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ATMOSPHERIC DEPOSITION OF HEAVY METALS AROUND THE LEAD AND COPPER-ZINC SMELTERS IN BAIA MARE, ROMANIA, STUDIED BY THE MOSS BIOMONITORING TECHNIQUE, NEUTRON ACTIVATION ANALYSIS AND FLAME ATOMIC ABSORPTION SPECTROMETRY

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Introduction

Heavy metals constitute one of the most dangerous groups of anthropogenic environmental pollutants due to their potential toxicity and their persistence in the environment. Evaluation of the levels of heavy metal deposition is, consequently, of vital importance.

Systematical surveys of the atmospheric deposition of heavy metals are performed in several European countries every 5 years[1-4] by means of the moss biomonitoring technique. It is well established that bryophytes are among the most effective types of organisms for biomonitoring due to a number of their biological features, widespread occurrence, and tendency to accumulate and retain pollutants.[5] As different from higher plants bryophytes lack an advanced root system. This inhibits significant absorption of pollutants from the substrate and consequently their uptake results mainly from the ambient atmosphere. Moss surveys have several advantages over conventional deposition monitoring based on precipitation samples: the sampling is simple and the chemical analyses are much easier due to higher concentrations and strongly reduced contamination problems.[6]

The most severe effects of air pollutants are likely to occur in the near vicinity of strong pollution sources.[7] Such a situation is evident at the town of Baia Mare in the north-western part of Romania, where polymetallic sulphides are extracted from factories in the town. Mining activities in Baia Mare are more than five centuries old and non-ferrous metallurgical industry has already existed for 150 years. The emissions from these metallurgical factories, reaching high intensity during the last decades (more than 30 tons of dust are emitted to the air each year, including more than 7 tons of lead) has caused severe environmental pollution with heavy metals [8, 9].

However, there is a lack of information about the real level of heavy metal pollution in this region. The primary purpose of this paper is to characterize qualitatively and quantitatively the regional atmospheric deposition of heavy metals and to indicate the extent of the areas polluted by these sources.

Materials and methods

The methods used in this study are based on the Scandinavian recommendations,[1] but adapted to the local environmental conditions as described below.

The studied area

Baia Mare is a district town with a population of 150,000. The town is situated in the valley of Sasar river and is bordered by mountains to the east, north, and west. The prevailing wind direction is from east-north-east, following the direction of the river. The most polluting plants are located upstream the town, so the dust is spread to the town.

Collection and preparation of samples

Three species of moss samples (*Pleurozium schreberi*, *Pseudoscleropodium purum* and *Rhytidiadelphus squarrosus*) were collected on 28 sites located 2 to 17 km from the center of the town (Fig. 1).

This selection of three species was necessary because no single species was present at all collection sites. Sampling was performed in 2000 during the period July-September. Sampling points were chosen at least 100 m from main roads, villages and industries and at least 50 m from smaller roads and houses. On each site, 5-10 samples were collected within a 50×50 m area. Whenever possible, the samples were taken from small forest clearings and always located away

from the nearest trees, so as not to be directly exposed to throughfall precipitation. Sampling and sample handling was performed using polyethene gloves and samples were stored in paper bags. In the laboratory, the samples were carefully cleaned from all dead material and attached litter, and only the green and green-brown shoots from the three latest years were analyzed, after 24 hours drying at 40 °C. Samples were not subjected to washing. For epithermal neutron activation analysis, moss samples of about 300 mg were packed in aluminum cups for long-term irradiation.

For short-term irradiation (conventional NAA) samples of about 300 mg were heat-sealed in polyethene foil.

For FAAS, weighted samples of about 1 g were digested overnight in a mixture of 20 mL concentrated HNO_3 and 1 mL HCl in Erlenmeyer flasks on a hot plate. After evaporation to dryness, 1 mL distilled water was added and the solution heated again to dryness. Then a mixture of 1 mL concentrated HNO_3 and 5 mL distilled water was added, and boiled for a short time. After filtration the solution was diluted with distilled water to 25 mL. For some elements further dilution was necessary to achieve optimal concentration levels for analysis.

Analysis

Neutron activation analysis

Neutron activation analyses were performed at the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia and Geological Institute of Russian Academy of Sciences, Moscow, Russia. Most elements were determined by ENAA with detection limits for most elements within the range of 0.01-10 µg/g. The samples were irradiated in the IBR-2 fast pulsed reactor, the flux parameters of which are shown in Table 1.

Two kinds of analysis were performed: long irradiation for 100 h in Ch1 were used to determine elements associated with long-lived radionuclides (As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, La, Rb, Sb, Sc, Se, Sm, Th, Zn) and short irradiation for 2 min in Ch2 was used for short-lived radionuclides (Al, Ca, Cl, I, K, Na, Mg, Mn, Ti, V). Gamma-ray spectra were recorded four times using a high-purity Ge detector; after decay periods of 5 min and 10 min following the short irradiation, and after 5 days and 13 days following the long irradiation. Four elements: Pb, Cd, Cu and Ni were determined by FAAS (Quant-2A) at Geological Institute of Russian Academy of Sciences.

Table 1. Flux parameters of the irradiation sites[10]

Irradiation site	$\Phi_{th} \cdot 10^{12}$, n/(cm²s)· E=0–0.55 eV	$\Phi_{th} \cdot 10^{12}$, n/(cm²s)· E=0.55–10⁵ eV	$\Phi_{th} \cdot 10^{12}$, n/(cm²s)· E=10⁵–25·10⁶eV
Ch1 (Cd-screened)	0.023	3.31	4.23
Ch2	1.23	2.96	4.10

As known, Pb cannot be determined by NAA, and for three other elements the detection limits are provided better by FAAS rather than by ENAA.

For AAS, the analytical performance was checked by the regular analyses of the reference materials IAEA-336, lichen, and IAEA-359, cabbage, issued by the International Atomic Energy Agency whereas IAEA-336, IAEA-359 and moss DK-1 (from a Nordic intercomparison exercise[1]) were used for NAA.

