Journal of Radioanalytical and Nuclear Chemistry (2020) 323:839–849
https://doi.org/10.1007/s10967-019-06978-9

Biomonitoring of elemental atmospheric deposition: spatial distributions in the 2015/2016 moss survey in Bulgaria

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Received: 16 September 2019 / Published online: 23 December 2019
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Abstract

In the most recent 2015/2016 campaign of the European-scale moss survey, Bulgaria joined for the fifth consecutive time. To investigate elemental atmospheric deposition patterns, 115 samples of moss biomonitors were collected. Instrumental neutron activation analysis was used to maximize the number of elements determined, including trace elements. The content of 34 elements was measured. Spatial and temporal variability trends and multivariate analysis indicated that coal mining and coal combustion for electricity production and domestic heating are major anthropogenic factors affecting the ecological situation in the country, followed by effects related to the construction of roads and related traffic pollution.

Keywords Air pollution · Deposition · Trace elements · Neutron activation analysis

Introduction

The moss technique, first used to assess metal accumulation from atmospheric deposition in terrestrial ecosystems in the late 1960's, is a well-established method for biomonitoring in Europe [1]. Bryophytes possess a certain set of distinctive morphological and physiological properties beneficial for biomonitoring of elemental atmospheric deposition [2]. Their root system is rudimentary, hence substrate uptake is negligible. Instead, nutrients are primarily obtained through wet and dry deposition; and the lack of vascular tissue implies no internal redistribution. The cell walls are characterized by high cation exchange capacity and the deposited elements are easily retained [3, 4]. This is an important advantage over conventional bulk precipitation collectors, often liable to sample contamination and problematic measurements of low concentrations. The wide geographical distribution and abundance of mosses facilitate economical large-scale biomonitoring with high-density networks [5].

In view of this, in 1990, the first European moss survey was initiated under the auspices of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation), under the Convention on Long-range Transboundary Air Pollution (Air Convention, formerly CLRTAP) of the United Nation's Economic Commission for Europe (UNECE) [6]. The main objective of the programme is to further the knowledge of transboundary air pollution by collecting data on a relatively large set of elements (namely Al, As, Cd, Cr, Cu, Fe, Ni, Pb, Sb, V, and Zn) determined in mosses. Additionally, element deposition maps are constructed and the effects of local pollution sources are delineated. The data are used to validate air pollution models by the International Cooperative Programme on Modelling and Mapping of Critical Levels and Loads and Air Pollution Effects, Risks, and Trends (ICP Modelling and Mapping).

Moss surveys have been conducted in parallel at 5-year intervals in an ever-growing number of participating countries. Since the start of the programme, it has been observed

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that median values for all investigated elements are relatively high in Eastern and Central European countries compared to data from Scandinavian and western European participants [7].

Bulgaria was first involved during the 1995/1996 campaign, and sampling has been performed regularly at non-uniform networks [8]. The predominant biomonitoring species has been *Hypnum cupressiforme* Hedw. It has been ascertained previously that local persistent "pollutant hotspots" correspond to contemporary and historical non-ferrous and ferrous facilities, mining and smelting activities, as well as coal-fired power stations [9].

During the last decades, many large soviet legacy industrial enterprises from the heavy industry and energy sectors were gradually closed down. Consequentially, the state Ministry of Environment and Water reported a reduction of local pollution emissions. Nevertheless, state air quality monitoring stations in over 20 towns often report exceedings of limit values for daily and annual particulate matter concentrations (PM10). This is attributed to vehicle emissions (due to obsolete fleets lacking catalytic converters), domestic heating (especially burning wood and coal), and to a lesser extent, electricity production and industrial activities [10].

The objective of this study was to determine the content of a relatively large set of elements deposited onto mosses so as to provide additional information to the few air quality indices investigated by the Bulgarian regulatory bodies (namely PM10, PM2.5, SO_2, NO_x, CO, O_3, C_6H_6, Pb, Cd, Ni, As, and PAHs). Instrumental neutron activation analysis (INAA) was chosen as a non-destructive multi-element method and inductively coupled plasma optical emission spectroscopy (ICP-OES) was employed in addition to ascertain the content of the environmentally important elements Cd, Cu, and Pb. To ascertain temporal trends of atmospheric deposition, a retrospective comparison with suitable data was performed. Multivariate statistics appointed possible sources of the elements determined. Spatial distribution maps constructed using GIS technology allowed for illustrating the regional extent of atmospheric deposition of elements regularly reported to the European programme.

Experimental

Moss sampling

The ICP Vegetation issues standardized sampling protocols listing appropriate moss biomonitor species and recommendations for: sampling density and number of subsamples, minimum distances between sampling sites and local emission sources, conditions for storage and transportation, as well as preferred analytical methods and standard reference materials [11, 12].

Study area

A substantial portion of the territory of Bulgaria was surveyed during the 2015/2016 campaign, as shown in Fig. 1. One hundred and fifteen composite moss samples were collected. Each comprised of 5–10 subsamples of a single moss species gathered within a 50 × 50 m area. The predominant species was *Hypnum cupressiforme* Hedw. (N = 79) and in its absence *Pleurozium schreberi* (Brid.) Mitt. (N = 21), and *Pseudoscleropodium purum* Hedw. (N = 15) were collected. The use of multiple moss species in a single survey is allowed and a preceding interspecies comparison and calibration are necessary for species not enlisted in the sampling protocols. No correction factors are to be used in calculating the final elemental content for the species approved by the Programme, as this introduces additional variability to the data [13].

