

R-MODE FACTOR ANALYSIS APPLIED TO THE EXPLORATION OF AIR POLLUTION IN THE SOUTH OF ROMANIA

C. D. OPREA, AL. MIHUL

*Dept. of Nuclear Physics, Faculty of Physics, Bucharest University,
Bucharest, Romania, Alexandru.Mihul@cern.ch*

(Received September 25, 2002)

Atmospheric deposition of heavy metals and other trace elements in the South of Romania was monitored by the moss biomonitoring technique. The goal of this study was to characterize the regional deposition pattern of polluting elements related to main pollution sources and to allow comparisons with similar studies done in Europe. A total of 52 moss samples were analyzed for heavy metals (Al, Sc, V, Cr, Mn, Fe, Co, Ni, Zn, As, Sr, Mo, Cd, W), halogens (Cl, Br, I), rare earth elements (La, Ce, Sm, Eu, Tb, Yb), Se, Sb, U and Th by epithermal neutron activation analysis. Lichen IAEA-336 was used as reference material to ensure the quality of the results. R-mode factor analysis was used to describe the relationship among 27 geochemical data in mosses. The mosses were classified into five groups according to the extracted factors. These factors are interpreted as contributions from crustal material, oil burning, general pollution, sea salt long-range transport, coal burning, and internal combustion engines, respectively. The moss monitoring programme showed up the highly industrialized and urban locations such as Ploiesti, Valea Prahovei, Motru-Rovinari, Petrosani and Buzau.

Key words: mosses, factor analysis, sources, air toxics

1. INTRODUCTION

Mosses have proven useful as bioindicators for atmospheric deposition of heavy metals [1-3]. Moss-biomonitoring technique [4] was applied in the South of Romania to provide important information on emissions from the surveyed area and perhaps long-range transport across the Europe, yet any study was not accomplished there to date. Studies in the South of Romania have been conducted as part of the project "The study of air pollution sources in the Southern part of Romania using epithermal neutron activation analysis and factor analysis". They have been included as part of the European Project "International Cooperative Programme On Effects Of Air Pollution On Natural Vegetation And Crops 2000-2001". Moss samples were collected in the 2000-year survey, from May to September. The moss samples were analyzed for 37 elements by epithermal neutron activation analysis and for 4 elements (i.e. Cd, Cu, Hg and Pb) were analyzed by flame atomic absorption spectrometry. The geographical distribution of moss concentrations is presented in the form of maps of isodepositions using the program Surfer.

Here we focus on the sources in the South of Romania, using a variant of factor analysis, R-mode factor analysis, for source identification [5]. R-mode factor analysis is based on the correlations among the variables (i.e. chemical elements) measured for each sample, which are assumed to be caused by main underlying sources.

The results from factor analysis are complemented by studies based on crustal enrichment factors. Furthermore, the air-mass trajectories are used in our studies to aid in interpreting spatial trends.

The specific matters we propose to answer in this paper are (1) What is the composition of mosses associated with each factor? (2) How can be extracted the soil component? (3) What are the main air pollution sources in the South of Romania? (4) How does the composition of mosses in South Romania compare with other European countries (excesses and similarities)?

2. EXPERIMENTAL

2.1. Study area, sample collection and analytics

The study area lying on south-central part of Romania comprises 11008 km². Because of its central geographical location it appears as an important transit route between the Middle East and the Central and Eastern Europe - a geographical fact that has led to an increased regional air pollution. The climate is moderated temperate continental, the annual average precipitation's is 500-600 mm and the dominant wind direction is from the east to west. The main sources of air toxics at this territory of Romania are the energy sector, coal mining and oil refining industry, ferrous and chemical industry [6]. Limited local pollution and long-range transport pollution (LRTP), as well as atmospheric transport from the marine environment influence the atmosphere of the investigated area.

The moss species of *Hylocomium splendens* and *Hypnum cupressiforme* were chosen to monitor atmospheric deposition of trace elements, as they are widely spread in the surveyed geographical territory [7], and they are recommended for simultaneous work in the other European states [1]. As reflected in the sampling performed, *Hylocomium splendens* mosses (found in 23.3 % of the sites) were more common in coniferous forests while *Hypnum cupressiforme* mosses (found in 97.7 % of the sites) were more abundant in deciduous and mixed forests. A total of 52 moss samples, from which 42 of *Hypnum cupressiforme* and 10 of *Hylocomium splendens* species were collected according to a grid network of 43 cells of 16 x 16 km² surface (Fig. [1]).

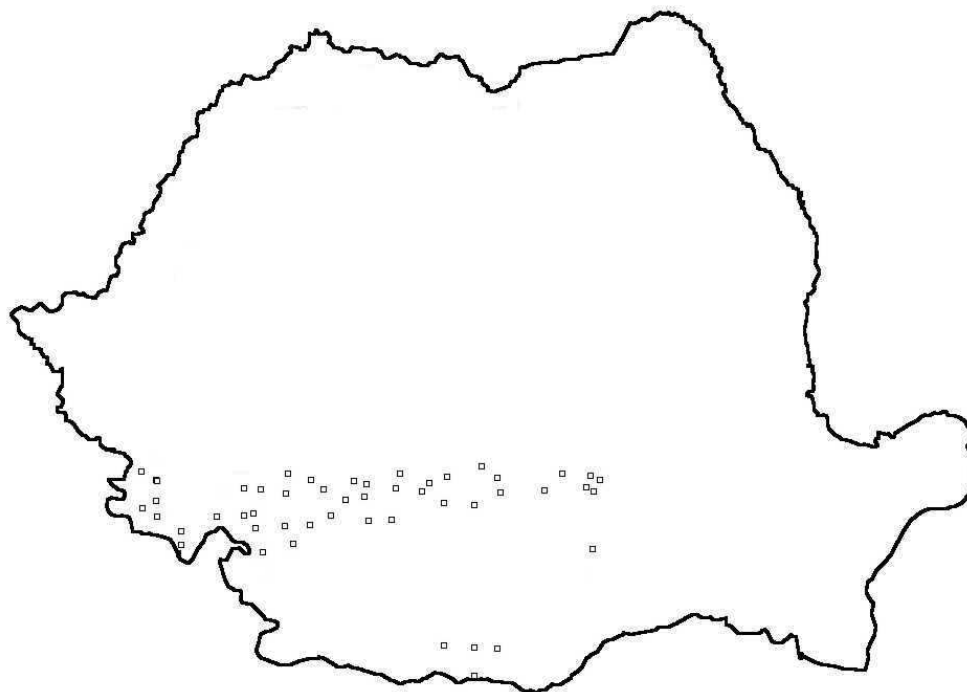


Fig. [1]- Map of Romania showing moss sampling sites.