Results and Discussion

In Fig. 2 the results obtained for Pb, Cd, As and I are compared with relevant data from similar work in other areas of Europe where the authors have been involved. Strongly elevated As values are evident in the Baia Mare region. The mean value of 2.17 mg/kg is similar to concentrations around the copper smelter in Karabash, South Ural Mountains, 3-4 times times higher than levels observed in other industrial areas and nearly 20 times higher than the current median level in Norway. The Cd mean value of 1.43 mg/kg is 2 to 5 times higher than in other European regions and again almost 20 times higher than the 2000 median in Norway. The values obtained for Pb (mean 46 mg/kg, range 11-175 mg/kg) are also higher than in Karabash and the Polish Copper Basin.(Table 2)

The Baia Mare region is well known not only for its high heavy metal pollution, but also for its endemic character due to iodine depletion. This fact is illustrated by our results. The mean iodine concentration (0.59 mg/kg) in mosses from Baia Mare is 5 times lower than the median level in Norway and also systematically lower than mean values elsewhere in Europe.[3]

Considering the obtained data for Cu and Pb we can clearly distinguish their different emission sources. The correlation coefficient calculated for these two elements for all collected samples is very low, only 0.46, but if we divide the samples in two categories with regard to their distribution around the main polluting sources, we observe much higher correlation coefficients for each direction (Fig. 3, a). A similar situation is noted for two other pairs of elements: As-Cd (Fig. 3, b) and As-Pb (Fig. 3, c).

Fig. 4(a-g) show isopleths of 14 elements representing somewhat different deposition patterns, which will be further discussed below. Lead, copper, arsenic and antimony are the fourth major elements emitted from the lead and copper-zinc industry in Baia Mare region. The major pollutant Pb shows a local distribution due to the fact that the lead smelter is located in the narrow valley of Firiza river and the atmospheric deposition is concentrated along the valley. The distribution maps for Cu, As, and Sb show very similar patterns with the highest values in the immediate surroundings of the smelters. Zn, Cr, and Cd demonstrate somewhat different patterns, but still pointing to local pollution sources. The maps presented in Fig. 4 show that major pollutants from the mining and smelting industry approach regional background levels within a distance of about 8 km from the main polluting sources.

