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AIR POLLUTION STUDIES IN BULGARIA USING THE MOSS BIOMONITORING TECHNIQUE, NAA AND AAS

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Маринова С. и др. E18-2009-53
Изучение загрязнений воздуха в Болгарии с использованием метода
мхов-биомониторов, НАА и ААС

Метод мхов-биомониторов использовался для изучения атмосферных выпадений следовых элементов в четырех районах Болгарии (западные и восточные Родопы, юго-восток и север-центр) в рамках европейской программы одновременного сбора мхов-биомониторов. Методом инструментального эпитеплового нейтронного активационного анализа (НАА) и атомной абсорбционной спектроскопии (ААС) были определены концентрации 41 элемента (Na, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rd, Sr, Mo, Cd, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Tb, Dy, Tm, Yb, Hf, Ta, W, Au, Pb, Th и U) в 97 образцах наземных мхов. В основном преобладали мхи вида *Hypnum cupressiforme*. Анализ главных компонентов (факторный анализ) использовался для идентификации и получения характеристик различных источников загрязнения и наиболее загрязненных точек в исследуемых областях. Интерпретация результатов факторного анализа позволила выделить природный компонент земной коры, морскую и растительную составляющие, а также источники антропогенного происхождения: сталелитейную (Пловдив, Хасково) и цветную (Пловдив, Карджали, Бургас) металлургию; нефтеперерабатывающие предприятия (Бургас) и центральные теплостанции (Пловдив, Хасково, Стара-Загора, Бургас). Сравнение медиан концентраций элементов во мхах, собранных в Болгарии, с концентрациями элементов во мхах, собранных на Балканах и в других странах Европы, свидетельствует о значительно более высоких концентрациях большинства элементов в образцах мха на Балканах, чем в других европейских странах, где проводился сбор мхов-биомониторов.

Работа выполнена в Лаборатории нейтронной физики им. И. М. Франка, ОИЯИ, в Пловдивском университете им. Паисия Хилендарски и в Институте ботаники БАН, София, Болгария.

Препринт Объединенного института ядерных исследований. Дубна, 2009

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Air Pollution Studies in Bulgaria Using the Moss Biomonitoring Technique, NAA and AAS

The moss biomonitoring technique was used to study trace element atmospheric deposition in four areas of Bulgaria (the western Thracian-Rhodope, the eastern Thracian-Rhodope, the south-eastern and the northern central regions) during the European moss survey in 2005. A total of 41 elements (Na, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rd, Sr, Mo, Cd, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Tb, Dy, Tm, Yb, Hf, Ta, W, Au, Pb, Th, and U) were determined by instrumental epithermal Neutron Activation Analysis (NAA) and Atomic Absorption Spectrometry (AAS) in 97 samples of terrestrial moss. The moss species used was *Hypnum cupressiforme*. Principal component analysis (factor analysis) was used to identify and characterize different pollution sources and to point out the most polluted areas. The interpretation of the factor analysis findings points to natural crust, marine, and vegetation components as well as to anthropogenic sources: ferrous (Plovdiv, Haskovo) and non-ferrous industries (Plovdiv, Kardzhali, Burgas); oil refining (Burgas), and central heating stations (Plovdiv, Haskovo, Stara Zagora, Burgas). Comparison of the medians of the elemental concentrations in moss samples collected in Bulgaria with those in the Balkan and other European countries reveals that the Balkan countries show considerably higher concentrations of most elements in moss than observed in other European countries where moss sampling has been employed.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR, at the Plovdiv University «Paisii Hilendarski» and at the Institute of Botany, Bulgarian Academy of Sciences, Sofia, Bulgaria.

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INTRODUCTION

The moss technique [1, 2] first introduced in Scandinavia, has shown to be very suitable for studying the atmospheric deposition of trace elements. It is now being used as part of monitoring programs for air pollutants in most European countries [3]. Mosses have a rudimentary root system and readily take up elements from the atmosphere. The advantage of the method is in the simplicity of sample collection, although the determination of the species needs an experienced hand. Data from existing surveys of heavy metal concentrations in mosses is an invaluable resource for international negotiations on heavy metal pollution.

The data from moss surveys allow examination of both spatial and temporal trends in heavy metal deposition, and identification of areas where there is high deposition of heavy metals from long-range atmospheric transport and local sources. In the Republic of Bulgaria the study of air pollution from heavy metals and other toxic elements based on moss analysis was undertaken since 2000 within the framework of a Bulgarian–Russian collaboration, in order to assess the general situation regarding heavy metal pollution and to jointly report these results to the European Atlas of Heavy Metal Atmospheric Deposition issued by UNECE ICP Vegetation [4, 5].

The presence of heavy metals in air within the Bulgarian territory had been previously studied only for some geographic regions using neutron activation analysis (NAA) [6] and inductively coupled plasma emission spectrometry (ICP-AES) for determination of a limited number of elements [7–11]. The primary task of the present study was to elucidate the present-day environmental situation in the sampling areas and to compare the results obtained with existing data from the previous moss surveys in Bulgaria. Furthermore the biomonitoring results could serve the purpose of risk assessment of certain endemic diseases such as Balkan nephropathy, arsenosis, etc., which are hypothetically connected with the environmental contamination with toxic substances [12]. This approach is in line with the European trend in establishing correlation of the environmental biomonitoring with human health aspects [13].

STUDY AREA

The Republic of Bulgaria is located in the south-east part of Europe and in the central-east part of the Balkan Peninsula. The area of the country is 110 910 km^2, mostly in mountainous territories. Four regions: the western Thracian-Rhodope, the eastern Thracian-Rhodope, the south-eastern and the northern central, comprising around 25% of the whole territory of Bulgaria, were sampled in this study. The climate in most of this area is continental with very hot and dry summers. In areas along the Black Sea coast there is a Mediterranean climate. In summer temperatures in the south of Bulgaria often exceed 40 °C, and the highest temperature ever of 47 °C was recorded at a site near Plovdiv. At such climatic conditions only a limited number of moss species are able to grow in arid areas.

