values and concentration ranges observed for 39 elements in moss samples from the northern half of Serbia and part of Bosnia are presented in Table 2, in comparison with corresponding data from other highly polluted areas studied by the authors in Bulgaria,[5] Poland,[6] Romania,[7] and Russia.[8] Data from the 2000 national deposition survey in Norway[9] are also included in order to demonstrate typical values in moss from an area with generally low levels of air pollutants. Isopleths for selected elements are shown in Figs. 3–6 in order to demonstrate deposition patterns for some elements representing different sources and source categories.

The moss data from Serbia were subjected to principal component factor analysis (Varimax with Kaiser Normalization). Loadings for the first six factors are shown in Table 3. These factors are interpreted as follows:

Factor 1 has particularly high loadings for Sc, Cr, Fe, REE, Hf, Ta, and Th. Also Na, Co, Ni, W, and U are mainly associated with this component. These elements are all typical of crustal material, and most probably this component at least in part reflects contamination of moss samples with soil particles. In Northern Europe where the moss biomonitoring method was first developed, epigeic mosses in most cases grow on a substrate (litter and raw humus) composed mainly of organic material. At more southerly latitudes where decomposition of organic matter goes faster the moss is more likely to pick up mineral soil particles. This problem was also encountered in some other surveys where the authors took part, as indicated by high median values for these lithogenic elements (*cfr.* Table 2). Under these circumstances it becomes difficult to identify industrial and other anthropogenic sources for the elements concerned. Still, when considering the geographical distribution of this component, as exemplified by Sc and Fe (Fig. 2, it is likely that anthropogenic activities involving silicate dust also contribute to Factor 1. One such activity is tilling of agricultural land. However, the high levels of these elements predominantly in the highlands near the Romanian/Bulgarian border and partly in the north near Becej (sites 8, 18, 24) indicate that industrial activities may be a more important source.

Factor 2 is an exceptionally clear-cut industrial component, with very high loadings for Cu, Zn, As, Se, Mo, Ag, Cd, In, Sb, and Au. These elements all show high levels at a limited number of sites surrounding the town of Bor and low levels almost everywhere else, as indicated in the case of Cu in Fig. 2. The main reason for the high pollution in this area is non-ferrous metal industry in the «Copper Basin» near the Romanian/Bulgarian border.

Factor 3, like Factor 1, is characterised by some elements typical of crustal material (Mg, Al, Ti, V). These elements are abundant in the same areas as those of Factor 1, but in addition they show high values at some sites (6, 32, 37) near Novi Sad, as illustrated for V in Fig. 2. Again a mixture of natural and anthropogenic sources is indicated.

Factor 4 contains Cs, Rb, and Sr. These elements are likely to be mainly of natural origin, and their presence in the moss may be associated with the so-called «vascular pump»[10] whereby the elements are supplied to the moss by the action of adjacently growing higher plants.

Table 2. Radionuclides, energies of γ-lines used for calculations, element concentrations (mg/kg) in moss samples collected in Serbia and Bosnis and in some other relevant areas used for comparison