In order to achieve a better resolution of contributions from different sources, the data set was subjected to factor analysis[11]. Five factors explaining 80% of the total variance can be distinguished (Table 3). Factor 1, comprising five major elements (Na, Mg, Al, Ti, Fe) and an additional number of trace elements (Sc, V, Cr, Cs, Ba, REE, Th) has the typical character of a crustal component. Such a component is frequently observed in deposition surveys based on the moss biomonitoring technique, and has been ascribed to windblown soil dust[12] in cases of extensive surveys in areas with low or moderate air pollution. In the present case this component with a crustal character appears to be mainly associated with the urban area, and predominantly with industrial activities. The map of Cr in Fig. 4d represents such a case The main contribution to factor1 have the collecting points number 1 and 4 (Fig.5). Factor 2, with high loadings for Cu, As, and Sb in addition to Pb seems to be a characteristic signature of emissions from the main lead smelter. The highest contribution to this factor have the points 12, 11, 17, 18, 21 (Fig.5). Similarly factor 4, with high loadings for Zn and Cd, appears to represent a distinctly different industrial source. Collecting points number 23, 21 and 25 contribute significantly to this factor. Factor 3, with high loadings for Cl and Br, seems more difficult to interpret. The presence of Ca in this factor however may suggest that it represents the use of calcium chloride to reduce the dust problem from gravel roads during the dry season.
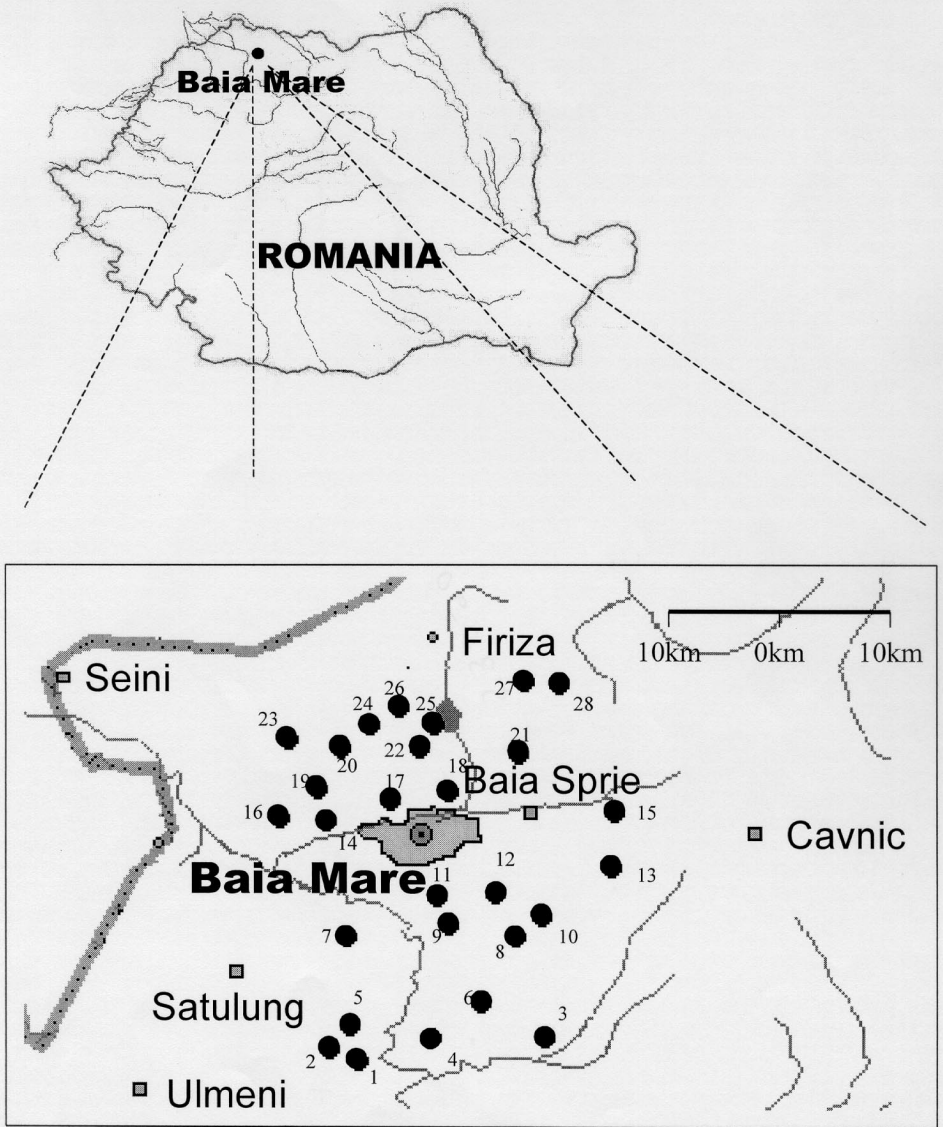
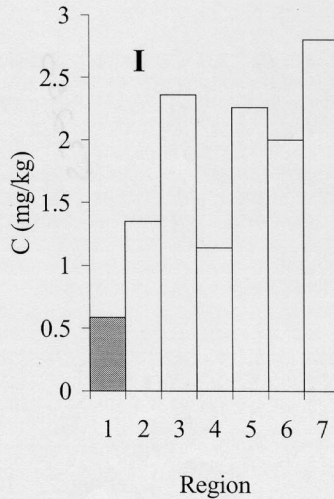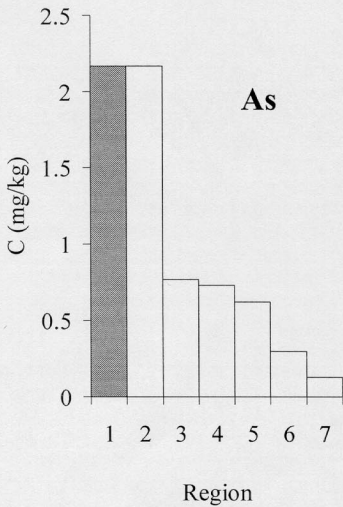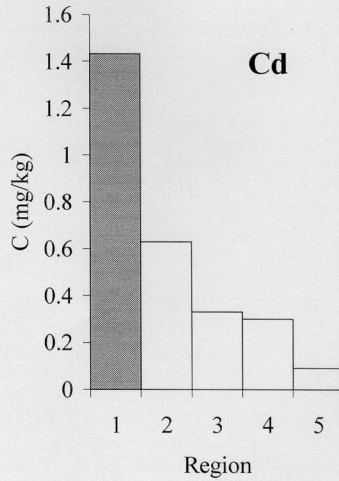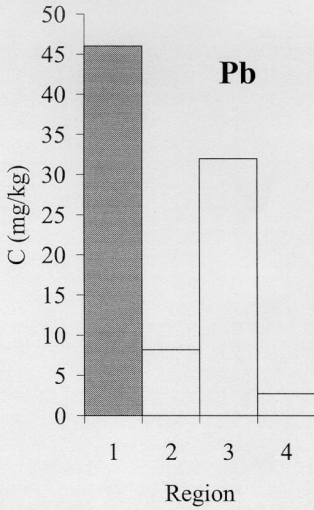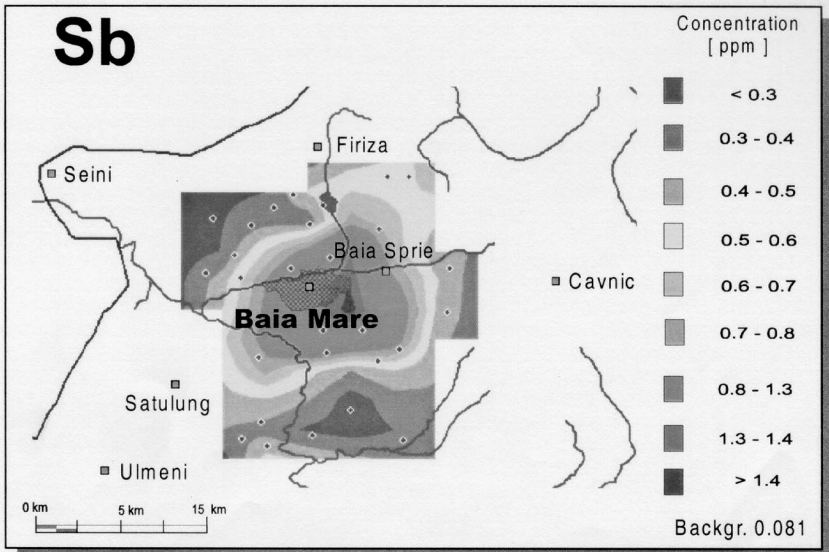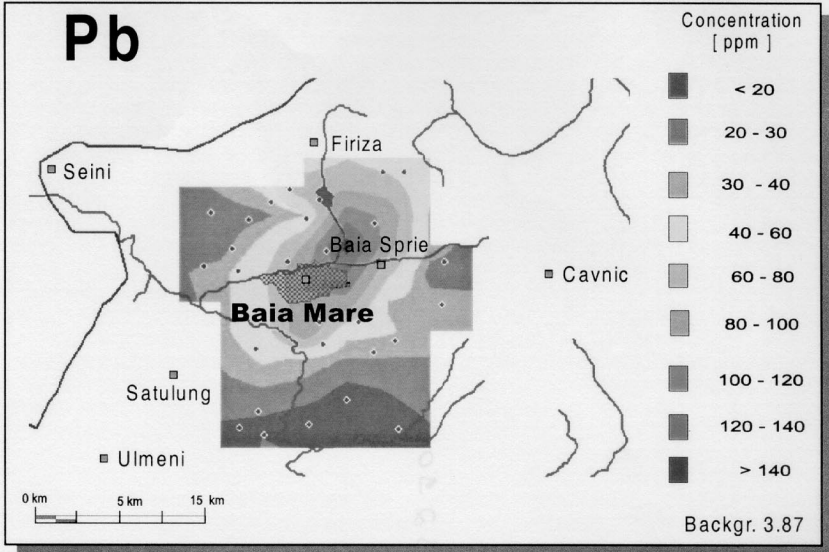*Fig.1.* Map of the Baia Mare region showing the sampling sites.