Industry plays a key role in the Bulgarian economy. Bulgaria is among the leading countries in Europe in production of lead, zinc, copper, caustic soda (NaOH), and nuclear energy. It possesses vast reserves of lignite, anthracite coal, and gold. Bulgaria has abundant non-metalliferrous minerals such as rock salt, gypsum, and marble. Ferrous metallurgy is of major importance. Much of the production of steel and pig iron takes place in Kremikovtsi and Pernik, with a third metallurgical base in Debelt. In production of steel and steel products per capita the country heads the Balkans. The largest refineries for lead and zinc operate in Plovdiv (the biggest refinery between Italy and the Ural Mountains), Kardzhali, and Novi Iskar; for copper in Pirdop and Eliseina; for aluminium in Shumen. Bulgaria ranks first in south-east Europe in production of many metals, measured per capita. About 14% of the total industrial production relates to machine-building, and 24% of the people work in this field. Electronics and electric equipment production have developed to a high degree. The largest industrial centres include Sofia, Plovdiv and the surrounding area, Botevgrad, Stara Zagora, Varna, Pravets and many other cities. These plants produce household appliances, computers, CDs, telephones, medical and scientific equipment. Many

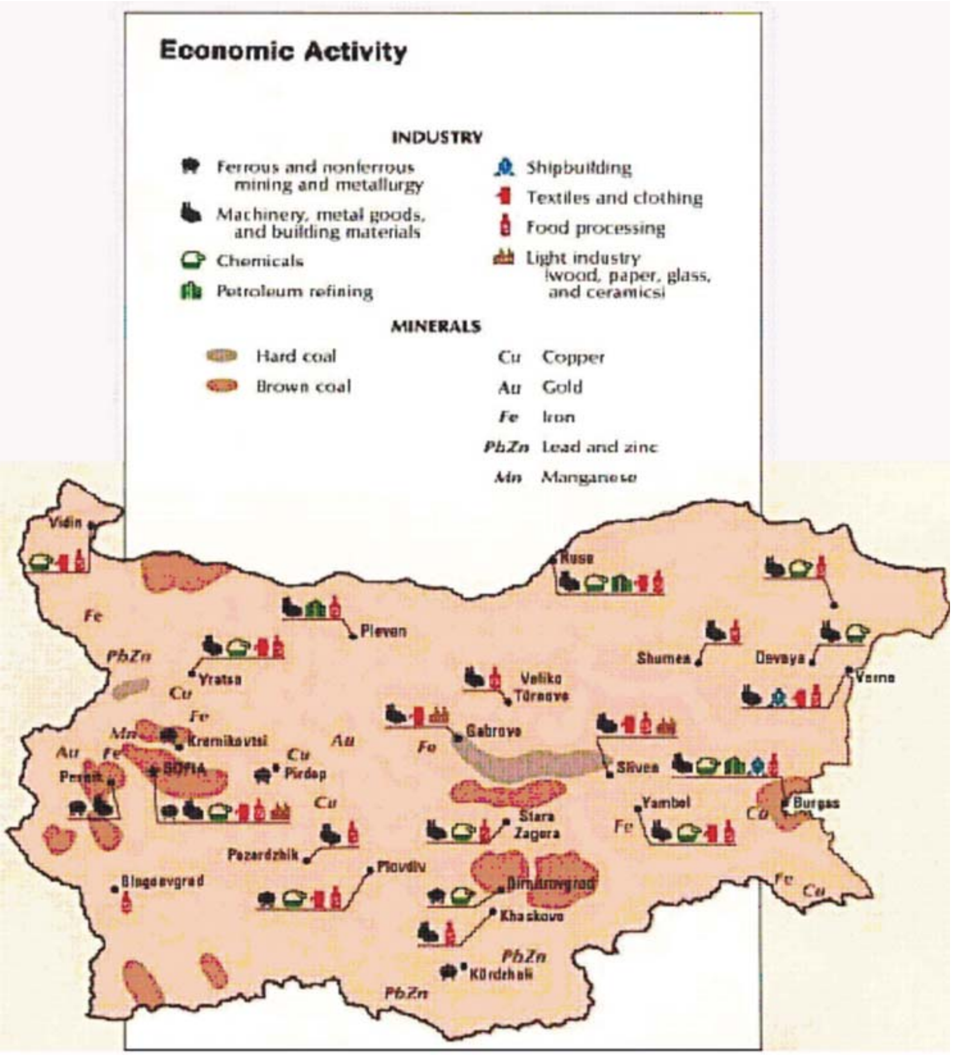

Fig. 1. The economic map of Bulgaria [14]

factories producing transportation equipment currently do not operate at full capacity. These factories produce trains (Burgas, Dryanovo), trams (Sofia), trolleys (Dupnitsa), buses (Botevgrad), trucks (Shumen), and motor trucks (Plovdiv, Lom, Sofia, Lovech). Lovech has an automotive assembly plant. Rousse serves as the main centre for agricultural machinery. Most Bulgarian shipbuilding takes place in Varna, Burgas and Rousse. Bulgarian arms production mainly operates in central Bulgaria (Kazanlak, Sopot, Karlovo). Foreigners seeking additional homes have recently boosted the Bulgarian properties market. Buyers come from across Europe, but mostly from the United Kingdom, encouraged by relatively low property prices and easy accessibility via air travel.

EXPERIMENTAL

Sampling. Samples of the moss species *Hypnum cupressiforme* were collected at 97 localities covering four geographic regions of the country during the period July–October, 2005. The sampling sites are shown on the map in Fig. 2.

The sampling was carried out in accordance with the strategy of the European moss survey program [5]. Samples were collected at a distance of at least 300 m from main roads, at least 100 m from roads and at least 200 m from villages, in forest glades or in open heath to reduce through-fall effects from the forest canopy. In order to make the moss samples representative for a reasonably large area, each sample was composed of five to ten subsamples collected within an area of 10 × 10 m. Collected samples were stored in paper bags. A separate set of disposable polyethylene gloves was used for collection of each sample.

Analysis. **NAA.** The neutron activation analysis (NAA) was performed at the pulsed fast reactor IBR-2 at the Frank Laboratory of Neutron Physics, Dubna, Russia.