To avoid the accidentally contamination, the moss samples were collected from isolated places, located at least 300 m from main roads and populated areas and at least 100 m from any road or single house. From each grid cell was collected a representative sample, which was obtained by mixing 5 to 10 samples taken within a 50 x 50 m area. The upper three fully developed segments of each *Hylocomium splendens* plant and corresponding green or green-brownish parts of the *Hypnum cupressiforme* plant representing the last 2-3 years growth were reaped. The concentrations of chemical elements in the moss samples reflect the three-year average content of pollutants estimated at the specific, corresponding geographic locations. The samples were cleaned from the extraneous material, divided in small pieces and homogenized in an agate mortar, excluding any further chemical homogenization [8]. Dried at room temperature, then the moss samples were kept at 40 °C for 48 hours in thermostat until constant weight. The same material was subjected both to epithermal neutron activation analysis and flame atomic absorption spectrometry.

The pulsed fast reactor IBR-2 is equipped with two irradiation channels for neutron activation purposes (Table 1).

Table 1.
Characteristics of the irradiation channels [9]

Irradiation channel	$\Phi \cdot 10^{12}, \text{ n cm}^{-2} \text{ s}^{-1}$			T (°C)	ϕ channel (mm)	L channel (mm)
	E=0–0.55 eV	E=0.55–10 ⁵ eV	E=10 ⁵ –25·10 ⁶ eV			
Ch1 (Cd-screened)	0.023 ± 0.002	3.31 ± 0.3	4.23 ± 0.4	70	28	260
Ch2	1.23 ± 0.1	2.96 ± 0.3	4.1 ± 0.4	60	28	260

The samples of 0.3 g and relevant reference materials (SRMs) were heat-sealed in polyethylene bags for short-term irradiation and packed in aluminum cups for long-term irradiation. To determine the elements which have short half-life nuclides such as Mg (²⁷Mg), Al (²⁸Al), Cl (³⁸Cl), Ca (⁴⁹Ca), V (⁵²V) and Mn (⁵⁶Mn), samples and standards were irradiated for 3 min in Ch2. Gamma-ray spectra were measured twice after 3-5 min of decay for 3 and 20 minutes, respectively. HPGe detector with a resolution of 2.5 keV for the ⁶⁰Co and relative efficiency of 20 % 1332 keV line was used.

The elements which have medium half-life nuclides such as Ca (⁴⁷Ca), As (⁷⁶As), Br (⁸²Br), La (¹⁴⁰La), Sm (¹⁵³Sm) and U (²³⁹Np), and long half-life nuclides such as Sc (⁴⁶Sc), Cr (⁵¹Cr), Fe (⁵⁹Fe), Co (⁶⁰Co), Ni (⁵⁸Co), Zn (⁶⁵Zn), Se (⁷⁵Se), Sr (⁸⁵Sr), Ag (^{110m}Ag), Cs (¹³⁴Cs), Ce (¹⁴¹Ce), Hf (¹⁸¹Hf) and Th (²³³Pa) were determined by irradiating the samples and standards for 4-5 days in Ch1. After cooling for 4 to 5 days (for medium half-lives) and for 14 to 20 days (for long half-lives), the gamma-ray spectra were measured for 40-50 min and 2 h 30 min - 3 h, respectively.

The gamma-ray spectra analysis was carried out using software developed in FLNP, JINR [10]. The element concentrations were determined by conventional relative standardization.

Cadmium, copper, lead and mercury were determined by flame atomic absorption spectrometry (FAAS) at the Centre of Environmental Protection from "Politehnica" University. The moss samples of 0.5 g (d. w.) were digested with 6 ml concentrated nitric acid at 120 °C for 6 h. After cooling to room temperature the samples were filtered and distilled water added up to 50 ml.

The lichen IAEA SRM L-336 (issued by the International Atomic Energy Agency) was used as reference material. The results on lichen IAEA SRM L-336 obtained by the both methods are presented in Table 2.

Table 2.
Acceptable limits established for standard reference material IAEA SRM L-336

Element	L-336, (mg/kg) (Certified)	L-336, (mg/kg) (Determined)
Na	320 ± 26	304 ± 26
Mg	610 ± 3	708 ± 101
Al	680 ± 3.4	720 ± 65
Cl	1920 ± 10	1927 ± 288
K	1840 ± 4	1910 ± 90
Ca	2600 ± 13	2810 ± 324
Sc	0.17 ± 0.011	0.176 ± 0.014
V	1.5 ± 0.44	1.38 ± 0.19
Cr	1.03 ± 0.08	1.10 ± 0.17
Mn	64 ± 2.9	69 ± 5.1
Fe	426 ± 0.6	430 ± 8.5
Co	0.287 ± 0.022	0.303 ± 0.070
Cu	3.55 ± 0.59	3.7 ± 0.5
Zn	31.6 ± 1.42	28.2 ± 2.3
As	0.639 ± 0.067	0.54 ± 0.71
Se	0.22 ± 0.011	0.22 ± 0.033
Br	12.9 ± 3.2	14.2 ± 2.3
Rb	1.72 ± 0.07	1.7 ± 0.17
Sr	9.2 ± 0.046	11.4 ± 0.55
Cd	0.117 ± 0.0006	0.13 ± 0.015
Sb	0.073 ± 0.0067	0.078 ± 0.01
Cs	0.11 ± 0.018	0.12 ± 0.024
Ba	6.4 ± 0.02	6.6 ± 0.7
La	0.66 ± 0.039	0.70 ± 0.06
Ce	1.27 ± 0.25	1.3 ± 0.25
Sm	0.106 ± 0.058	0.106 ± 0.06
Tb	0.014 ± 0.001	0.015 ± 0.0006
Yb	0.037 ± 0.0018	0.042 ± 0.0026
Pb	4.9 ± 0.96	5.0 ± 1.0
Hg	0.20 ± 0.02	0.19 ± 0.1
Th	0.14 ± 0.0014	0.14 ± 0.006

2.2. Statistical data analysis

The data were subjected to statistical analysis by using the statistical package SPSS 10.0.7 for Windows. The descriptive statistics of elemental concentrations contains few extremely high or extremely low score loadings, than the mean is biased by these outermost values and the median was further chosen to define the representative pollution levels in the studied region. The total range between minimal and maximal concentration values characterized the measure of variability in the data set. A statistical multivariate analysis of each element concentration in suites of related samples is done to seek communality of variation at different sampling sites. R-mode factor analysis is a well described mathematical method to reduce the dimensionality of the variable space on the basis of the reduced factor solution [11, 12]. R-mode factor analysis usually proceeds in four steps: (1) the

correlation matrix for all variables is computed, (2) factor extraction, (3) factor rotation and (4) score calculation between the original values and the extracted factors.