Fig. 2. Comparison of present results with concentration levels in moss from selected sites in Europe investigated by the authors: 1 - Baia Mare; 2 - Karabash, South Ural Mountains (copper smelter); 3 - Tula, central Russia (mixed industry); 4 - «Copper Basin», Poland; 5 - Mo, northern Norway (ferro-alloy smelters); 6 - Median value, Norway 2000.

Pb

Seini

Firiza

Baia Sprie

Baia Mare

Cavnic

Satulung

Ulmeni

0 km   5 km   15 km

Concentration [ppm]

< 20
20 - 30
30 - 40
40 - 60
60 - 80
80 - 100
100 - 120
120 - 140
> 140

Backgr. 3.87

Sb

Seini

Firiza

Baia Sprie

Baia Mare

Cavnic

Satulung

Ulmeni

0 km   5 km   15 km

Concentration [ppm]

< 0.3
0.3 - 0.4
0.4 - 0.5
0.5 - 0.6
0.6 - 0.7
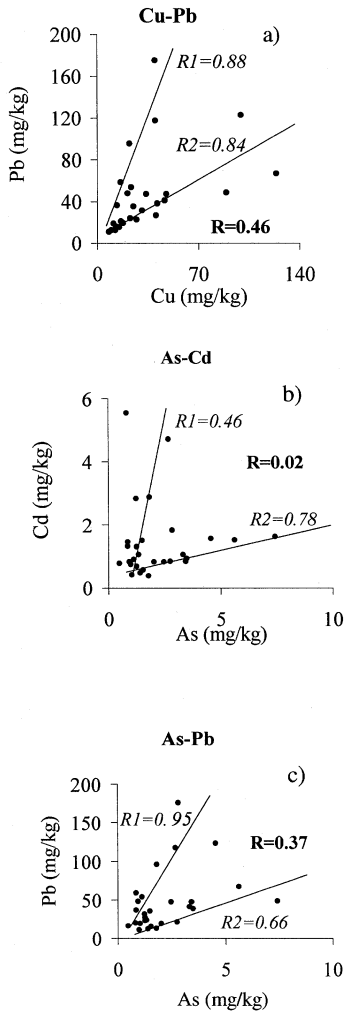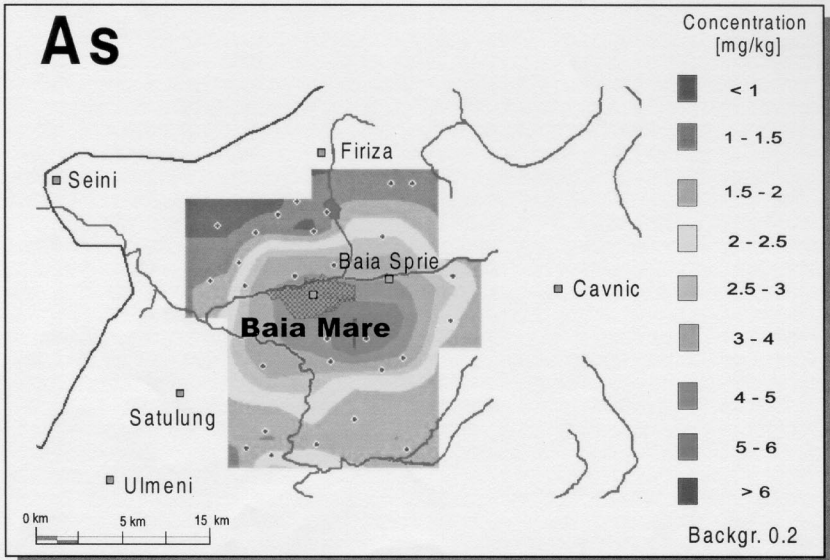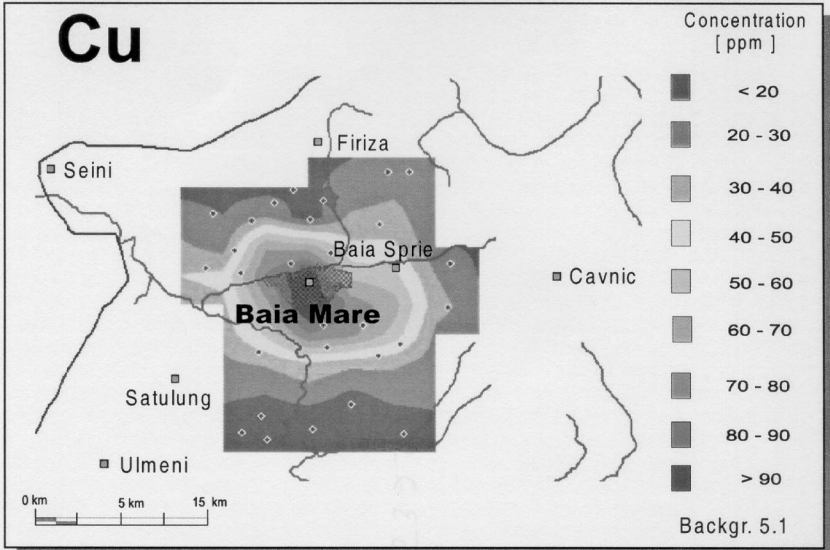0.7 - 0.8
0.8 - 1.3
1.3 - 1.4
> 1.4

Backgr. 0.081

Fig. 3. Correlation graphs of Cu *versus* Pb (a), As *versus* Cd (b), and As *versus* Pb (c) in moss.

Cu

Concentration [ppm]	
	< 20
	20 - 30
	30 - 40
	40 - 50
	50 - 60
	60 - 70
	70 - 80
	80 - 90
	> 90

Firiza

Seini

Baia Sprie

Cavnic

Baia Mare

Satulung

Ulmeni

0 km   5 km   15 km

Backgr. 5.1

As

Concentration [mg/kg]	
	< 1
	1 - 1.5
	1.5 - 2
	2 - 2.5
	2.5 - 3
	3 - 4
	4 - 5
	5 - 6
	> 6

Firiza

Seini

Baia Sprie

Cavnic

Baia Mare

Satulung

Ulmeni

0 km   5 km   15 km

Backgr. 0.2

Zn

Concentration [ppm]

■	< 50
■	50 - 60
■	60 - 70
■	70 - 80
■	80 - 90
■	90 - 100
■	100 - 150
■	150 - 200
■	> 200

Seini
Firiza
Baia Sprie
Cavnic
Baia Mare
Satulung
Ulmeni

0 km   5 km   15 km

Backgr. 39.3

Cd

Concentration [ppm]

■	< 0.5
■	0.5 - 0.8
■	0.8 - 1.1
■	1.1 - 1.4
■	1.4 - 1.7
■	1.7 - 2.0
■	2.0 - 4.0
■	4.0 - 5.0
■	> 5.0