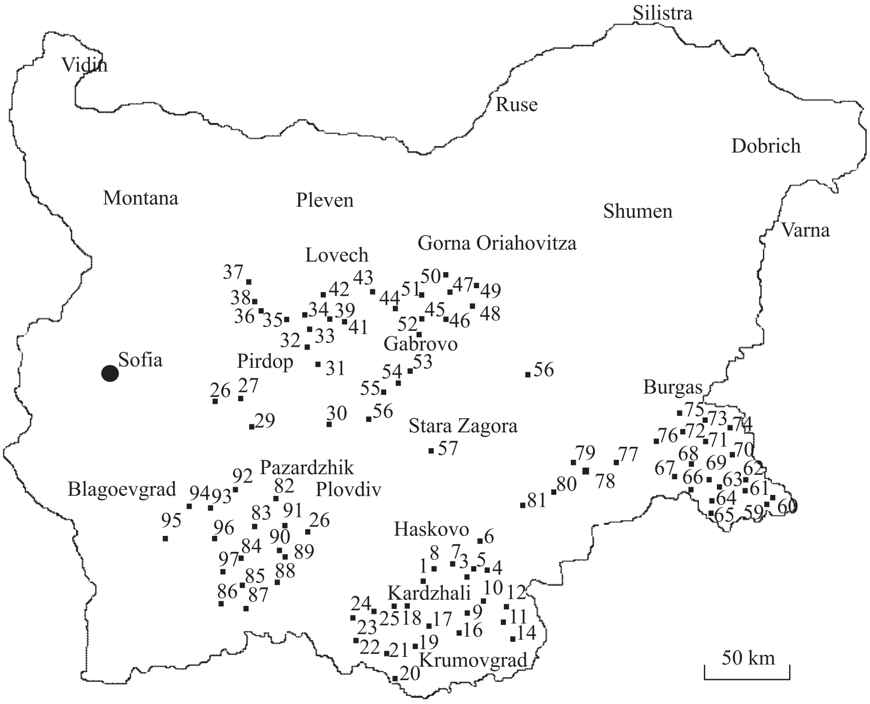

Fig. 2. Study area — Republic of Bulgaria [15]

Table 1. Flux parameters of irradiation positions [17]

Irradiation position	$\Phi_{\text{th}} \cdot 10^{12}$, $\text{n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ $E = 0 \div 0.55$ eV	$\Phi_{\text{th}} \cdot 10^{12}$, $\text{n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ $E = 0.55 \div 10^5$ eV	$\Phi_{\text{fast}} \cdot 10^{12}$, $\text{n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ $E = 10^5 \div 25 \cdot 10^6$ eV
Ch1 (Cd-screened)	0.023	3.3	4.2
Ch2	1.23	2.9	4.1

Table 2. List of selected peak energies for NAA

Element	Isotope	Half-life	Gamma-ray peak (keV)	Element	Isotope	Half-life	Gamma-ray peak (keV)
Na	^{24}Na	14.7 h	2753.6	Rb	^{86}Rb	18.7 d	1076.6
Al	^{28}Al	2.2 m	1778.9	Sr	^{85}Sr	64.8 d	514.0
Cl	^{38}Cl	37.2 m	2168.8	Mo	^{99}Mo	66.0 h	140.5
K	^{42}K	12.4 h	1524.7	Cd	^{115}Cd	53.5 h	527.7
Ca	^{49}Ca	8.7 m	3084.4	Sb	^{124}Sb	60.2 d	1691.0
Sc	^{46}Sc	83.8 d	889.2	I	^{128}I	25.0 m	442.9
Ti	^{51}Ti	5.8 m	320.1	Cs	^{134}Cs	2.1 y	795.8
V	^{52}V	3.8 m	1434.1	Ba	^{131}Ba	11.8 d	496.8
Cr	^{51}Cr	27.7 d	320.1	La	^{140}La	40.2 h	1596.5
Mn	^{56}Mn	2.6 h	1810.7	Ce	^{141}Ce	32.5 d	145.4
Fe	^{59}Fe	44.5 d	1099.2	Tb	^{160}Tb	72.3 d	879.4
Co	^{60}Co	5.3 y	1173.1	Hf	^{181}Hf	42.4 d	482.0
Ni	^{58}Co	70.9 d	810.8	Ta	^{182}Ta	114.4 d	1221.4
Zn	^{65}Zn	244.0 d	1116.0	W	^{187}W	23.9 h	685.8
As	^{76}As	26.3 h	559.1	Au	^{198}Au	2.7 d	411.8
Se	^{75}Se	119.8 d	264.7	Th	^{233}Pa	27.0 d	312.0
Br	^{82}Br	35.3 h	776.5	U	^{239}Np	2.4 d	228.2

At the laboratory the samples were cleaned from extraneous plant material and air-dried to constant weight at 30–40 °C for 48 h. The samples were not washed and not homogenized. Green-brown moss shoots representing the last three years' growth were subjected to analysis, as they correspond approximately to the deposition over the last three years. Previous experience from the use of NAA in moss biomonitoring employing *Hylocomium spelendens* has shown that samples of 0.3 g are sufficiently large to be used without homogenization [16]. The samples were pelletized before irradiation using simple press-forms. For short irradiation unwashed samples of about 0.3 g were heat-sealed in polyethylene bags. For long irradiation samples of the same weight (about 0.3 g) were packed in aluminium cups. Characteristics of neutron flux density in the channels equipped with a pneumatic system are given in Table 1.