A matrix of measured values X_{mn} or its standardized matrix Z_{mn} can be split into the product of the loading matrix of extracted common factors F_{mp} (the arithmetic mean concentrations of the elements) and the matrix of factor scores S_{pn} (the contributions of each factor to the sample) plus the residual matrix R_{mn}

$$Z_{mn} = F_{mp} S_{pn} + R_{mn} \quad (1)$$

where m , n si p are number of variables, subjects and extracted factors, respectively. After estimation of communalities in the main diagonal of the correlation matrix, we solve the eigenvalue problem by the principal component method [13].

To maximize the source-identification power of factor analysis, we selected elements with precise source information. The variables we used in the factor analysis were Na, Mg, Al, Cl, K, Ca, Sc, V, Cr, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Cd, Sb, I, Cs, Ba, La, Ce, Pb, Hg, Th, U. The factors obtained were subjected to orthogonal rotation by the varimax method to minimize the medium loaded elements in the extracted factors and to maximize low and high loadings of the elements. Factor scores were used to eliminate the outliers and to identify the single source samples in the data set. Because the R-mode factor analysis, like other factor-analysis models is subjective to a degree, we evaluated the source elemental profiles by (1) examining the enrichments of the crustal factors relative to Sc and average crustal material and (2) comparing the composition of the factors obtained to known pollution sources.

3. RESULTS AND DISCUSSION

3.1. The data interpretation by the method of descriptive statistics

We will focus our discussion to the arithmetical mean (including standard deviation), median, minimum, maximum and Max./Min. ratios (Table 3).

Table 3.
Concentrations of 41 elements ($\mu\text{g/g d. w.}$) in moss samples

<i>Statistics</i> Element	<i>Mean</i>	<i>Median</i>	<i>Min.</i>	<i>Max.</i>	<i>Max./Min.</i>
Na	895 \pm 47	773	276	2136	7.7
Mg	2145 \pm 109	1895	759	6510	8.6
Al	5498 \pm 298	5087	1783	18570	10.4
Cl	285 \pm 6	275	185	480	2.6
K	7175 \pm 381	6043	2270	25150	11.1
Ca	5269 \pm 169	4816	2874	10410	3.6
Sc	0.53 \pm 0.02	0.52	0.23	1.31	5.8
V	8.4 \pm 0.5	7.2	3.6	32.7	9.1
Cr	12.1 \pm 0.6	12.2	2.6	30.0	11.6
Mn	265 \pm 9	251	108	504	4.7
Fe	2361 \pm 103	2327	777	5213	6.7
Co	1.05 \pm 0.03	1.07	0.48	2.00	4.2
Ni	7.8 \pm 0.4	6.8	3.4	29.3	8.7
Cu	18.4 \pm 0.6	17	9.3	32.7	3.5
Zn	69 \pm 2	65	33	121	3.7
As	1.72 \pm 0.06	1.54	0.86	3.62	4.2
Se	0.21 \pm 0.01	0.21	0.03	0.50	17.2
Br	6.3 \pm 0.25	5.6	2.2	14.7	6.7
Rb	18.9 \pm 0.6	18.7	8.8	35.1	4
Sr	17.2 \pm 0.8	17.0	3.5	41.3	12
Zr	14.6 \pm 0.7	11.3	5.3	32.8	6.2
Mo	0.37 \pm 0.03	0.31	0.01	1.13	113
Ag	0.12 \pm 0.01	0.10	0.02	0.35	19.5
Cd	0.40 \pm 0.23	0.32	0.11	1.08	9.8
Sb	0.63 \pm 0.02	0.59	0.38	1.17	3.1
I	1.05 \pm 0.05	0.90	0.36	2.45	6.8
Cs	0.53 \pm 0.02	0.46	0.19	1.23	6.4
Ba	75 \pm 3	75	27	157	5.9
La	3.6 \pm 0.2	3.4	0.7	7.7	11.8
Ce	6.1 \pm 0.3	5.5	1.5	14.3	9.6
Pb	14.5 \pm 2	6.3	2.3	86.2	37.5
Hg	0.17 \pm 0.008	0.15	0.07	0.35	5
Sm	0.65 \pm 0.03	0.56	0.24	1.76	7.2
Tb	0.053 \pm .002	0.050	0.021	0.110	5.2
Yb	0.10 \pm 0.05	0.090	0.040	0.220	5.5
Hf	0.35 \pm 0.02	0.32	0.09	0.69	7.7
Ta	0.07 \pm 0.003	0.06	0.02	0.13	6.5
W	0.16 \pm 0.01	0.13	0.07	0.45	6.4
Au	0.011 \pm 0.001	0.009	0.002	0.025	12.1
Th	0.76 \pm 0.03	0.70	0.16	1.42	8.7
U	0.22 \pm 0.01	0.09	0.09	0.62	6.8

The data were standardized versus background (i.e. the ratios between the median value of a variable and the corresponding background value were computed). A rural site west of the Southern Carpathians was evaluated to represent background conditions most closely. The ratios of median/background values for the main pollutants were represented graphically in Fig. [2].