Seini
Firiza
Baia Sprie
Cavnic
Baia Mare
Satulung
Ulmeni

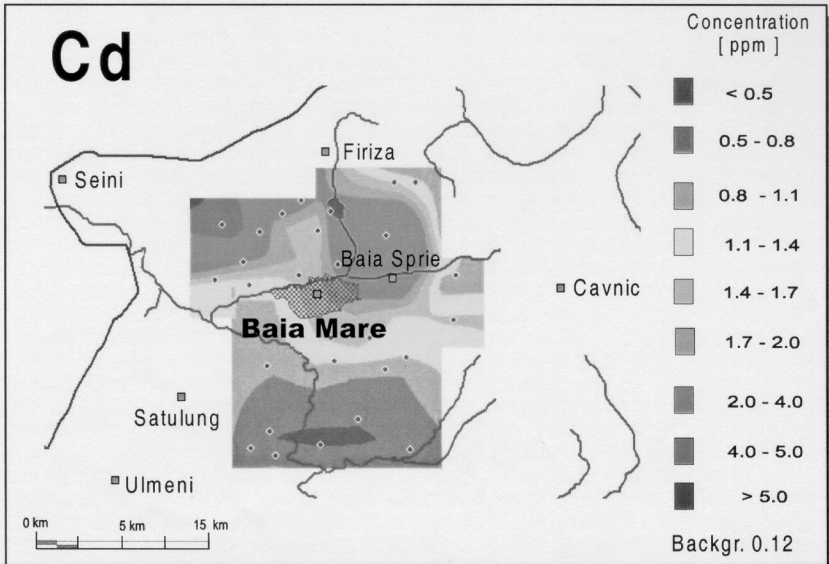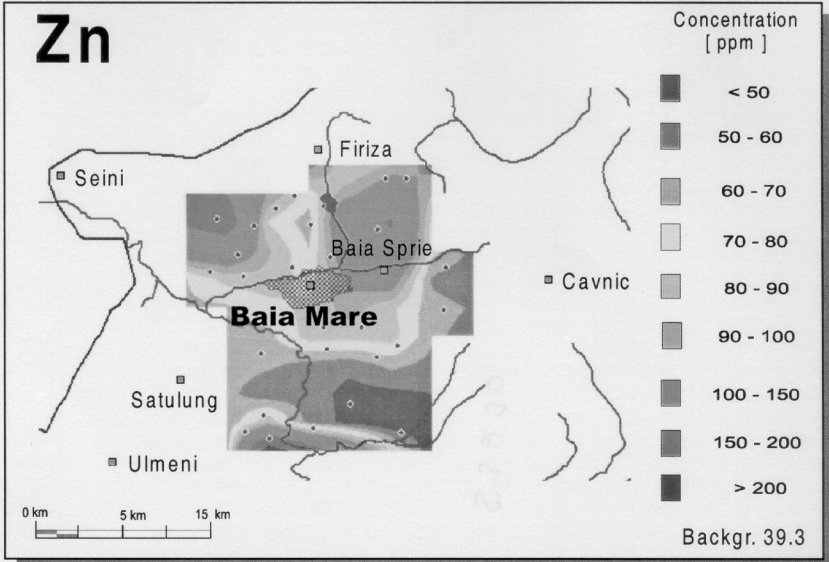0 km   5 km   15 km

Backgr. 0.12

Table 2. Mean, median, minimum and maximum values (in mg/kg)
of 31 elements in moss samples from Baia Mare

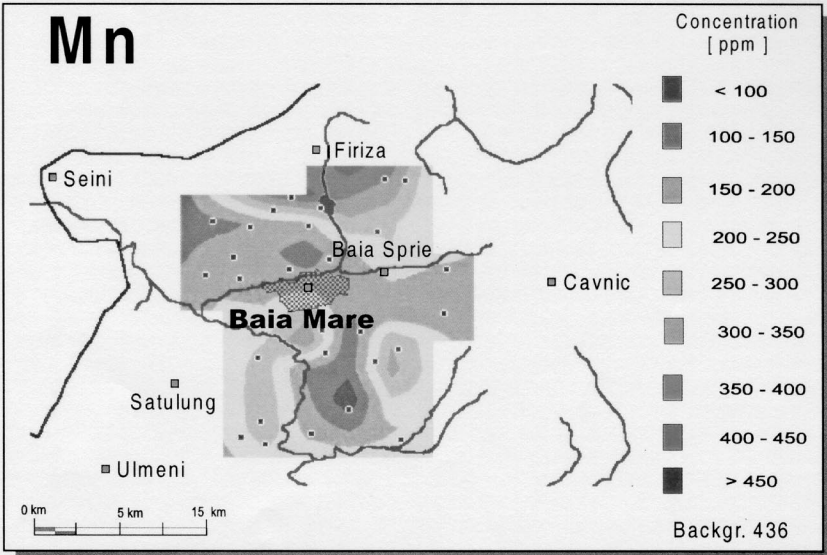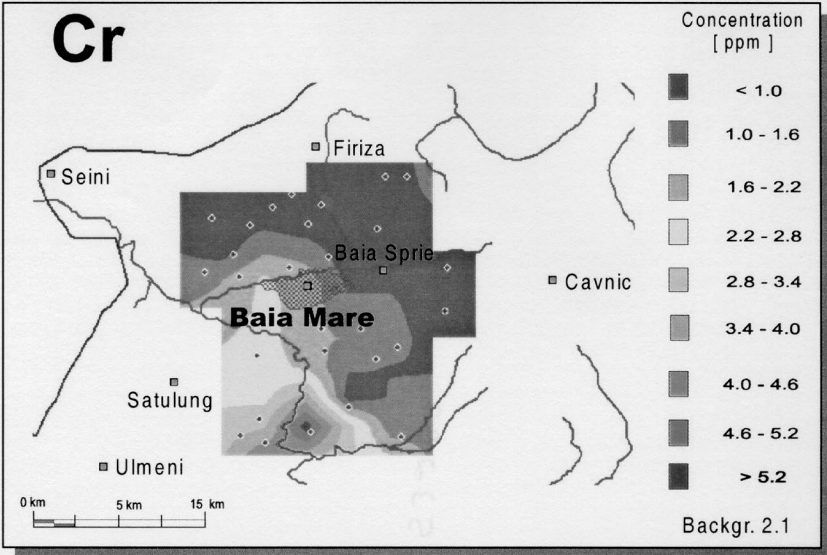| Element	Na	Mg	Al	Cl	K	Sc	Ca	Ti
Mean	432	1629	2427	395	11160	0.404	4896	26
Median	328	1544	2015	341	11300	0.287	4503	18
Min	158	758	681	100	5000	0.037	2120	4
Max	1863	3232	7204	1795	17410	2.276	9798	119
Element	V	Cr	Mn	Ni*	Fe	Co	Cu*	Zn
Mean	5.18	1.475	222	1.96	1032	5.91	33	86
Median	3.82	1016	206	1.47	937	5.18	23	68
Min	1.65	0.5	40	0.77	338	0.4	8	37
Max	16.7	6.28	505	5.68	4956	14.36	124	237
Element	Se	As	Br	Rb	Cd*	Sb	I	Ba
Mean	0.431	2.17	1.67	52	1.43	0.56	0.59	43
Median	0.401	1.51	1.33	44	0.98	0.396	0.50	39
Min	0.09	0.48	0.41	16	0.37	0.183	0.50	17
Max	1.192	7.42	9.46	166	5.54	1.66	0.94	105
Element	Cs	La	Ce	Eu	Sm	Th	Pb*	
Mean	0.262	1.395	1.959	0.022	0.179	0.303	46	
Median	0.189	1.029	1.305	0.012	0.130	0.196	36	
Min	0.068	0.337	0.3	0.012	0.052	0.035	11	
Max	0.911	6.08	7.416	0.097	0.491	1.5	175	