Table 3. NAA data and recommended/certified values of reference materials, mg/kg

Element	DK-1 (determined)	DK-1 (recommended)	Lichen-336 (determined)	Lichen-336 (certified)
Na	303 ± 25	315 ± 31	304 ± 26	320 ± 40
Al	830 ± 84	810 ± 81	720 ± 65	680 ± 109
Cl	328 ± 35	328 ± 33	1927 ± 288	1900 ± 304
K	3350 ± 165	3300 ± 297	1910 ± 90	1840 ± 202
Ca	1604 ± 180	1630 ± 40	—	—
Sc	0.16 ± 0.02	0.16 ± 0.02	0.176 ± 0.014	0.17 ± 0.20
V	4.12 ± 0.31	3.8 ± 0.3	1.38 ± 0.19	1.47 ± 0.22
Cr	1.94 ± 0.15	1.7 ± 0.4	1.10 ± 0.17	1.06 ± 0.17
Mn	143 ± 10	120 ± 10	69 ± 5.1	63 ± 7
Fe	575 ± 53	550 ± 50	430 ± 8.5	430 ± 51
Co	0.26 ± 0.01	0.23 ± 0.01	0.303 ± 0.070	0.29 ± 0.05
Ni	1.58 ± 0.33	1.8 ± 0.2	—	—
Zn	30.8 ± 4.0	29 ± 2	28.2 ± 2.3	30.4 ± 3.3
As	0.64 ± 0.02	0.64± 0.02	0.54 ± 0.71	0.63 ± 0.08
Se	0.43 ± 0.04	0.43 ± 0.04	0.22 ± 0.033	0.22 ± 0.04
Br	13.5 ± 0.94	12.8 ± 1.0	14.2 ± 2.3	12.9 ± 1.6
Rb	12.9 ± 0.86	12.6 ± 0.9	1.7 ± 0.17	1.76 ± 0.22
Sr	15.1 ± 3.0	10 ± 0.1	11.4 ± 0.55	9.3 ± 1.1
Zr	11.0 ± 1.2	11 ± 1.2	—	—
Mo	0.21 ± 0.02	0.2 ± 0.02	—	—
Sb	0.347 ± 0.02	0.347 ± 0.02	0.078 ± 0.01	0.073 ± 0.0067
I	3.8 ± 0.07	3.8 ± 0.3	—	—
Cs	0.285 ± 0.02	0.30 ± 0.02	0.12 ± 0.024	0.110 ± 0.013
Ba	12.5 ± 0.12	12 ± 2	6.6 ± 0.7	6.4 ± 1.1
La	1.22 ± 0.34	1.22 ± 0.1	0.70 ± 0.06	0.66 ± 0.10
Ce	2.92 ± 0.53	2.92 ± 0.22	1.3 ± 0.25	1.28 ± 0.17
Sm	0.231 ± 0.05	0.231 ± 0.01	0.106 ± 0.06	0.106 ± 0.014
Tb	0.0218 ± 0.01	0.0216 ± 0.002	0.015 ± 0.002	0.014 ± 0.002
Hf	0.21 ± 0.06	0.21 ± 0.009	—	—
Ta	0.026 ± 0.005	0.026 ± 0.0036	—	—
W	0.73 ± 0.11	0.73 ± 0.21	—	—
Au	0.00074 ± 0.0014	0.00074 ± 0.00004	—	—
Th	0.16 ± 0.08	0.15 ± 0.0011	0.14 ± 0.01	0.14 ± 0.02
U	0.192 ± 0.02	0.192 ± 0.015	—	—

For determinations involving short-lived radionuclides samples were irradiated for 3 min. After irradiation two gamma-spectrometric measurements were performed; the first one for 5 min after 2–3 min of decay, and the second for 20 min after 9–10 min decay.

Determinations using long-lived radionuclides were performed following an irradiation for 100 h in the cadmium-screened channel 1. After irradiation samples were repacked into clean containers and gamma spectra were registered after 4–5 and 20–23 d for 45 min and for 3 h, respectively, as described elsewhere [18].

Table 2 lists selected peak energies for NAA and method of analysis. The gamma spectra of the induced activities were analyzed using software developed at the Frank Laboratory of Neutron Physics [19].

AAS. The environmentally important element lead cannot be determined by INAA, and cadmium and copper are difficult at low concentration levels. These elements were therefore determined by flame atomic absorption spectrophotometry (Perkin Elmer 303) with background correction and acetylene as fuel at the Institute of Botany, BAS, Sofia. About 1 g of the moss material was treated with 15 ml nitric acid (9.67 M) overnight. The wet-ashing procedure was continued by heating on a water bath, following by addition of 2 ml portions of hydrogen peroxide (30 %). This treatment was repeated until complete digestion. The filtrate was diluted with doubly distilled deionized water ($0.06\,\mu S\ \mathrm{cm}^{-1}$) to 25 ml. All solutions were stored in plastic flasks.

Quality Control. The quality of NAA results was ensured by simultaneous analysis of the examined samples and reference materials (RM) Lichen 336 IAEA (International Atomic Energy Agency) and NORD DK-1 (moss reference sample prepared for intercomparison in 1990). The NAA data and recommended/certified values of reference materials are given in Table 3. The quality control (QC) of AAS determinations was based on the standard addition method and it was found that the recovery of the investigated elements ranged between 98.5 and 101.2 %. Besides standard addition method, blanks parallel to the decomposition of samples and preparation of sample solutions for analysis were analyzed. Moreover the quality of the determinations was checked by simultaneous analysis of the moss reference materials M2 and M3 prepared in Finland for the European moss surveys. The obtained concentrations of Cu, Pb and Cd were in good agreement with the corresponding recommended values [20]. Deviations between duplicate sample solutions analyzed simultaneously was always below 5%.

RESULTS AND DISCUSSION

Median values and ranges of the elements studied are presented in Table 4 along with corresponding data from similar studies in the neighboring Balkan countries Macedonia, Romania, and Serbia [5, 19–21].

For comparison with a pristine territory corresponding data for northern Norway [22] are shown in the right-hand column. The Norwegian values were obtained by ICP-MS analysis and were based on nitric-acid solutions, potentially leaving out fractions of the elements in moss samples contained in silicate minerals (attached soil particles). The same argument may apply to the present AAS results.

Based on the data of Table 4 countries can be ranged according to the median values for each element. This presents a generally favourable picture for Bulgaria in comparison with the other three Balkan countries concerning elements predominantly of industrial origin. In comparison with the pristine northern Norway however the Bulgarian data are substantially higher for typical air pollution elements (V, Cr, As, Ag, Cd, Sb, Pb). The opposite is the case for halogens of presumed marine origin where the Norwegian data are higher. The Norwegian data are also much lower for elements that have been previously ascribed mainly to soil particles attached to the moss (Sc, Ti, Fe, REE, Th and U). In this case, the fact that INAA determines the whole content could be one factor contributing to this difference. For elements where the local microenvironment is known to be a more dominant source to the moss than atmospheric deposition (Mg, Ca, Mn, Rb, Sr, Cs, Ba, partly Zn) the Norwegian data are of the same order of magnitude as the Balkan values.