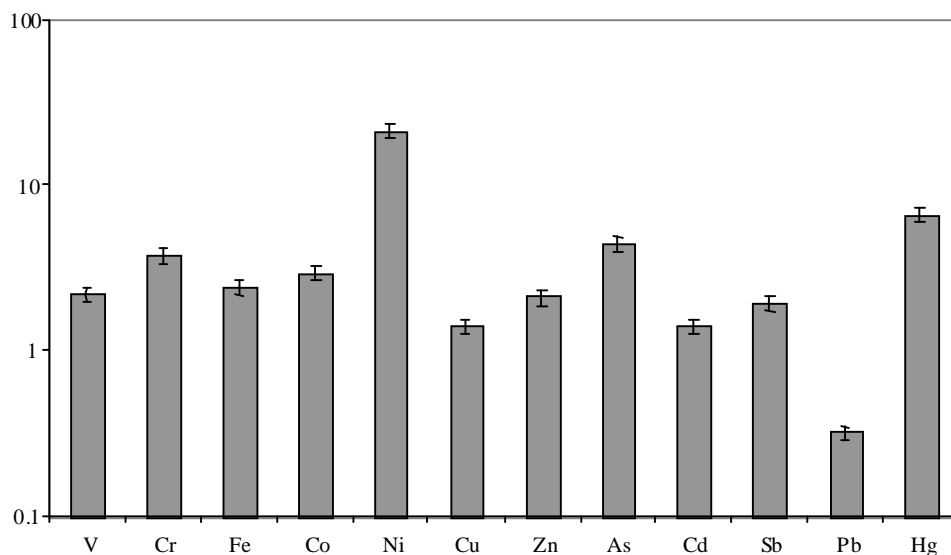


Fig. 2- The main atmospheric pollutants (median/background) in the monitored area

The ratio for Pb is very low and is connected with a moderated high value of Pb at the reference site. We can see low values of the ratio pollution/background for vanadium, iron and cobalt. As the three elements have a crustal nature and consequently they could be accumulated in mosses from windblown dust, the information given by the considered ratio is not relevant (or insufficient) in air pollution study. For copper, zinc, cadmium and antimony we obtained relatively small indices, as the nonferrous industry is not very well represented in the investigated area. Chromium and arsenic values exceed 5 times the background value and indicate a moderate atmospheric pollution level. The highest pollution/background ratio determined for nickel is related to the local oil and heavy industries [14]. Another high pollution/background ratio was obtained for mercury and can be attributed to internal combustion engines emissions.

The highest concentrations were determined for Al, Ca, V, Fe, Ni, Zn, and As (originated mainly from local source emissions), Na, Cl, Br (transported from marine environment), Sr, Rb and Cs (transferred to mosses from substrata).

Molybdenum presents a high Max./Min. ratio (113) and this value can be related to the analytical uncertainties. The rest of the elements showed not significant Max./Min. ratios, pointing that the variation of elemental atmospheric deposition differ not substantially from one locality to another, moreover it indicates a regional character.

3.2. Source interpretation

The five factors extracted by R-mode factor analysis are represented as factor loadings (Table 4). The eigenvalue and variance (%) for each factor and cumulative variance are included. A separation of 81.4 % was achieved.

Table 4.
Sources for atmospheric deposition of chemical elements expressed as factor loadings.

Factor / Component	F1	F2	F3	F4	F5
Na	0.887	0.163	0.114	0.132	-0.036
Ba	0.877	0.092	0.022	0.113	-0.119
Al	0.864	0.214	0.201	0.240	0.103
Ni	0.852	0.096	0.209	0.199	0.157
Mg	0.850	0.257	0.260	0.030	0.089
V	0.819	0.153	0.218	0.294	0.188
La	0.765	0.136	0.353	0.165	-0.052
Sc	0.759	0.084	0.188	0.165	0.270
Th	0.759	0.187	0.260	0.405	0.063
Sr	0.661	0.056	-0.283	-0.170	-0.399
Cs	0.649	0.274	0.027	-0.045	-0.398
As	0.273	0.900	0.116	-0.002	-0.086
Cd	0.008	0.895	0.014	0.080	0.102
Zn	0.352	0.864	-0.035	0.178	-0.025
Sb	0.228	0.861	-0.013	-0.075	0.134
Cu	0.141	0.821	0.018	0.340	0.096
Hg	0.021	0.740	-0.073	0.199	0.467
Br	0.077	-0.054	0.968	0.089	0.064
I	0.173	0.058	0.949	0.044	0.040
Cl	0.305	-0.087	0.862	0.105	0.023
U	0.478	0.190	0.657	0.250	-0.140
Cr	0.256	0.138	0.087	0.887	0.041
Fe	0.432	0.163	0.097	0.826	0.048
Se	-0.192	-0.065	0.227	0.787	-0.184
Co	0.619	0.281	-0.102	0.623	0.042
Rb	0.308	0.148	0.050	0.050	-0.522
Pb	0.261	0.427	0.029	-0.129	0.714
Eigenvalue	8.5	5.0	3.6	3.5	1.3
% of Variance	31.4	18.6	13.5	13.0	4.9
Cumulative %	31.4	50.0	63.5	76.5	81.4

The first factor contains crustal elements such as Al, Sc, Fe and Th and the others, such as Ni and V. It represents a mixed signal of the crustal source profile with contributions from oil burning. It explains 31.4 % of the total variance in the data set. This factor was isolated from the survey dataset and further processed to separate the different mixed source profiles. Consequently a second-generation data set was achieved, with new variances. The soil (F11) and vegetation (F13) contributions were removed (Table 5). The pollution source was obviously identified (F12); it is most loaded with V, Ni, Co, Zn and Pb and can be assigned mainly to oil burning and less to coal burning.

Table 5.
Source profiles in Factor 1 expressed as factor loadings.

Factor / Component	F11	F12	F13
Al	0.809	0.387	0.330
V	0.370	0.889	0.308
Th	0.789	0.308	0.120
Ni	0.288	0.881	0.376
Sc	0.753	0.209	0.279
Mg	0.749	0.262	0.459
Na	0.720	0.305	0.472
La	0.717	0.304	0.325
Ba	0.563	0.237	0.637
Rb	0.154	0.018	0.761
Co	0.473	0.733	0.193
Fe	0.718	0.506	-0.106
Zn	0.127	0.671	0.397
Sr	0.165	-0.016	0.861
Cs	0.346	0.431	0.488
Pb	0.063	0.586	-0.052
Eigenvalue	6.4	3.3	2.5
% of Variance	40.2	20.4	15.5
Cumulative %	40.2	60.6	76.1

The second factor is most loaded with As, Cd, Zn, Sb, Cu and Hg and represents a general pollution signal. This factor explains 18.6 % of the variance [15]. The third factor is most loaded with Br, I, Cl and U and represents a long-range marine transport from the Mediterranean Sea. The sea salt transport from the Black Sea could accidentally contribute to this factor, but usually it has a character strict local. The marine factor signs for 13 % of the variance. The fourth factor is most loaded with Cr, Fe, Se, Co and Cu, suggesting a coal burning signal released by industry -mainly of ferrous type, power plants and heating. It describes 13.5 % of the variance. The fifth factor is most loaded with Pb and small amount of Hg and can be attributed to internal combustion engines. This factor includes also a small negative component of Sr, Mn, Cs and Zn of vegetative origin [16]. This factor describes 4.9 % of variance.