* determined by FAAS

Table 3. Rotated factor matrix for moss samples from Baia Mare. Loadings and explained variance for the first 5 factors are listed.
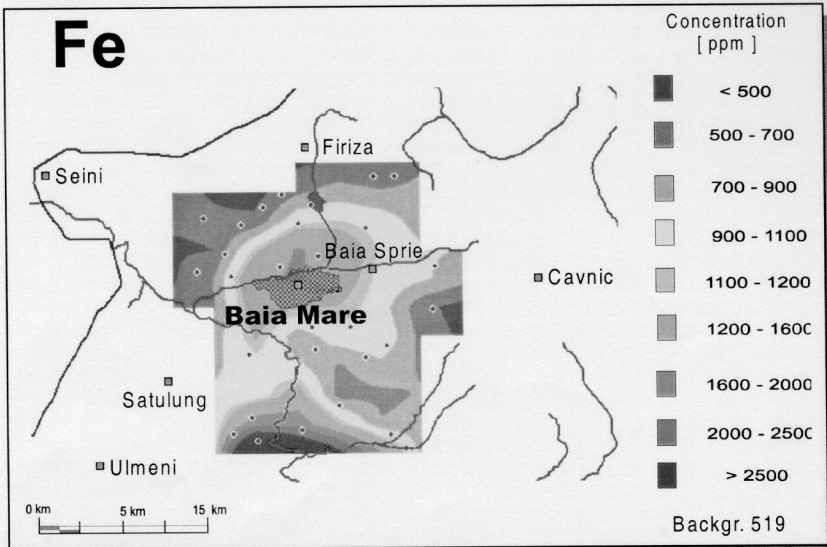
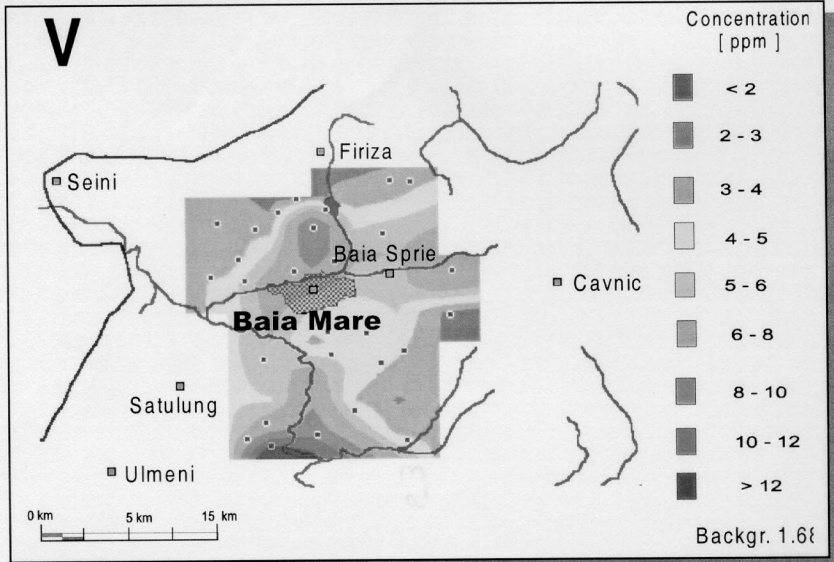| Component	1	2	3	4	5
% of Variance	*37.40*	*13.90*	*10.30*	*7.20*	*5.30*
Na	**0.80**	-0.19	0.38	0.23	0.04
Mg	**0.75**	0.06	0.32	0.14	0.44
Al	**0.78**	-0.05	0.35	-0.01	0.29
Cl	-0.01	-0.10	**0.87**	-0.13	0.24
K	0.23	0.35	0.16	0.23	0.47
Sc	**0.91**	0.00	0.14	0.16	0.15
Ca	0.27	0.24	**0.58**	0.04	**0.65**
Ti	0.91	-0.11	-0.12	0.05	0.11
V	**0.78**	0.01	0.41	0.07	0.29
Cr	**0.87**	-0.05	-0.17	-0.16	0.14
Mn	0.00	0.09	-0.05	0.03	**-0.78**
Ni	0.49	0.29	0.02	-0.05	-0.29
Fe	**0.90**	0.13	0.09	0.19	0.14
Co	0.32	0.19	0.38	0.00	-0.10
Cu	-0.06	**0.86**	-0.14	-0.05	0.19
Zn	0.35	0.07	0.01	**0.82**	-0.02
Se	-0.32	**0.75**	0.13	0.24	-0.12
As	0.19	**0.89**	-0.13	-0.04	0.25
Br	0.02	0.03	**0.93**	-0.01	-0.04
Rb	-0.07	0.01	0.10	0.47	**-0.57**
Cd	-0.29	0.13	0.07	**0.79**	0.18
Sb	0.04	**0.88**	0.08	0.13	-0.12
I	0.14	0.12	-0.20	0.48	-0.05
Ba	**0.54**	0.05	-0.06	0.57	-0.16
Cs	**0.53**	0.09	0.04	0.26	-0.04
La	**0.98**	-0.01	0.00	0.04	-0.03
Ce	**0.95**	-0.05	0.04	-0.04	-0.05
Eu	**0.85**	-0.29	0.07	0.06	0.04
Sm	**0.70**	0.22	-0.02	-0.07	-0.21
Th	**0.97**	-0.05	-0.11	0.09	0.04
Pb	-0.13	**0.68**	0.25	0.34	-0.23

Extraction Method: Principal Component Analysis
Rotation Method: Varimax with Kaiser Normalization
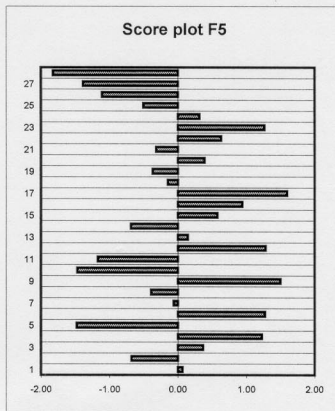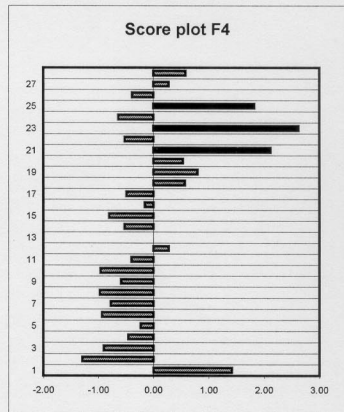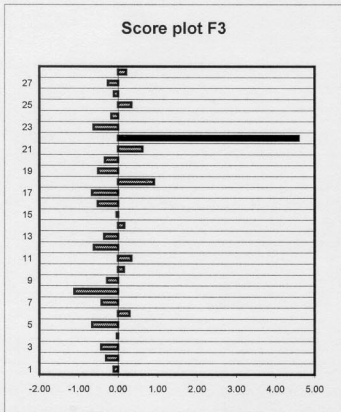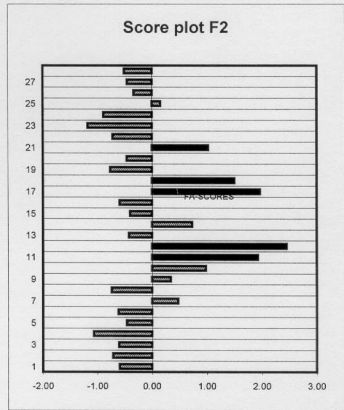Rotation converged in 7 iterations