A similar comparison (cfr. Fig. 3) with data from the European Moss Atlas [4] reveals that the Balkan countries show considerably higher concentrations of most elements in moss than observed in other European countries where moss sampling has been employed. This simple comparison confirms that the East and the West of Europe differ greatly by the levels of many contaminants in the atmospheric deposition, and indicates that some eastern European countries still have a long way to go in order to bring their emissions down to a satisfactory level. The only exception in the west is Belgium where high levels of Cu, Cr, V and Zn in moss are explained by smelter emissions in this industrialized country.

The unfavorable air pollution situation may adversely affect not only the natural environment, but also human health. An environmental hypothesis suggests that endemic distributions of diseases directly correlate with the geographic patterns of soil deficiencies or excess of essential elements, which could be of natural or anthropogenic origin. Examples of adverse health in the Balkans associated with trace element deficiencies and excesses have been described in the literature [23]. For example, environmental chronic exposure to non-essential elements such as arsenic has been considered to possibly affect human health, given the fact that elevated concentrations of arsenic were observed in drinking water in some areas of Serbia (Zrenjanin), Romania (Baia Mare), and other Balkan countries.

Considering heavy metal atmospheric deposition in the Balkans specific geographical distribution patterns of several elements are evident. The highest median value for As (present data) were observed in Bulgaria, mainly connected with the mining and smelting of copper ores and coal combustion. Still the most severe metal pollution in Bulgaria comes from old iron mines and metallurgic plants (Cu, Fe, Cr, As, V, Zn).

Multivariate statistical analysis (factor analysis) was used to identify and characterize different pollution sources and to point out the most polluted areas. Factor analysis is a multivariate technique for reducing matrices of data to their lowest dimensionality by the use of orthogonal factor space and transformations that yield predictions and/or recognizable factor [27]. Values of the five factors are given in Table 5.

Factor scores representing the contributions of individual sampling sites to the relevant factor are given in Fig. 4. Five identified factors are interpreted as follows:

Factor 1 has particularly high values of Na, Al, Sc, Ti, Cr, Fe, Co, Ni, As, Rb, Sr, Cs, Ba, W, U, and REEs (rare-earth elements). Most of these elements are typical for crustal material, and most probably this component at least partly reflects the contamination of moss samples with soil particles. Another possible source could be fly-ash particles resulting from high-temperature processes such as coal burning, which may have a major element composition similar to crustal material.

Table 4. Comparison of the results obtained in the present study (mg/kg) with other Balkan countries and a pristine area (northern Norway)

	Bulgaria		Bulgaria		Macedonia		Romania		Northern Serbia		Northern Norway	
	(Present work)		(West and South) [6, 8]*		[21]		(Transilvania) [24]		[25]		[22]	
No. of samples	*99*		*103*		*73*		*70*		*92*		*100*	
Element	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
Na	725	189-8210	523	155-5580	419	118-8670	902	192-4330	694	178-2440	–	–
Al	6930	1532-43600	3840	1110-46400	3740	825-17600	5550	830-23000	6800	1280-22100	200	67-820
Cl	232	84-1330	161	59-1180	149	43-693	370	160-1300	256	105-1030	–	–
K	6020	2750-13800	5760	3270-20500	8620	2860-18200	7770	4770-20000	5090	2710-11800	–	–
Ca	8960	4530-32200	7280	2270-19700	5590	1210-23640	5770	1250-23500	7720	2890-18120	2820	1680-5490
Sc	0.92	0.21-7.20	0.65	0.2-6.4	0.81	0.12-6.79	0.94	0.21-6.13	1.31	0.27-4.13	0.052	0.009-0.220
Ti	340	94-2590	–	–	163	12-1370	–	–	71	11-297	23.5	12.4-66.4
V	8.7	2.23-64	8.4	2.2-113	6.9	1.79-43	8.7	1.95-32	11	2.85-39	0.92	0.39-5.1
Cr	5.6	1.18-55	3.2	0.5-26.9	7.47	2.33-122	13.8	2.72-51.9	6.51	1.14-22	0.55	0.10-4.2
Mn	243	45-1270	251	32-986	186	37-1480	265	27-1470	217	30-2340	256	22-750
Fe	3000	689-19400	2310	692-14700	2460	424-17380	3290	815-21340	3110	720-9230	209	77-1370
Co	1.49	0.35-28	1.08	0.23-10.6	1.09	0.24-13.6	1.41	0.32-7.0	8.24	1.42-39	0.202	0.065-0.654
Ni	5	1.08-29	4.1	0.5-18.6	2.4	0.09-24	5.4	0.6-32	6.73	1.96-26	1.14	0.12-6.6
Cu*	6.84	0.1-63.9	14.5*	5.34-1860	22	3-83	21.5	2.21-2420	16.9	6.31-3140	3.6	2.1-9.2
Zn	45	23-774	41	19-379	39	14-203	135	39-2950	44	14-415	26.5	7.9-173
As	0.97	0.27-8.76	1	0.3-59.0	0.8	0.12-8.0	2.2	0.59-45.1	3.35	0.46-61	0.093	0.020-0.505
Se	1.31	0.09-4.71	0.24	0.01-1.18	0.18	0.013-0.61	0.36	0.08-5.01	0.39	0.046-10	0.33	0.05-1.30
Br	4.4	1.33-18	3.6	1.1-11.6	2.16	0.06-7.7	8.6	2.03-20.9	5.75	1.83-18.0	4.5	1.4-20.3
Rb	15	5.16-68	12	3.0-69	10.9	5.0-87	15	5.8-135	13	17200	7.7	1.3-51.5
Sr	36	14-170	25	7-106	31	11.8-136	37.4	1.8-290	22	34900	15.8	3.6-43.3
Mo	0.37	0.01-1.22	0.99	0.16-3.36	0.19	0.03-1.12	0.65	0.13-10	0.85	0.12-23	0.135	0.065-0.70
Cd*	0.23	$< 0.1 - 5.56$	–	–	0.16	0.016-2.95	–	–	0.4	0.4-6.5	0.058	0.025-0.171
Sb	0.29	0.07-8.7	0.23	0.07-20.2	0.2	0.039-1.4	0.88	0.16-51	0.52	0.13-7	0.033	0.004-0.240
I	2.6	0.85-6.31	1.4	0.6-4.4	1.18	0.36-2.8	2.17	0.76-5.55	2.09	0.87-4	2.5	0.6-41.7
Cs	0.52	0.18-5.71	0.4	0.10-2.96	0.39	0.097-1.7	0.51	0.12-3.4	0.76	0.11-18.2	0.072	0.016-0.88
Ba	79	21-294	68	17-517	54	14-256	101	20-658	39	13-130	17.1	5.6-50.5
La	3.3	1-61.79	2.9	0.8-23.7	2.32	0.50-22	2.4	0.4-15.2	4.66	41518	0.189	0.045-2.56
Ce	6.8	1.75-143	–	–	5.6	0.83-42	6.1	0.9-42.5	9.2	1.84-28	0.342	0.095-4.61
Nd	3.15	0.01-47	–	–	–	–	–	–	–	–	–	–
Sm	0.6	0.19-8.30	–	–	–	–	–	–	–	–	–	–
Tb	0.076	0.02-0.98	0.068	0.016-0.610	0.06	0.01-0.56	0.07	0.01-0.42	0.11	0.02-0.36	0.003	0.002-0.030
Dy	0.43	0.01-4.40	–	–	–	–	–	–	–	–	–	–
Tm	0.057	0.02-0.67	–	–	–	–	–	–	–	–	–	–
Yb	0.22	0.05-3.32	–	–	–	–	–	–	–	–	–	–
Hf	0.45	0.11-12.1	0.46	0.11-4.78	0.26	0.05-3.8	0.56	0.12-4.66	0.78	0.15-2.6	–	–
Ta	0.127	0.03-1.52	0.076	0.018-0.563	0.09	0.013-0.79	0.1	0.01-0.66	0.11	0.024-0.29	–	–
W	1.22	0.25-13	0.193	0.03-1.39	1.21	0.25-3.9	1.02	0.12-8.74	1.34	0.19-3.3	0.127	0.009-1.23
Au	0.015	0.0007-0.043	0.0042	0.0009-0.047	0.0061	0.001-0.034	0.025	0.003-0.114	0.0041	0.00029-0.087	–	–
Pb*	11.7	0.5-368	18.9*	4.55-887	6	1.5-37.2	14.3	6.45-31.5	–	–	1.17	0.64-6.12
Th	0.86	0.27-23	0.56	0.11-4.53	0.67	0.12-7.6	0.81	0.21-4.16	0.82	0.18-2.4	0.033	0.004-0.240
U	0.3	0.09-6.28	0.2	0.03-1.87	0.21	0.03-1.45	0.28	0.04-1.36	0.32	0.08-1.03	0.015	0.001-0.138