To study whether these factors are related to each other, we examined the correlations of the factor scores; R^2 was negligible proving the fact that the factors are essentially independent of each other (Fig. [3]). Crustal and general pollution sources increase with the coal burning source, hinting that all three are associated to a degree with the same emission sources.











F1	0.01	0.01	0.23	0.00
	F2	0.03	0.11	0.00
		F3	0.00	0.00
			F4	0.03
				F5

Fig. 3 - Log-log correlation matrix plot of the factor score

3.3. Crustal enrichment factors

The crustal enrichment factors (EFs), relative to scandium and average crustal rock [21, 22] were constructed (Fig. [4]), where the enrichment factor EF is defined as

$$EF(\text{Sc, soil}) = (X/\text{Sc})_{\text{moss}} / (X/\text{Sc})_{\text{soil}} \quad (2)$$

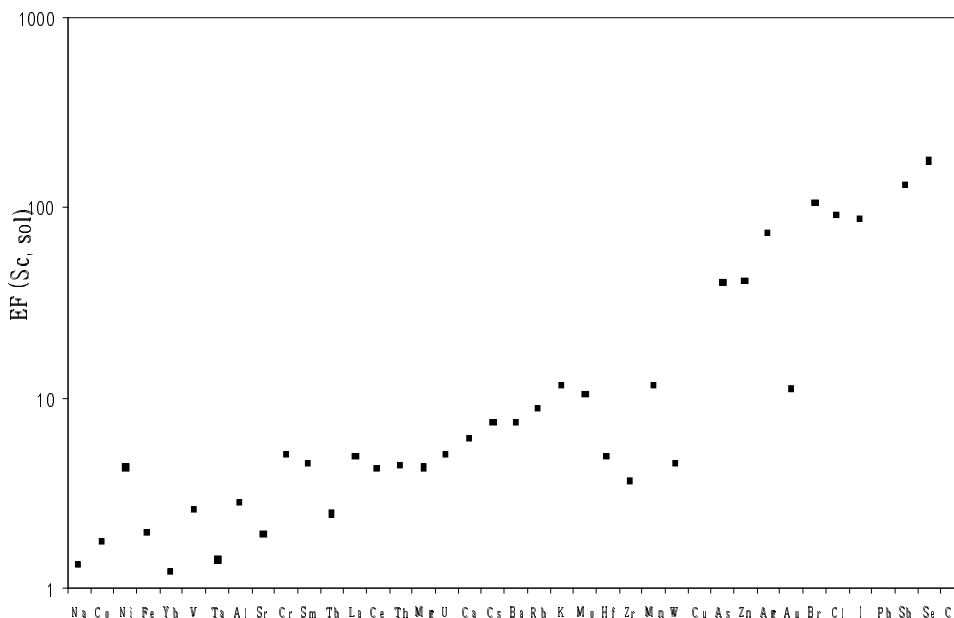


Fig.4 - Crustal enrichment factors (EFs), relative to Sc and average crustal rock [22] for the studied elements

According to the crustal enrichment factors (EF), the elements may be grouped in three categories: (1) The highly enriched elements ($EF > 70$) such as Cd, Se, Sb, Pb, I, Cl and Br - consequently the first four of them can be attributed to anthropogenic sources and the following three to sea-salt processes, (2) Moderately enriched ($EF 10-70$) such as Ag, Zn, As, Cu, W and Mn - they can be attributed to anthropogenic sources associated with mineral particles and (3) The less enriched elements ($EF < 10$) were in decreasing order of the observed enrichments Zr, Hf, Mo, K, Rb, Ba, Cs, Ca, U, Mg, Th, Ce, La, Tb, Sm, Cr, Sr, Al, Ta, V, Yb, Fe, Ni, Co, Na - these elements have few sources other than windblown soil dust.

3.4. Sources of air toxics

The isodeposition maps of air toxic concentrations in mosses were built to study geographical distribution of the air pollution sources. Further the results for each factor are discussed with respect to contributing sources.

First factor (F1)

The behaviour of V and Ni are typical of fuel oil and coal burning, corresponding to F1 (Fig. [5]-[7]). Elevated levels were found in Petrosani, Motru-Rovinari and Tirgu Jiu lignite basins and in Banat pit-coal basin. Other sources of airborne nickel and vanadium are the thermal power stations in Anina and Rogojelu. The high emissions of nickel from Ploiesti, Valea Prahovei (up to 15.5 $\mu\text{g/g}$) and Buzau regions (up to 13.7 $\mu\text{g/g}$) correlate strongly with those of vanadium and are related to local industry with an old tradition in oil mining and refining.

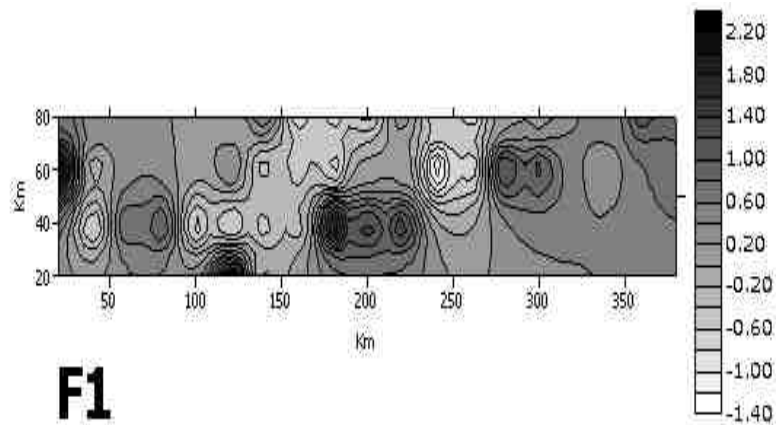


Fig. 5 - Geographical distribution of the first factor (F1)