	Serbia *Present work*		***Bosnia*** *Present work*		***Romania*** ***(Transilvania)***		***Bulgaria*** ***(West and South)***		***Poland*** ***(Copper Basin)***		***Russia*** ***(South Urals)***		*Norway* *Moss survey 2000*	
N of samples	*92*		*23*				*103*		*86*		*56*		*464*	
Element	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
Na	694	178-2440	360	91-1100	902	192-4330	523	155-5573	152	74-302	346	104-1304		
Mg	2780	1100-8130	2670	1040-9520	2850	480-6840	2026	748-12500	1694	800-6480	3096	1188-15400	1543	645-3678
Al	6800	1280-22090	6270	2305-20740	5545	830-23000	3843	1111-46350	815	237-2590	2300	810-8877	350	97-10970
Cl	256	105-1030	344	156-715	370	160-1300	161	59-1180	226	123-537	250	55-1114		
K	5090	2710-11750	4820	1950-6820	7770	4770-19980	5764	3274-20490	5000	515-8708	6954	3011-13260		
Ca	7720	2890-18120	10310	5323-34330	5770	1250-23500	7283	2266-19650	2230	1190-12800	3972	1720-13800	3120	1379-22512
Sc	1.31	0.27-4.13	0.47	0.13-1.37	0.94	0.21-6.13	0.65	0.2-6.4	0.15	0.03-0.63	0.53	0.10-1.78		
Ti	71	11-297	57	14-222									31	10-414
V	11	2.85-39	11	2.89-34	8.7	02.09 36	8.4	2.2-112.6	2.5	1.14-8.13	7.0	2.0-28.8	1.35	0.28-22.6
Cr	6.51	1.14-22	5.09	0.94-19	13.8	03.07 56	3.2	0.5-26.9	1.43	0.80-3.16	11	1.5-194.3	0.69	0.058-259
Mn	217	30-2340	503	38-1770	265	27-1470	251	32-986	222	70-896	285	59-1402	333	28-5415
Fe	3110	720-9230	1600	439-4750	3290	815-21340	2314	692-14700	357	147-845	1689	335-20730	362	99-11216
Co	8.24	1.42-39	1.09	0.18-7	1.41	0.32-7.0	1.08	0.23-10.6	0.26	0.11-1.48	0.57	0.14-2.75	0.17	0.014-2.6
Ni	6.73	1.96-26	7.14	0.92-25	5.4	0.6-32	4.1	0.5-18.6	1.83	0.09-3.55	3.2	0.41-93.9	1.1	0.057-72.1
Cu	94	6.31-3140	22	10-67	68	18-810			(73*) 20	7.3-2040	22	3.4-200	4.2	1.7-52.7
Zn	44	14-415	25	10-57	135	39-2950	41	19-379	45	31-110	58	15-304	32	9.7-661
As	3.35	0.46-61	1.12	0.31-3.7	2.2	0.59-45.1	1	0.3-59.0	0.61	0.25-6.04	1.57	0.37-9.68	0.135	0.0023-2.63
Se	0.39	0.046-10	0.09	0.035-0.18	0.36	0.08-5.01	0.24	0.01-1.18	0.33	0.22-077	0.29	0.02-2.21		
Br	5.75	1.83-18	4.31	1.99-8.1	8.6	2.03-20.9	3.6	1.1-11.6	1.38	0.89-2.85	4.3	0.09-25.40		
Rb	13	3-47	9	3-19	15.0	5.8-135	12	3.0-69	22.4	2.0-45.5	10	2.8-38.6	9.9	1.2-50.7
Sr	22	6.8-95	14	5.8-32	37.4	1.8-290	25	7-106	12.4	0.69-339			11.5	2-74.2
Mo	0.85	0.12-23	0.97	0.26-3	0.65	0.13-10	0.99	0.16-3.36	0.29	0.05-2.42			0.108	0.0087-2.42
Ag	0.078	0.012-1.5	0.052	0.015-0.076	0.13	0.03-4.54			0.09	0.04-1.7	0.09	0.01-0.47	0.021	0.0017-0.27
Cd	<0.4	<0.4-6.5											0.087	0.001-2.65

Table 2. (continued)