Cr — Concentration [ppm]

	< 1.0
	1.0 - 1.6
	1.6 - 2.2
	2.2 - 2.8
	2.8 - 3.4
	3.4 - 4.0
	4.0 - 4.6
	4.6 - 5.2
	> 5.2

Seini, Firiza, Baia Sprie, Cavnic, Baia Mare, Satulung, Ulmeni

0 km 5 km 15 km

Backgr. 2.1

Mn — Concentration [ppm]

	< 100
	100 - 150
	150 - 200
	200 - 250
	250 - 300
	300 - 350
	350 - 400
	400 - 450
	> 450

Seini, Firiza, Baia Sprie, Cavnic, Baia Mare, Satulung, Ulmeni

0 km 5 km 15 km

Backgr. 436

Concentration [ppm]

	< 2
	2 - 3
	3 - 4
	4 - 5
	5 - 6
	6 - 8
	8 - 10
	10 - 12
	> 12

V

Seini
Firiza
Baia Sprie
Cavnic
Baia Mare
Satulung
Ulmeni

0 km   5 km   15 km

Backgr. 1.68

Concentration [ppm]

	< 500
	500 - 700
	700 - 900
	900 - 1100
	1100 - 1200
	1200 - 1600
	1600 - 2000
	2000 - 2500
	> 2500

Fe

Seini
Firiza
Baia Sprie
Cavnic
Baia Mare
Satulung
Ulmeni

0 km   5 km   15 km

Backgr. 519

Fig.5. Plots of factor scores for moss samples

Ni

Concentration [ppm]

■	< 1
■	1 - 1.5
■	1.5 - 2
■	2 - 2.5
■	2.5 - 3
■	3 - 3.5
■	3.5 - 4
■	4 - 4.5
■	> 4.5

Seini Firiza Baia Sprie Cavnic **Baia Mare** Satulung Ulmeni

0 km   5 km   15 km

Backgr. 1.9

Se

Concentration [ppm]

■	< 0.1
■	0.1 - 0.2
■	0.2 - 0.3
■	0.3 - 0.4
■	0.4 - 0.5
■	0.5 - 0.6
■	0.6 - 0.7
■	0.7 - 0.8
■	> 0.8

Seini Firiza Baia Sprie Cavnic **Baia Mare** Satulung Ulmeni

0 km   5 km   15 km
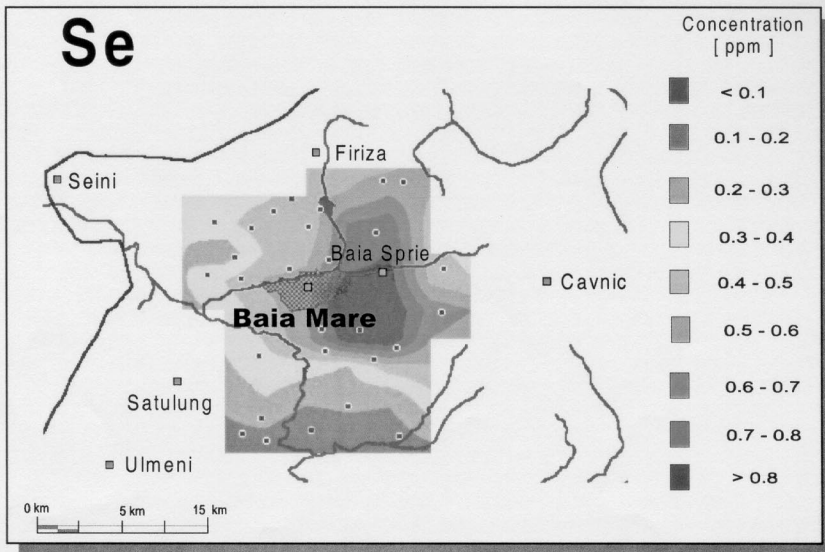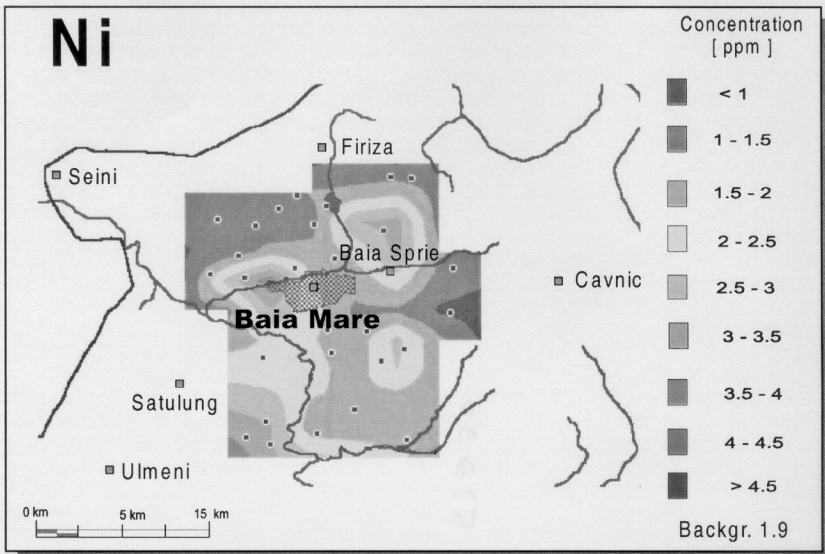
Some elements tend to occur in mosses in concentrations far higher than would be possible if atmospheric deposition was the only source.[12] This mainly concerns elements that are essential to the moss, such as K, Ca, and Mn. In spite of the fact that the moss lacks a root system it is able to absorb these elements in relatively large quantities, either from leaching of higher plants or from the substrate on which it grows. Factor 5 seems to represent this group of elements, showing negative values for Mn and Rb, and positive for Ca. This could be associated with cation exchange competition on the moss surface. In areas with a higher dust load Ca^{++} dissolved from dust particles may displace Mn^{++} and Rb^{+}. A similar phenomenon is observed in areas with a strong marine gradient where Mg^{++} and Na^{+} from sea-spray are supplied with precipitation and strongly reduce the Mn content of the moss[12].