***Determined by ICP-AES [8].**

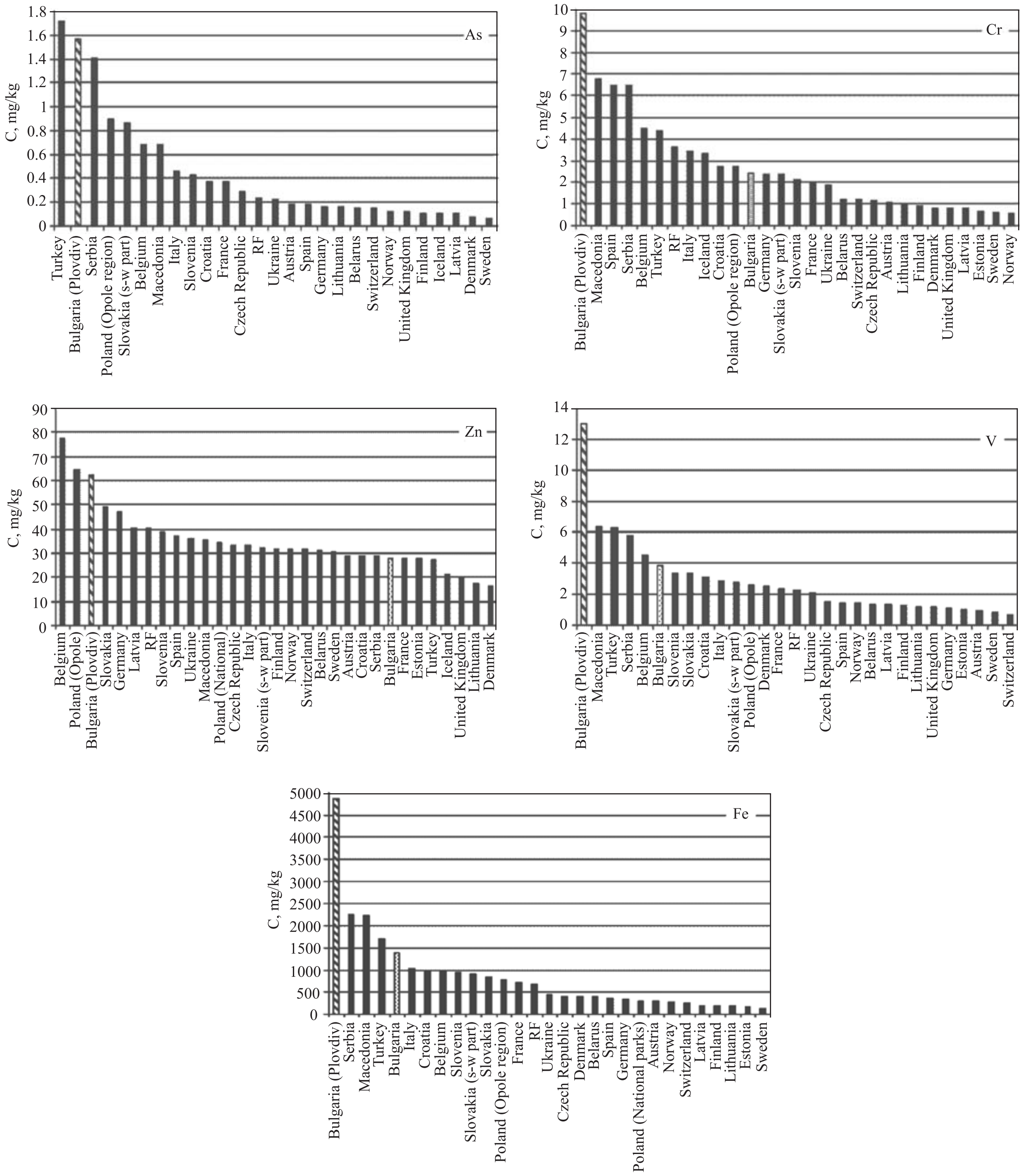

Fig. 3. Range of median values for selected elements is moss according to simultaneous moss surveys in different European countries [4]. Data for Turkey are from [26] and represent the European part of the country

Factor 2 is an exceptionally clear-cut industrial component with high values for Zn, Mo, Cd, Sb, and Pb. These elements show particularly high concentrations at a limited number of sites located within the region of Kardzhali. The main source of high pollution in this region is extraction of lead–zinc ores. Elements such as Cd and Sb are used in chemical industry, which explains their high concentration in regions of Burgas, Gabrovo, Troyan, Panagiurishte and Pazardzhik.