	Serbia *Present work*		*Bosnia* *Present work*		*Romania* *(Transilvania)*		*Bulgaria* *(West and South)*		*Poland* *(Copper Basin)*		*Russia* *(South Urals)*		*Norway* *Moss survey 2000*	
N of samples	*92*		*23*				*103*		*86*		*56*		*464*	
Element	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
In	0.025	0.0036-0.34	0.019	0.0057-0.048										
Sb	0.52	0.13-7	0.25	0.068-1.5	0.88	0.16-51	0.23	0.07-20.2	0.25	0.16-0.79	0.50	0.08-3.46	0.056	0.001-0.46
I	2.09	0.87-4	1.80	0.60-3	2.17	0.76-5.55	1.4	0.6-4.4	1.11	0.35-2.68				
Cs	0.76	0.11-18.2	0.39	0.079-2.5	0.51	0.12-3.4	0.4	0.1-2.96	0.416	0.16-1.3	0.21	0.03-0.61	0.129	0.01-2.06
Ba	39	13-130	41	8-90	101	20-658	68	17-517	10.3	5.5-79.2	43	6-129	19.2	4.3-217
La	4.66	1.09-13	3.11	0.82-8	2.4	0.4-15.2	2.9	0.8-23.7	0.5	0.14-1.61	1.3	0.37-12.58	0.28	0.049-9
Ce	9.2	1.84-28	3.31	0.87-12	6.1	0.9-42.5			1.1	0.24-3.74	2.7	0.53-18.10	0.54	0.098-17.6
Eu	0.08	0.02-0.48	0.17	0.019-0.48									0.010	<0.0003-0.24
Tb	0.11	0.02-0.36	0.13	0.041-0.31	0.07	0.01-0.42	0.068	0.016-0.610	0.01	0.003-0.09	0.024	0.004-0.171	0.005	<0.0001-0.16
Hf	0.78	0.15-2.6	1.06	0.29-3.8	0.56	0.12-4.66	0.46	0.11-4.78	0.09	0.01-0.58	0.21	0.02-1.78	0.006	0.001-0.16
Ta	0.11	0.024-0.29	0.13	0.04-0.36	0.10	0.01-0.66	0.076	0.018-0.563	0.02	0.004-0.13	0.029	0.004-0.108	<0.0005	<0.0005-0.14
W	1.34	0.19-3.3	0.21	0.03-0.52	1.02	0.12-8.74	0.193	0.03-1.39	0.19	0.02-0.67	0.23	0.05-1.27	0.04	0.002-0.89
Au	0.0041	0.00029-0.087	0.0057	0.0017-0.017	0.025	0.003-0.114	0.0042	0.0009-0.0465	0.003	0.001-0.015	0.006	0.002-0.086		
Hg	0.55	0.056-2.7	0.53	0.047-4.9									0.054	0.021-0.467
Th	0.82	0.18-2.4	0.38	0.11-1.5	0.81	0.21-4.16	0.56	0.11-4.53	0.13	0.08-0.45	0.29	0.05-2.42	0.054	<0.0002-1.7
U	0.32	0.08-1.03	0.21	0.05-0.61	0.28	0.04-1.36	0.20	0.03-1.87	0.08	0.02-0.99	0.19	0.05-4.60	0.017	<0.0004-0.37

Table 3. The results of FA for Serbia

	1	2	3	4	5	6
Na	**0.768**	0.054	0.248	0.037	0.023	0.093
Mg	**0.567**	0.067	**0.690**	0.077	0.312	-0.014
Al	**0.598**	0.200	**0.686**	0.074	0.101	-0.086
Cl	-0.038	-0.055	-0.029	0.013	**0.867**	-0.063
K	0.472	-0.009	0.125	0.071	**0.658**	-0.023
Sc	**0.883**	0.209	0.311	0.027	0.036	-0.009
Ca	0.011	-0.126	0.135	0.015	**0.800**	-0.019
Ti	**0.581**	0.069	**0.756**	0.071	0.032	0.018
V	**0.608**	0.296	**0.672**	0.045	0.090	-0.099
Cr	**0.931**	-0.039	0.076	0.027	0.099	0.051
Mn	0.039	0.018	0.110	0.111	0.020	0.070
Fe	**0.882**	0.270	0.178	0.020	0.049	-0.003
Co	**0.664**	0.247	0.214	-0.102	-0.058	-0.209
Ni	**0.771**	0.002	0.014	-0.057	0.058	-0.170
Cu	-0.030	**0.963**	0.150	-0.013	-0.046	-0.063
Zn	0.105	**0.945**	-0.019	0.016	0.000	0.048
As	0.051	**0.969**	0.130	0.111	-0.033	-0.074
Se	-0.007	**0.986**	0.013	0.002	-0.006	-0.021
Br	0.148	-0.070	-0.124	0.032	0.026	**0.852**
Rb	0.712	0.044	0.073	**0.555**	0.009	-0.071
Sr	0.181	0.214	0.057	**0.824**	0.109	0.139
Mo	0.003	**0.961**	-0.014	0.022	0.014	-0.037
Ag	0.016	**0.978**	-0.012	0.048	-0.039	-0.034
Cd	-0.086	**0.873**	0.140	-0.021	-0.085	-0.117
In	0.003	**0.956**	0.164	-0.031	-0.080	-0.035
Sb	0.042	**0.947**	0.063	0.253	-0.045	-0.034
I	0.328	-0.064	0.076	-0.035	-0.188	**0.680**
Cs	0.104	-0.025	0.035	**0.946**	-0.029	-0.088
Ba	**0.644**	0.018	0.089	0.201	0.040	0.182
La	**0.950**	0.004	0.102	0.002	0.005	0.127
Ce	**0.935**	-0.059	0.111	0.093	0.054	0.168
Nd	**0.893**	-0.120	0.150	-0.010	0.003	0.140
Eu	**0.898**	-0.075	0.006	0.127	0.010	0.064
Tb	**0.822**	0.046	0.152	0.047	0.097	0.228
Lu	**0.714**	0.003	-0.029	0.017	-0.053	-0.056
Hf	**0.855**	-0.021	0.098	0.084	0.029	0.300
Ta	**0.947**	-0.041	0.057	0.041	-0.019	0.128
W	**0.749**	0.137	0.112	0.301	0.108	-0.038
Au	0.066	**0.941**	-0.030	-0.004	0.014	0.095
Hg	0.327	**0.549**	-0.223	-0.071	0.032	0.056
Th	**0.930**	-0.046	0.096	0.109	0.112	0.190
U	**0.872**	0.114	0.075	0.095	-0.011	0.054