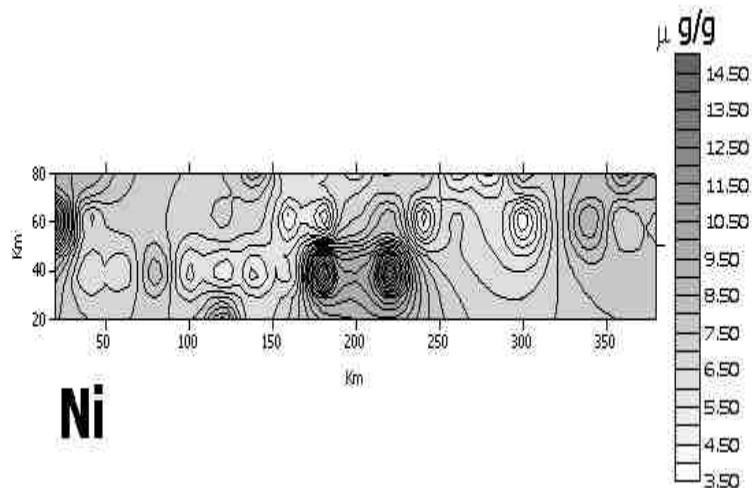


Fig. 6
Geographical distribution of nichel concentrations ($\mu\text{g/g}$) in *Hypnum cupressiforme*

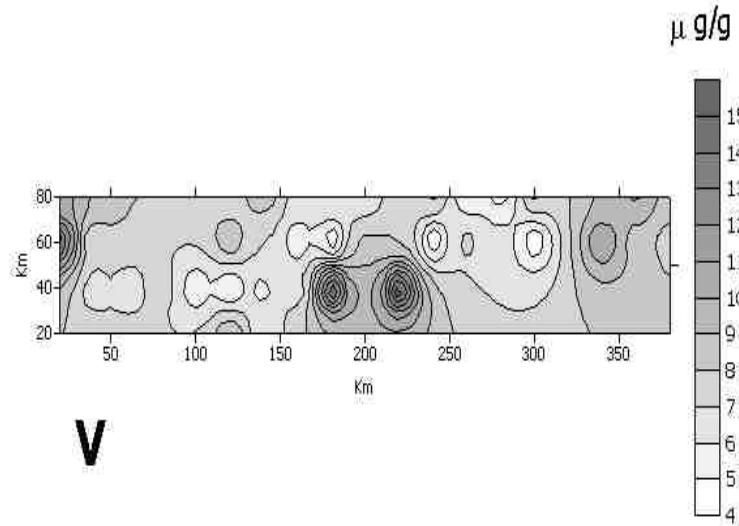


Fig. 7 - Geographical distribution of vanadium concentrations ($\mu\text{g/g}$) in *Hypnum cupressiforme*
Second factor (F2)

The general pollution source (F2) have a strict regional character, showing quite similar profiles for all pollutants loading F2, namely As, Cd, Zn, Sb, Cu and Hg (as seen, for example, in Fig. [8], [9]). The main air pollution sources are the highly industrialized and densely populated areas of Ploiesti, Buzau, Ramnicu Valcea, Pitesti and Drobeta- Turnu Severin towns.

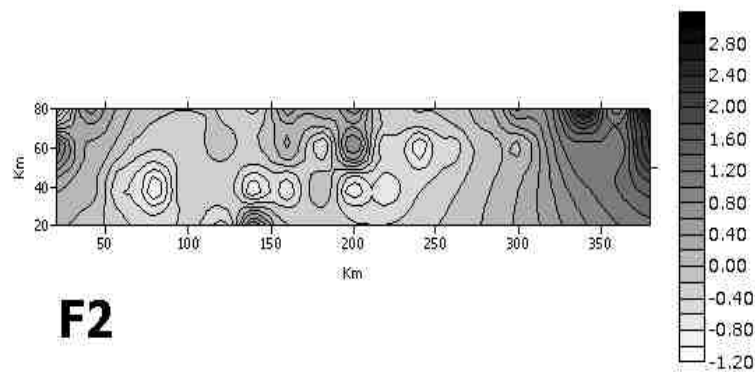


Fig. 8 - Geographical distribution of the second factor (F2)

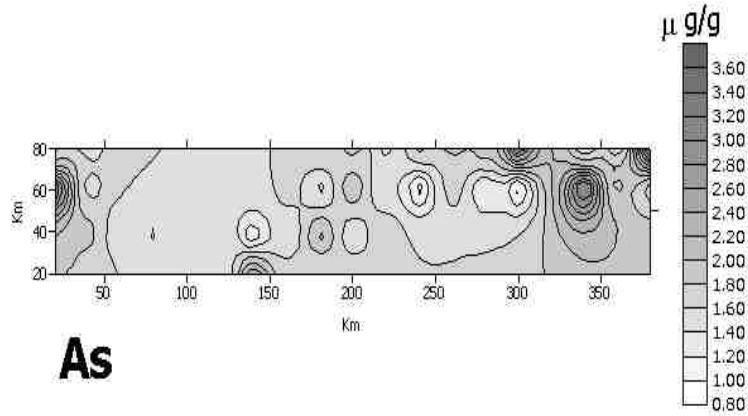


Fig. 9 - Geographical distribution of arsenic concentrations ($\mu\text{g/g}$) in *Hypnum cupressiforme*
Fourth factor (F4)

The areas affected by airborne deposition of elements loaded in F4 are lignite basin of Petrosani and another, situated between Arges and Buzau and the highly industrialized area of Ploiesti and Buzau (by thermal power plant emissions). The profiles can be seen in Figs. [10] and [11].

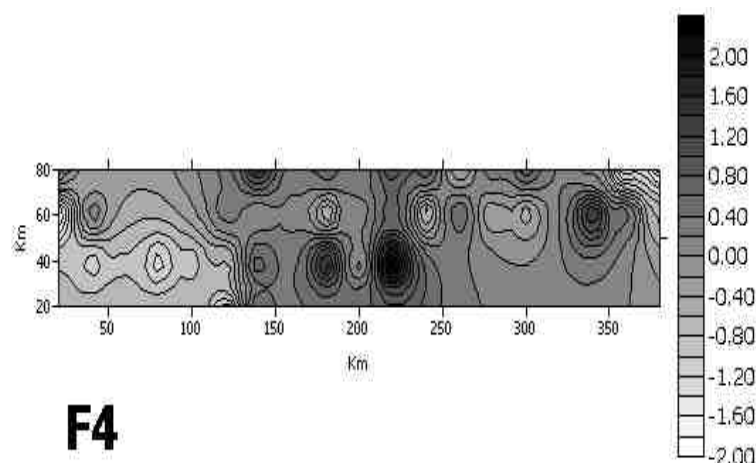
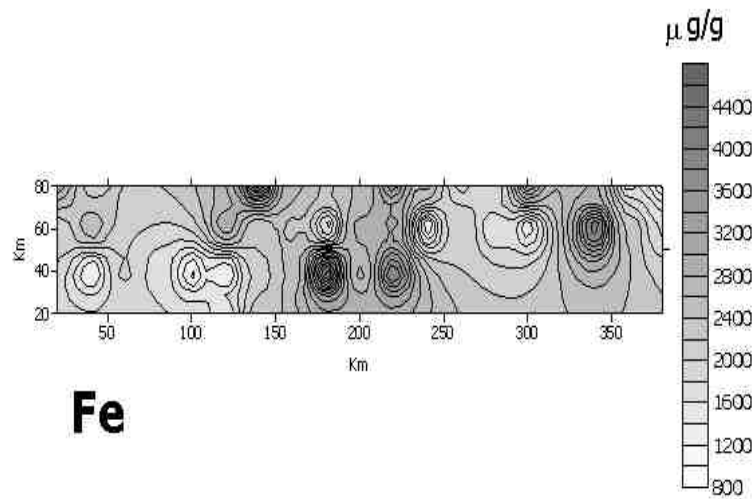