Factor 3 has high values for Ti, V, Cr, Fe, Ni and As. These elements may be associated with metallurgical and chemical industries. The main contribution to the concentration of V and Ni may come from oil-fired power plants. For the other elements the main source may be mining of iron and chromium ores in areas around Medet, Teteven and Burgas, and Ivailovgrad, respectively.

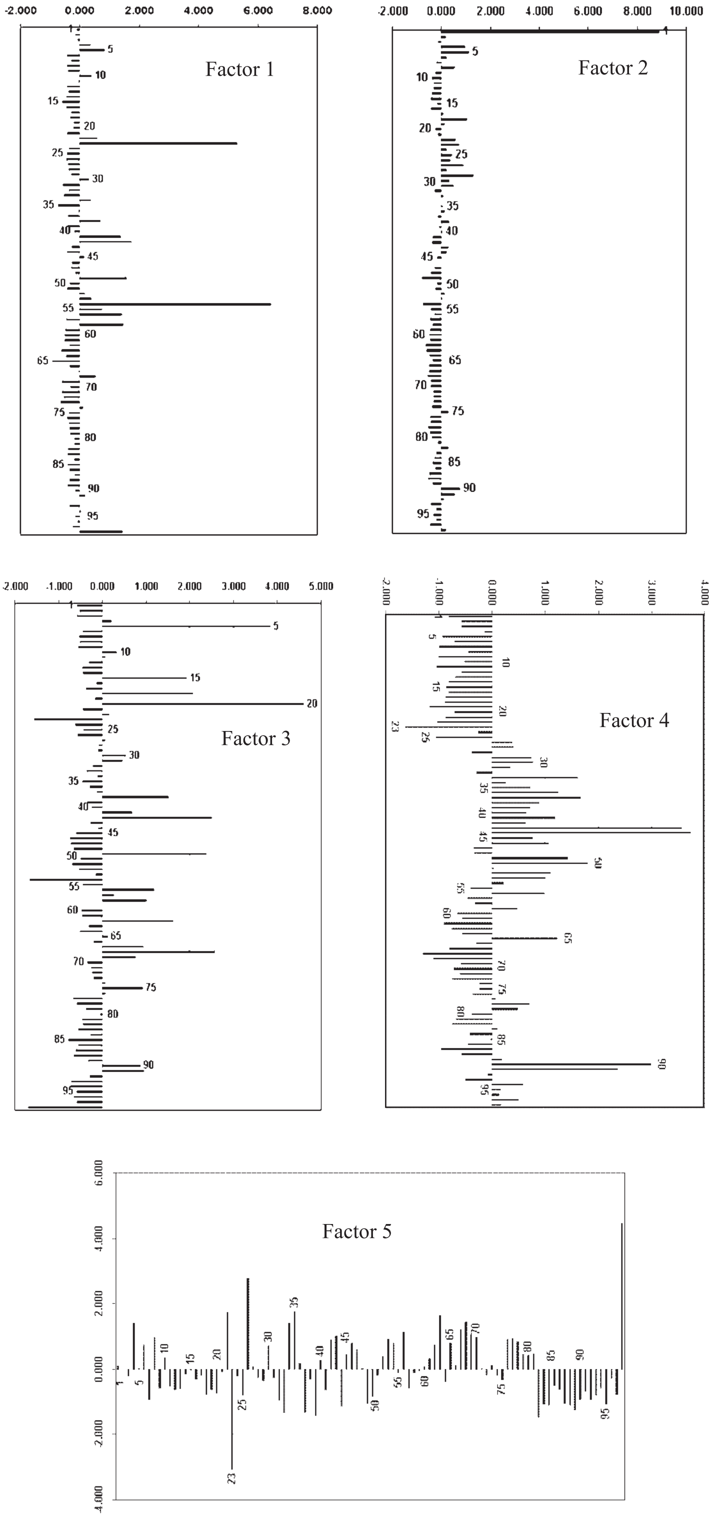

Fig. 4. Plots of factor scores for moss samples from Bulgaria

Factor 4 has high levels of Cl, Ca, and Au. These elements may be associated with emissions from metallurgical industry in Balkan Mountain region and from gold mining in Zlatitza.

Factor 5 has high levels for Br and I, which are associated with atmospheric deposition of aerosol influenced by processes in the marine environment. In our case this is strongly supported by high Br and I concentrations in samples from the Black Sea.

Arsenic. The elevated concentrations of this toxic and carcinogenic element are mainly related to the copper and gold mines, as well as to coal combustion. The relatively high values at sites 67, 68, 74 might be from the copper mining in the «Rosen basin» and coal combustion at Burgas region, which is another plausible source of air pollution. A high correlation of As with Fe (R = 0.79) and Ni (R = 0.67) is noted.

Chromium. Cr is mainly associated with the crustal component. The median value of Cr in the investigated region is similar to the corresponding values in the neighboring countries. Cr correlates most strongly with Sc (R = 0.93), Ti (R = 0.86), and V (R = 0.74). The highest factor scores are observed at sites 38, 42, 49, 54, 58, 67, 75 where high concentration of V are also evident. Chromium may originate from the nearby metallurgical plant. Combustion of coal may also lead to an increased chromium load on the ecosystem.

Iron. The concentration in moss is accounted for by the soil factor as indicated by the high Fe–Sc correlation (R = 0.96) and the principal component analysis (sites 53, 56, 58, 68, 91), pointing to iron ores in region near Troyan. However, high concentration of iron was also observed within the Burgas region (sites 67, 68), which is likely to be due to local emission sources such as the metallurgic plant in Debelt.