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

Factor 5 with the highest loadings for Cl and Ca is most probably anthropogenic. One possible candidate activity is the use of $CaCl_2$ on gravel roads during dry periods to reduce dust problems.

Factor 6, characterised by Br and I, would typically be associated with atmospheric deposition of aerosols influenced by processes in the marine environment.[11] In this case however the highest Br concentrations are typically observed in samples from an area in the north of Serbia (sites 18, 24, 60, 83) very distant from the sea, and some industrial source is therefore more likely.

As concerns the data from Bosnia, the number of samples was considered too small for a valid factor analysis, and these data will therefore not be discussed in detail here. In general the areas of Bosnia represented seem to be less influenced by air pollution by heavy metals than the Serbian territory in question, as indicated by lower median values for elements such as Fe, Co, Cu, Zn, As, Se, and Sb.

In the following some elements of particular interest are discussed one by one:

Chlorine

The chlorine concentration in Serbian mosses is very constant and the median value is similar to those observed in other continental regions (Table 2). A few high values (sites 7, 37, 47) might be associated with emissions from chemical industries under normal operation or damaged during the NATO military action. Sites 7 and 37 are located only several kilometres from damaged industrial objects in Novi Sad and Pancevo. Another potential source of high Cl in samples of epigeic moss could be animal urine, but the samples concerned do not show correspondingly high Na concentrations.

Vanadium

The median value of V in Serbia (and also in Bosnia) is similar to the corresponding values from the neighbouring areas of Transilvania and Western Bulgaria. V in the present material is most strongly correlated with Mg, Al, and Ti (Factor 3). The highest values (Fig. 2) are observed in the "Copper Basin", and one likely source is sulphuric acid production where vanadium is used as a catalyst.

Vanadium and nickel are normally found in relatively high concentrations in crude oil, and these elements are therefore often used as markers of fuel oil combustion in air pollution studies (including moss surveys). The general correlation between V and Ni in this material is only moderate (R=0.57), but at some sites (35, 41, 42, 61, 78, 85) high V content in the moss are matched by Ni values of the same order. In two of these cases (61, 85) the sampling sites are not far from industries damaged by the NATO bombs, and especially fires at the Pancevo refinery appears to be a likely source in this case.

Iron

High iron concentrations in the moss are most often observed at sites associated with Factor 1. In addition an area just south-east of Belgrade (sites 64, 72) shows elevated Fe level (Fig. 2). Sample 64 is also very high in the light REE, whereas 72 is not particularly high in any other element studied, and may be affected by an iron smelter in nearby Smederevo. Iron is considerably higher in Serbia than in any of the areas shown in Table 2 for comparison, with the exception of the neighbouring region Transilvania.