Fig. 10 - Geographical distribution of F4

Fig. 11 - Geographical distribution of iron concentrations ($\mu\text{g/g}$) in *Hypnum cupressiforme*

Fifth factor (F5)

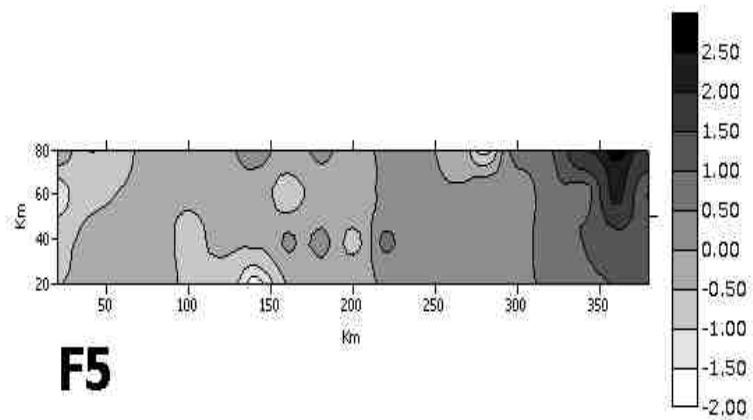


Fig. 12 - Geographical distribution of F5

Lead and mercury, the constituents of F4, are emitted into the atmosphere by internal combustion engines of stationary and mobile sources (Figs. [12] and [13]). On the map the isopleths are more densely around Ploiesti, Ramnicu Valcea, less around Pitesti and in the rest the gradients are oriented along the main roads.

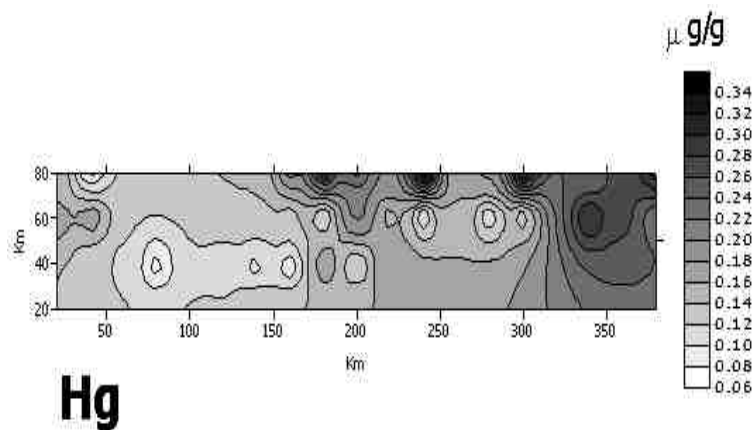


Fig. 13 - Geographical distribution of mercury concentrations ($\mu\text{g/g}$) in *Hypnum cupressiforme*

3.5. Comparison with studies outside Romania

Table 6 gives a comparison of median and maximal concentrations of trace metals in mosses from Romania and those from monitoring programs in the other South-East European countries as Bulgaria [19], Poland [20], Serbia [21], and Slovakia [22] and a background European country as Norway [23]. The present median values of air toxics are generally similar to those reported from Eastern-European countries and characterize the same major sources in the region. In the same time, those values are significantly higher than the Norwich data. The comparison with the concerned areas showed maximum value of cadmium in mosses from Romania.

Table 6.

Trace metal concentrations ($\mu\text{g/g d. w.}$) in mosses from the present work compared with data from other countries in Eastern Europe and data from a background European country - Norway.

	South Romania		Bulgaria		Norway		Poland		Serbia		Slovakia	
	Mediana	Max	Mediana	Max	Mediana	Max	Mediana	Max	Mediana	Max	Mediana	Max
	<i>52 probe</i>		<i>103 probe</i>		<i>464 probe</i>		<i>86 probe</i>		<i>92 probe</i>		<i>86 probe</i>	
V	7.2	32.7	8.4	113	1.35	22.6	2.5	8.1	11.3	39	5.7	30.3
Cr	12.2	30.0	3.2	26.9	0.69	259	1.43	3.2	6.5	20	6.5	42.7
Fe	2327	5213	2314	14700	362	11216	357	845	3110	9230	1561	13750
Co	0.77	6.03	1.08	10.6	0.17	2.6	0.26	1.48	8.2	39	0.85	8.2
Ni	6.8	29.3	4.1	18.6	1.1	72.1	1.8	3.6	6.7	26	3.2	12.6
Cu	17	32.7			4.2	52.7	73	2040	94	3140	23	136
Zn	65	121	41	379	32	661	45	110	44	415	55	179
As	1.54	3.62	1.0	59	0.135	2.63	0.61	6.0	3.35	61	0.71	2.21
Cd	0.32	1.08			0.09	2.65			<0.4	6.5	0.59	1.49
Sb	0.59	1.17	0.23	20.2	0.056	0.46	0.25	0.79	0.52	7	0.87	14.3
Pb	6.4	86.2			2.7	22.7					28	109
Hg	0.147	0.347			0.054	0.467						

4. CONCLUSIONS

On the basis of factor structure and estimations from crustal enrichment factors, R-mode factor analysis was reliable enough to classify moss samples according to deposition types and to known pollution sources. The elements can be classified as follows: (1) crustal elements reached in mosses by windblown dust such as Fe, Sc, Th, Sm, Hf, V, Cs, La, Na, U, Ce, Mg, Rb, Al, Ba, and Co (2) long-range atmospheric transport of pollutants (LRTP) from the strong anthropogenic sources of the areas monitored such as Pb, Cd, Zn, Cu, As, Sb and Ca (3) local stationary sources of airborne pollutants related to monitored area such as Ni, Co, Cu (4) marine elements of atmospheric transport of sea-salt such as Br, I, Cl and Se and (5) vegetative elements of foliar leaching such as Rb, Cs, Sr, (Zn), Ba, and K.