Baia Mare is considered to be one of the main "hot spots" of heavy metal pollution in Romania. Although the present investigation is far from clearing up all aspects of metal pollution in this region, it adds substantially to the existing knowledge about the character and extent of the atmospheric supply of heavy metals to the town of Baia Mare and the surrounding local environment.

<center>*</center>
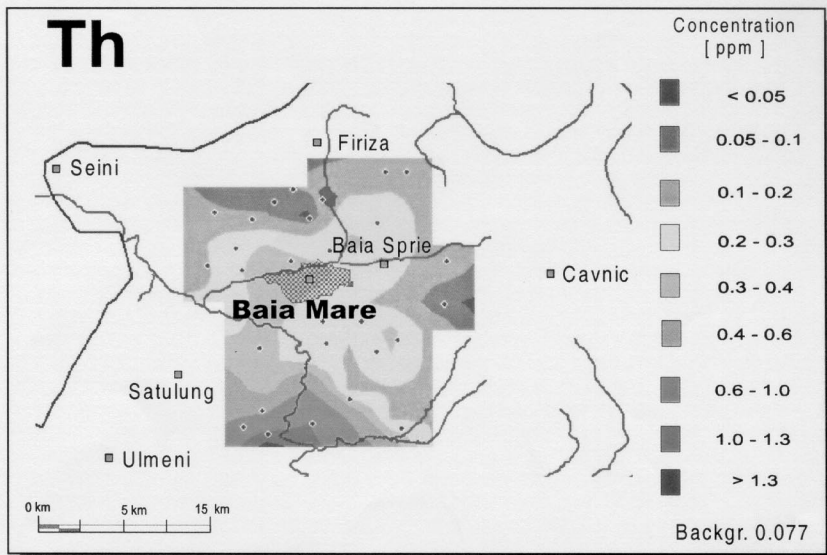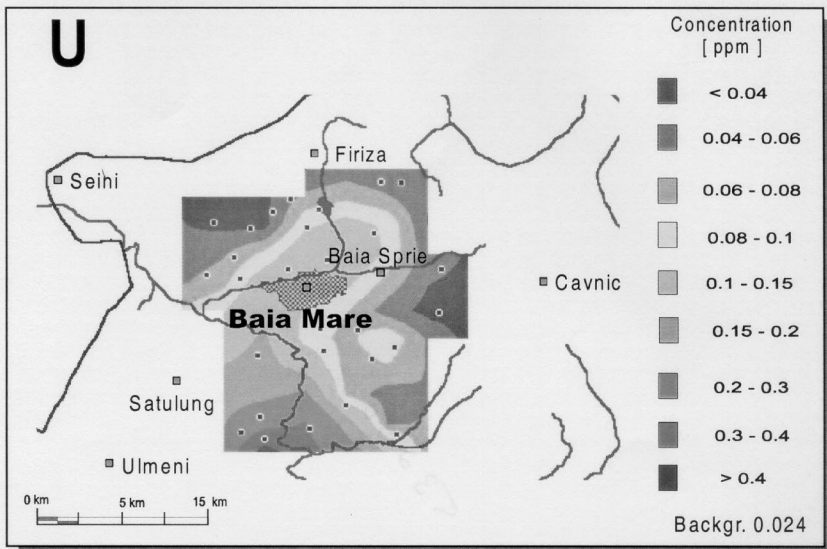
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Куликов О. А. и др. E14-2002-102

Изучение атмосферных выпадений тяжелых металлов в районе свинцового и медно-цинкового комбинатов в Бая-Маре, Румыния, с помощью мхов-биомониторов, нейтронного активационного анализа и пламенной атомной абсорбционной спектрометрии

Мхи *Pleurozium schreberi*, *Pseudoscleropodium purum* и *Rhytidiadelphus squarrosus* использовались как биомониторы для изучения атмосферных выпадений тяжелых металлов в районе свинцового и медно-цинкового комбинатов в Бая-Маре. Образцы, представляющие собой три последних годовых сегмента прироста мхов, или их зеленой части, были собраны с 28 площадок пробоотбора, расположенных в 2–17 км от источников обследования. Элементный состав образцов определялся с помощью эпитеплового нейтронного активационного анализа и пламенной атомной абсорбционной спектрометрии. В целом был определен 31 элемент, включая большинство тяжелых металлов, типичных для данных видов производств. Концентрации Pb, As, Cu и Cd являются самыми высокими в Европе для сходных производств, но уже на расстоянии 8 км от источников загрязнения они сравнимы с региональным фоном. Факторный анализ позволил выделить два «промышленных» компонента: первый — Pb, Cu, As и Sb и второй — Zn и Cd. Сильный компонент, включающий пять макроэлементов (Na, Mg, Al, Ti, Fe) и, кроме того, следовые элементы (Sc, V, Cr, Cs, Ba, REE, Th), по-видимому, также связан с промышленным производством. Концентрации йода в данном экспериментальном материале в пять раз ниже фоновой концентрации йода в норвежских мхах и систематически ниже всех известных европейских значений. Это свидетельствует об эндемичности (обеднении) исследуемой территории по йоду.

Culicov O. A. et al. E4-2002-102

Atmospheric Deposition of Heavy Metals around the Lead and Copper-Zinc Smelters in Baia Mare, Romania, Studied by the Moss Biomonitoring Technique, Neutron Activation Analysis and Flame Atomic Absorption Spectrometry

The mosses *Pleurozium schreberi*, *Pseudoscleropodium purum* and *Rhytidiadelphus squarrosus* were used as biomonitors to study the atmospheric deposition of heavy metals around the lead and copper-zinc smelters in Baia Mare. Samples representing the last three years' growth of moss or its green part, collected on the ground at 28 sites located 2–17 km from the source area, were analyzed by instrumental neutron activation analysis using epithermal neutrons and by flame atomic absorption spectrometry. A total of 31 elements were determined, including most of the heavy metals characteristic of emissions from this kind industry. The observed data for Pb, As, Cu, and Cd are all high compared with those observed in other regions of Europe with similar industries, but the concentrations in moss approach regional background levels at a distance of about 8 km from the main source area. Factor analysis of the data distinguishes two industrial components, one characterized by Pb, Cu, As, and Sb, and another one by Zn and Cd. A strong crustal component including five major elements (Na, Mg, Al, Ti, Fe) and an additional number of trace elements (Sc, V, Cr, Cs, Ba, REE, Th) also appears to be derived mainly from industrial sources. The mean I value in the present material is 5 times lower than the corresponding level in moss in Norway, and also consistently lower than elsewhere in Europe, a fact which evidence the endemic character of the examined area due to iodine depletion.