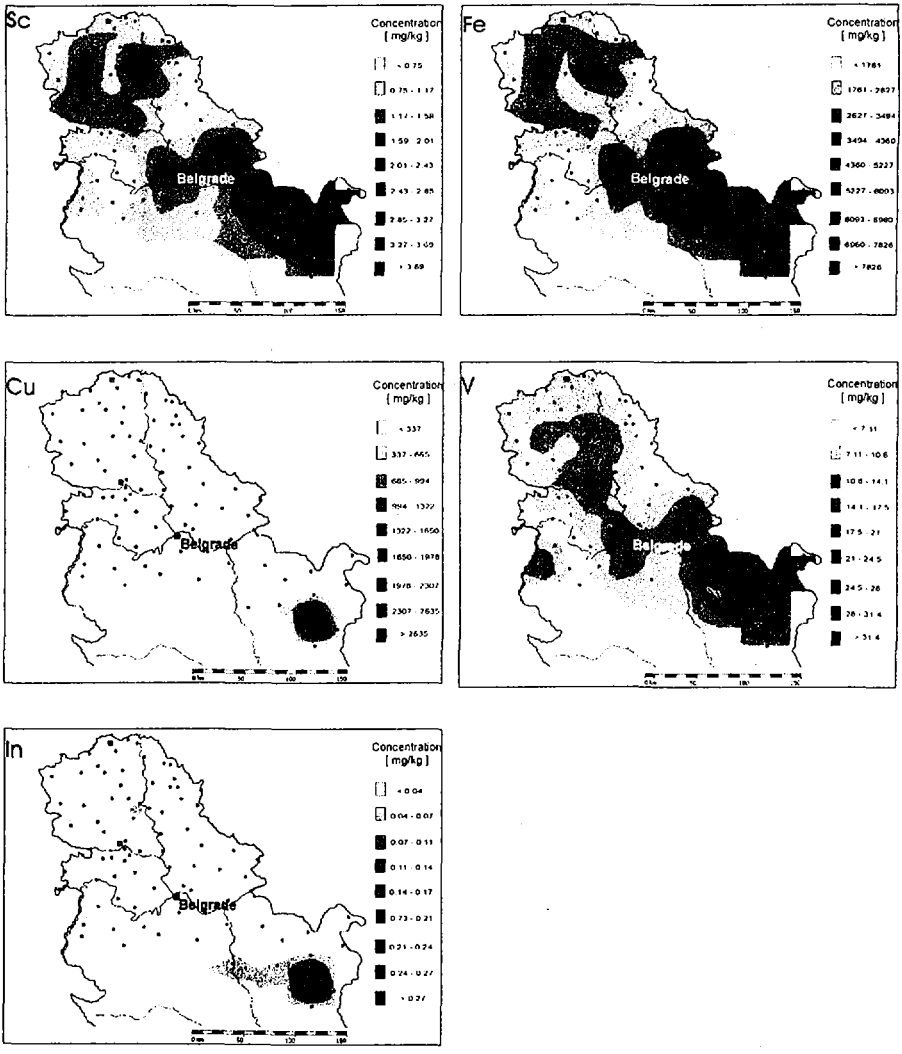

Figure 2. Distribution maps of some heavy metals in moss samples from Serbia

Cobalt

The median and maximum values of cobalt in Serbian mosses are considerably higher than corresponding values in other areas. High Co concentrations are observed near Bor (sites 12,66, 89), near the border with Romania (35, 41) and near the Smederevo iron smelter (72). The highest Co value is for site 89 where none of the other elements studied show correspondingly high values.

Nickel

The median concentration of Ni in Serbia (and Bosnia) is higher than in most of the other areas shown in Table 2, but the maximum value is only 3–4 times the median. This means that no strong point source for Ni exists in the area. A high correlation with Cr (R=0.86) may be noted. Correlations with other elements are considerably weaker. Association with Factor 1 indicates that the generally high Ni level in Serbia mainly reflects the geochemistry of the area. Relatively high values at sites 4, 61, 77 and 85 might be from fires at the Pancevo refinery, as mentioned above for V.

Copper

Non-ferrous metal industry in the «Copper basin» in east Serbia, near the Romanian and Bulgarian borders, is a very strong source of air pollution. From Table 2 it is evident that the copper deposition in the vicinity of Bor is comparable to some very polluted sites in other countries. The copper deposition (Fig. 2) is mainly limited to an area within a distance of about 50 km from Bor. So is also the deposition of a series of other elements characterised by Factor 2 and showing very similar deposition patterns (Zn, As, Se, Mo, Ag, Cd, In, Sb, Au). The deposition map for In is shown in Fig. 2 as an example. It is very clear that these elements all are derived from the same source area. In the case of Se and Mo the maximum values from Serbia are probably the highest ever recorded in moss samples used as biomonitors of air pollution.

Bromine

The bromine values observed in this work are not particularly high compared to other areas (Table 2). However, most of the high values (>10 μg/g) are concentrated in a relatively limited area in the north (sites 18, 24, 60, 83) and it is reasonable to assume that they are due to some industrial source.