Air toxic concentrations vary from one site to another reflecting the initial emissions at different distances to the main sources. The highest concentrations were measured for some elements such as Al, Ca, V, Fe, Ni, Zn, As, Na, Cl, Br, Sr, Rb and Cs as they are related with specific sources. The concentration values in the present study are similar to those found by the other East-European countries participating in 2000 European moss survey. On the other hand, the trace metal levels were significantly higher in Romania compared with Norway, indicating an increased general level of pollution in the studied area.

REFERENCES

1. A., RUHLING, L., RASMUSSEN, K., PILEGAARD, A., MAKINEN, and E., STEINNES, *Survey of Atmospheric Heavy Metal Deposition in The Nordic Countries in 1985 - Monitored by Moss Analysis*, (Nordic Council of Ministers), NORD 1987:21, Copenhagen, 21, 1987.
2. A., RUHLING, G., BRUMELIS, N., GOLTSOVA, K., KVIETKUS, E., KUBIN, S., LIIV, S., MAGNUSSON, A., MAKINEN, K., PILEGAARD, L., RASMUSSEN, E., SANDER, and E., STEINNES, *Atmospheric Heavy Metal Deposition in Northern Europe 1990*, (Nordic Council of Ministers), NORD 1992:12, Copenhagen, 38, 1992.
3. A., RUEHLLING, and E., STEINNES, *Atmospheric Heavy Metal Deposition in Europe 1995-1996*, (Nordic Council of Ministers), NORD 1998:15, Copenhagen, 67, 1998.
4. A., RUHLING and G., TYLER, Ecology of heavy metals, a regional and historical study, *Botaniska Notiser*, 122, 248-259, 1969.
5. T., BERG, O., ROYSET, E., STEINNES and M., VADSET, Atmospheric trace element deposition: principal component analysis of ICP-MS data from moss samples, *Environmental Pollution*, 88, 67-77, 1995.
6. A.E. PINCOVSCI and I.I. GEORGESCU, Radionuclide and Heavy Metal Pollution in Romania, Radionuclides and Heavy Metals in Environment, (Kluwer Academic Publishers), Dordrecht-Boston-London, 313-318, 2001.
7. I., CRISTUREAN and L., LUNGU, *The systematic botany* (in Romanian), Bucharest University, 600, 1974.
8. E., STEINNES, J.E., HANSEN, J.P., RAMBAEK and N.B., VOGT, Atmospheric deposition of trace elements in Norway: Temporal and spatial trends studied by moss analysis, *Water, Air, Soil Pollution*, 74, 121-140, 1994.
9. M.V., FRONTASYEVA, S.S., PAVLOV, Analytical investigations at the IBR-2 reactor in Dubna, JINR Reprint E14-2000-177, Dubna, RF, 10, 2000.T.M., OSTROVNAYA, L.S., NEFEDYEVA, V.M., NAZAROV, S.B., BORZAKOV and L.P., STRELKOVA, Software for INAA on the Basis of Relative and Absolute Methods Using Nuclear Data Base, Activation Analysis in Environment Protection, D-14-93-325, JINR, Dubna, RF, 319-325, 1993.
- 10.K. UBERLA, Factor Analiz, *Statisticheskoe Metody za rubezhom*, Matematiko, Moskva, 247, 1980.
11. L.R., TUCKER and R.C., MACCALLUM, *Exploratory factor analysis*, <http://www.utexas.edu/cc/stat>.
12. T., BERG, O., ROYSET, E. STEINNES, & M., VADSET, Atmospheric trace element deposition: principal component analysis of ICP-MS data from moss samples, *Environmental pollution* 88, 67-77, 1995.
13. E. STEINNES, J. P. RAMBAEK and J. E. HANSEN, Large scale multi-element survey of atmospheric deposition using naturally growing moss as biomonitor, *Chemosphere*, 25, 735-752, (1992).
14. J. M., PACYNA, Estimations on the atmospheric emissions of trace elements from anthropogenic sources in Europe, *Atmospheric Environment* 18, 1, 41-50, 1984.
15. E., STEINNES, J. P., RAMBAEK and J. E., HANSEN, Large scale multi-element survey of atmospheric deposition using naturally growing moss as biomonitor, *Chemosphere*, 25, 735-752, 1992.
16. K., RAHN, A graphical technique for determining major components in a mixed aerosol. I. Descriptive aspects, *Atmospheric Environment* 33, 1441-1455, 1999.
17. B., MASON, *Principles of Geochemistry*, Wiley, New York 329, 1966.

18. J., STAMENOV, M., IOVCHEV, B., VACHEV, E., GUELEVA, L., YURUKOVA, A., GANEVA, M., MITRIKOV, A., ANTONOV, A., SRENTZ, Z., VARBANOV, I., BATOV, K., DAMOV, E., MARINOVA, M.V., FRONTASYEVA, S.S., PAVLOV, L.P., STRELKOVA, New results from air pollution studies in Bulgaria: Moss survey 2000, JINR Reprint, Dubna 2001 (in press).
19. K., GRODZIŃSKA, M.V., FRONTASYEVA, G., SZAREK-ŁUKASZEWSKA, M., KLICH, A., KUCHARSKA, S.F., GUNDORINA, T.M., OSTROVNAYA. Trace element concentrations in *Pleurozium schreberi* (Brid.) Mitt. in industrial regions of Poland - mosses as indicators of atmospheric contamination. Environ. Monit. and Assess. (in press).
20. M.V., FRONTASYEVA, T.YE., GALINSKAYA, M., KRMAR, M., MATAVULY, S.S., PAVLOV, D., RADNOVIC, E., STEINNES, Atmospheric deposition of heavy metals in Serbia studied by moss biomonitoring, neutron activation analysis and GIS technology. J. Radioanal. Chem. (in press).
21. M., FLOREK, M.V., FRONTASYEVA, B., MANKOVSKA, C.D., OPREA, S.S., PAVLOV, I., SYKORA, Air-pollution with heavy metals and radionuclides in Slovakia studied by the moss biomonitoring technique, Proceedings of ISINN-9 May 23-26, Dubna, 442-449, 2001.
22. E. STEINNES, Atmospheric Heavy Metal Deposition in Norway - estimation based on moss analysis, 2000 (in press).