Table 5. Factor analysis of NAA and AAS data on moss samples from Bulgaria

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Na	**0.893**	0.030	0.070	0.111	-0.026
Al	**0.668**	0.138	**0.596**	0.077	0.205
Cl	0.060	0.032	-0.027	**0.782**	0.090
K	**0.526**	-0.027	0.175	0.419	0.322
Ca	0.058	0.089	0.034	**0.695**	0.145
Sc	**0.732**	0.027	**0.626**	0.011	0.115
Ti	**0.605**	0.106	**0.703**	0.074	0.147
V	0.229	0.159	**0.837**	-0.159	0.087
Cr	**0.598**	0.077	**0.737**	0.025	-0.001
Mn	0.215	0.150	0.278	-0.092	**0.573**
Fe	**0.710**	0.030	**0.628**	0.113	0.158
Co	**0.691**	-0.084	0.274	0.173	0.071
Ni	0.424	0.023	**0.824**	-0.011	0.105
Cu*	0.033	0.355	0.176	0.259	0.037
Zn	0.148	**0.954**	0.070	0.021	0.081
As	**0.470**	0.172	**0.580**	0.158	0.225
Se	-0.130	0.125	0.158	-0.348	0.096
Br	0.214	0.091	0.097	0.048	**0.779**
Rb	**0.729**	0.136	0.390	0.044	0.292
Sr	**0.737**	0.228	0.057	0.123	0.352
Mo	0.145	**0.479**	0.149	0.075	0.327
Cd*	0.026	**0.956**	0.053	-0.008	-0.014
Sb	0.041	**0.954**	0.068	0.022	0.066
I	0.112	-0.090	0.330	-0.034	**0.750**
Cs	**0.605**	0.180	0.377	-0.006	0.292
Ba	**0.687**	0.097	0.424	0.099	0.255
La	**0.954**	0.074	0.163	-0.028	0.003
Ce	**0.943**	0.088	0.137	-0.066	-0.019
Nd	**0.912**	0.030	0.206	0.013	-0.070
Sm	**0.955**	0.064	0.205	-0.031	0.026
Tb	**0.924**	0.061	0.300	-0.048	0.005
Dy	**0.776**	0.001	0.406	0.011	0.230
Tm	**0.872**	0.053	0.371	0.050	0.163
Yb	**0.924**	0.025	0.294	0.042	0.121
Hf	**0.868**	-0.037	0.168	0.080	0.134
Ta	**0.817**	0.072	0.383	0.109	0.232
W	**0.736**	0.164	0.116	0.077	-0.092
Au	-0.049	-0.032	-0.014	**0.721**	-0.307
Th	**0.975**	0.110	0.049	-0.029	0.052
U	**0.904**	0.106	0.094	0.049	0.191
Pb*	0.131	**0.929**	0.058	-0.009	-0.076
expl.var	16.665	4.313	5.582	2.181	2.615
prp.totl	0.406	0.105	0.136	0.053	0.064

Vanadium. The median value of V in south Bulgaria is similar to the corresponding values in the neighbouring areas in Romania and Serbia [24, 25]. V in the present samples is most strongly correlated with Al, Se, Ti, and Ni. Vanadium and nickel are usually 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 overall correlation between V and Ni in this material is R = 0.78, and high factor scores are evident at sites 75, 74, 76, and 73 in the Burgas region. The reason for high vanadium deposition is associated with the oil refinery and chemical industry in the town of Burgas and with the nearby metallurgic plant.

Nickel. The element distribution pattern of nickel corresponds closely to that of vanadium. The slightly elevated Ni concentrations in sites 67, 68, 69 may thus also be related to the Burgas oil refinery and to the nearby metallurgic plant.

Zinc. The median value of zinc in the investigated region is similar to the corresponding values in other continental regions of Europe. Only a few sampling sites (1, 5, 8, 18, 22, 23, 91) showed high Zn values. Apparently the extraction of lead–zinc ores are mainly responsible for these values.

Bromine and Iodine. These elements are strongly correlated and show high loadings in Factor 5. The highest scores of this factor are observed at sites near the Black Sea coast, confirming the marine origin of these elements.

Thorium and Uranium. The concentrations of these elements in the present samples are of the same order as those found in neighbouring areas in other Balkan countries. The highest values were observed at two sampling sites (58, 68) located in the vicinity of a uranium mine, which may be a source of windblown soil material.

Aluminum. The regional distribution of Al is typical for the group of crustal elements predominantly supplied to the moss by windblown soil dust, showing relative uniform mean values for different regions. However, it is also a typical representative of ferrous industry and cement plants.

Calcium. The level of Ca in moss is high and uniform, probably reflecting a contribution from higher vegetation. Calcium sulphate is used as construction material. Quicklime is calcium oxide (CaO) and may be responsible for high concentrations at the other sampling sites.

Manganese. The concentration of this element shows a high, relatively uniform level in the interior areas of the country, and decreases rapidly towards the coast. This is probably due to the low retention capacity of Mn in moss, where Mn may be lost by exchange with Na and Mg ions from marine aerosols.

Antimony. The association with Factor 2 suggests a predominantly industrial origin of this element.

Gold. The concentration of this element shows a high, relatively uniform level in the interior areas of the country. Bulgaria is rich in gold ores. Mines such as «Chelopech» in the Central Balkan Mountains and the nearby Krumovgrad mine «Ada Tepe» in the Eastern Rodopi may be responsible for high concentrations of gold and other related elements such as As used for gold extraction along with cyanide.

CONCLUSIONS

This study confirms that the moss method is suitable for detecting temporal and spatial trends in heavy metal deposition. The effects of newly introduced measures in order to decrease heavy metal emissions are clearly visible. The method is thus a valuable tool for the evaluation of atmospheric input of metals to the environment. Although deposition levels in Bulgaria decreased, we still found very high levels of some heavy metals (Pb, Cd) in mosses due to still heavily contaminated soils around ferrous industry, polymetal works and old mines, appeared local emissions, and site-specific characteristics as serpentine spots. It thus appears to be important that new technologies and preferably also new environmental legislation and controls are implemented and that the monitoring of deposition of heavy metals is continued.

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