Indium

To the knowledge of the authors this is the first time the atmospheric deposition of In has been studied by the moss biomonitoring technique. this is mainly thanks to the very high sensitivity offered by neutron activation analysis for the determination of In, in particular when the epithermal variant is used. The In distribution in Fig. 2 appears almost identical to that of Cu.

Antimony

In addition to the area around Bor there is some Sb pollution in western Serbia (Sites 46, 28). The source here is probably an antimony mine near site 46.

Caesium

This element is normally observed in moss as a result of natural processes.[11] In the present material there is one obvious exception: the 18.2 µg/g value at site 46, which may also be associated with the antimony mine.

Uranium

The U median value in Serbia is similar to the neighbouring areas of Romania and Bulgaria, and the maximum value is just 3 times the median. That indicates a crustal origin of this uranium, as also indicated by the high loading for U in factor 1. The present results do not indicate any appreciable deposition of U due to possible use of depleted uranium in weapons during the 1999 NATO military action.

Conclusion

From the presented results it can be concluded that atmospheric deposition of heavy metals is a considerable problem in Serbia even at the current level of industrial activity. The most obvious problems are present in the Bor region, where the maximum deposition levels are observed not only for elements associated with the extraction of sulfide ores there, but also for most elements which are representative of the general composition of the Earth's crust. Industrial sources are also evident in the northern and western parts of Serbia. It may seem surprising that the factor analysis was not able to distinguish a separate component due to coal fired power plants. However, elements such as As and Se, normally good markers of emissions from coal burning, are so strongly dominated in the present material by the emissions from the Bor industry that the contribution from power plants elsewhere in the country would be very difficult to distinguish. Still it may be assumed that fly ash from coal burning is a significant part of the strong «crustal» component evident from the factor analysis.

Some trends possibly associated with the NATO military action in the spring of 1999 seem to be distinguishable, but they are not very evident on the top of a generally high pollution load. This may seem surprising considering the fact that thousands of tons of crude oil were set on fire and large amounts of combustion products of nitrogen, sulfur and carbon were emitted. Using ENAA trace elements characteristic of crude oil such as V and Ni can be determined in mosses. It is essential to have in mind however that the emission of vanadium and other trace elements from refineries lasted only about 10 days. High concentrations of V observed in moss samples from the copper basin on the other hand are the result of continuous emissions over the last three years. It means that the NATO action may still have caused substantial air concentrations of the mentioned elements in some places and subsequent atmospheric deposition in nearby regions.

References

1. FR Yugoslavia Report. The Consenquences of NATO Bombing for the Environment in FR Yugoslavia. Ed. Yugoslav Federal Ministry for Development, Science and the Environment. Belgrade 2000. pp. 1-87.
2. Å. RÜHLING, E. STEINNES (eds.). Atmospheric Heavy Metal Deposition in Europe 1995 - 1996. Report Nord 1998:15, Nordic Council of Ministers, Copenhagen 1998, 66 pp.
3. M.V.FRONTASYEVA, S.S.PAVLOV. Analytical Investigations at the IBR-2 Reactor in Dubna, *JINR Preprint*, E14-2000-177, Dubna, 2000.
4. Å. RÜHLING, G. BRUMELIS, N. GOLTSOVA, K. KVIETKUS, E. KUBIN, S. LIIV, S. MAGNUSSON, A. MÄKINEN, K. PILEGAARD, L. RASMUSSEN, E. SANDER, E. STEINNES. Atmospheric Heavy Metal Deposition in Northern Europe 1990. Report Nord 1992:12, Nordic Council of Ministers, Copenhagen 1992, 41 pp.
5. J. STAMENOV et al. New results from air pollution studies in Bulgaria:Moss Survey 2000. JINR Preprint, E-14-2002-xx (in press), 2002.
6. K.GRODZINSKA, M.V.FRONTASYEVA, G.SZAREK-LUKASZEWSKA, M.KLICH, A.KUCHARSKA, S.F.GUNDORING, T.M.OSTROVNAYA. Trace element concentrations in *Pleurozium schreberi* (Brid.) Mitt. in industrial regions in Poland – mosses as indicators of atmospheric contamination (submitted to the *J. Environ. Monitor.*).
7. A. LUCACIU, M.V. FRONTASYEVA, E. STEINNES, Ye.N.CHEREMISINA, C.OPREA, T.B.PROGULOVA, S.SPIRIDON, L.STAICU, L.TIMOFTE: Atmospheric deposition of heavy metals in Romania studied by the moss technique employing nuclear and related analytical techniques and GIS technology. *J. Radioanal. Nucl. Chem.*, v. 240, No.2 457-458, 1999.
8. M.V.FRONTASYEVA, E.STEINNES, S.M.LYAPUNOV, V.D.CHERCHINTSEV, L.I.SMIRNOV. Biomonitoring of heavy metal deposition in South Ural region: Some preliminary obtained by nuclear and related techniques, *J. Radioanal. Nucl. Chem.*, vol. 245, No.2, 415-420, 2000.
9. E. STEINNES, T. BERG, T.E. SJØBAKK, H. UGGERUD, M. VADSET. Report 838/2001, State Pollution Control Authority, Oslo 2001, 28 pp (In Norwegian).
10. E .STEINNES. A critical evaluation of the use of naturally growing moss to monitor the deposition of atmospheric metals. Sci. Total Environ. 1995;160/161.
11. E.STEINNES, J.P.RAMBAEK, J.E.HANSSEN. Large Scale Multi-Element Survey of Atmospheric Deposition Using Naturally Growing Moss as Biomonitor, *Chemosphere*, 1992, vol. 25, p. 735-752.

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Фронтасьева М. В. и др. E18-2002-144
Изучение атмосферных выпадений тяжелых металлов на территории Сербии с помощью нейтронного активационного анализа мхов-биомониторов и ГИС-технологий

Представлены результаты экспериментального исследования мхов-биомониторов, используемых для изучения атмосферных выпадений тяжелых металлов и других следовых элементов в северной части Сербии и некоторых районах Боснии. Образцы мха *Hypnum cupressiforme*, наряду с некоторыми другими типами мхов, были собраны в 92 точках летом 2000 г. 44 элемента определены методом инструментального нейтронного активационного анализа с использованием эпитепловых нейтронов. Наблюдаемые уровни концентрации элементов Cu, Zn, As, Ag, Cd, In, Sb в районе г. Бор (Сербия) сопоставимы с уровнями концентраций этих элементов в других промышленных областях, например в Медном Бассейне (Польша) и на Южном Урале (Россия). В этом районе отмечены предельно высокие концентрации элементов Se и Mo. По результатам факторного анализа элементов Fe и Ni представляют почвенную компоненту в сербских мхах, что связано с выветриванием поверхностного слоя почв (большинство образцов мхов были взяты в сельскохозяйственных районах), а также с выпадениями этих элементов в процессе сжигания угля на электростанциях. Содержание некоторых элементов во мхах (например, Cl и V) может быть результатом деятельности различных промышленных объектов, но в некоторых районах высокие концентрации элементов во мхах, возможно, связаны с пожарами на нефтеперерабатывающих заводах в результате военной операции НАТО на территории Сербии в 1999 г.

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Frontasyeva M. V. et al. E18-2002-144
Atmospheric Deposition of Heavy Metals in Serbia Studied by Moss Biomonitoring, Neutron Activation Analysis and GIS Technology

The results of a pilot study on atmospheric deposition of heavy metals and other trace elements using the moss biomonitoring technique in the northern part of Serbia and some areas of Bosnia are presented. Samples of *Hypnum cupressiforme* along with some other moss types were collected at 92 sites during the summer of 2000. A total of 44 elements were determined by instrumental neutron activation analysis using epithermal neutrons. The observed levels of Cu, Zn, As, Ag, Cd, In, Sb, etc. in the area surrounding the town of Bor (Serbia) are comparable to those reported from similar industrial areas in other countries such as the Copper Basin in Poland and the South Urals of Russia. In the same region the maximum Se and Mo concentrations are the highest ever recorded in biomonitoring studies using mosses. High median concentrations of Fe and Ni in Serbian mosses are associated with a crustal component as apparent from factor analysis of the moss data. This component could be a result of windblown soil dust (most of the samples were taken from agricultural regions) or deposition of ash from coal-burning power stations. Some specific elements such as Cl and V may originate from known industrial sources, but at certain places high values in the moss samples are suspected to be associated with fires in oil refineries damaged during the 1999 NATO military action.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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