The climate in the country is temperate continental and transitions to subtropical and Mediterranean to the south. Summers are hot and dry, hampering moss growth in arid regions, hence the lack of samples in valleys (Fig. 1). Longitude, latitude, and elevation were noted for all sampling sites. The sampling procedure, conditions for storage, and transportation were carried out in accordance with the ICP Vegetation protocols.

Sample preparation and analysis

After the removal of extraneous plant material, the unwashed samples were sorted, so that only the green part of the moss was subjected to analysis. The samples were air-dried to constant weight at 40 °C for 48 h.

Instrumental epithermal neutron activation analysis was performed in the radioanalytical laboratory REGATA at the Frank Laboratory of Neutron Physics (FLNP JINR), Dubna, Russia. The samples were not digested, as the method is non-destructive. Two subsamples of 0.3 g from each sample were prepared: one packed in polyethylene foil bags for short-term irradiation, and another—in aluminum cups for long-term irradiation.

Long term irradiation was performed using a cadmium-screened irradiation channel to determine elements characterized by long-lived isotopes. Samples were irradiated for 4 days, re-packed and then measured twice: after 3–6 days and after 20 days of decay. The time of measurement varied from 1 to 5 h. To determine elements characterized by short-lived isotopes (Cl, V, I, Mg, Al, and Mn), a conventional irradiation channel was used. Samples were irradiated for 3 min and measured for 15 min.

Quantitative analysis and quality assurance were conducted on the basis of flux comparators (namely Zr) and

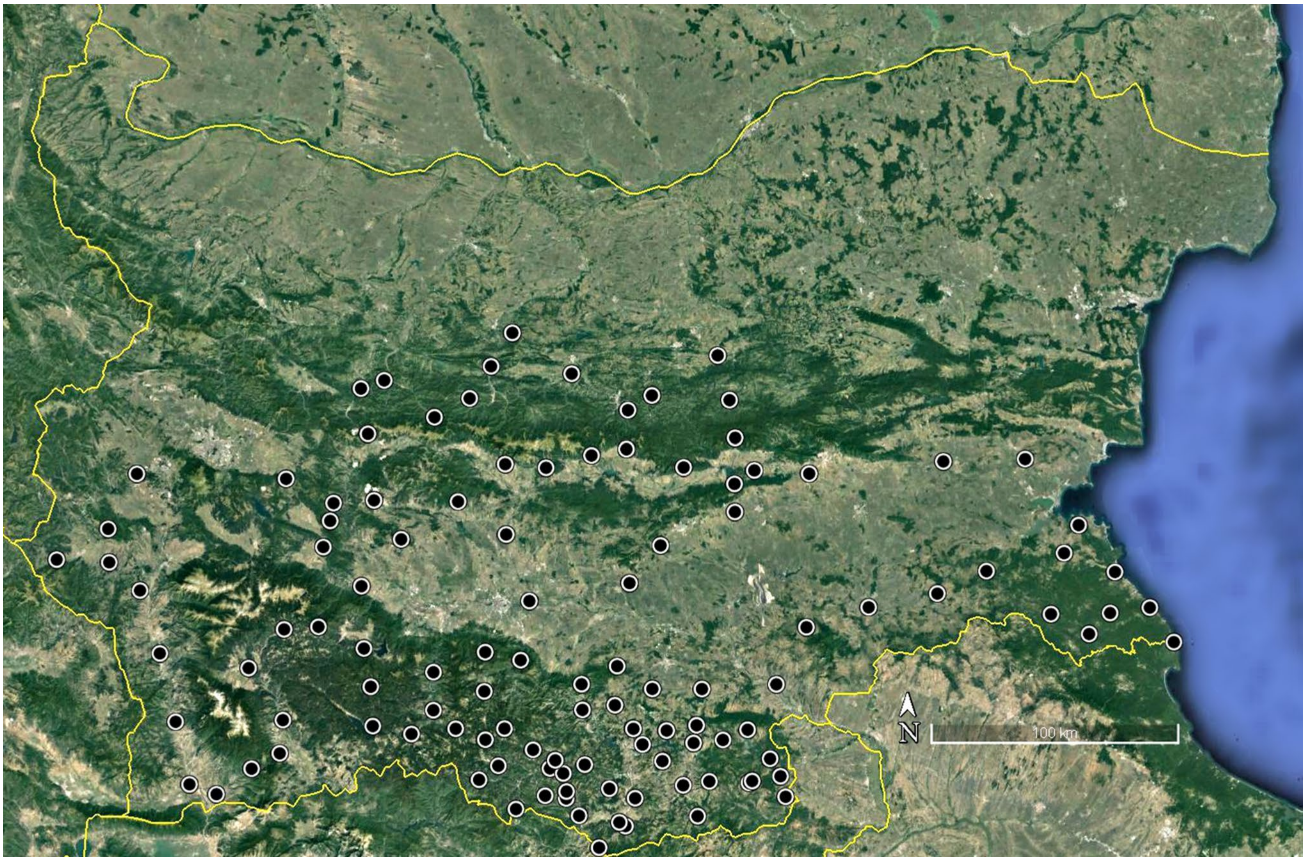

Fig. 1 Sampling sites for the 2015/2016 ICP vegetation moss survey in Bulgaria

certified reference materials, irradiated with the samples (Table 1).

A variety of standard reference materials was used: IAEA-443—Marine sediment, IRMM BCR-667—Estuarine sediment, NIST SRM 1572—Citrus leaves, NIST SRM 1573a—Tomato leaves, 1632c—Trace elements in coal, NIST SRM 1633b—Coal fly ash, NIST SRM 2710—Montana soil, and Finnish Forest Research Institute moss reference materials M2 and M3. Using software developed at FNLP, JINR the content of each element was calculated using the reference material showing the least deviation between the measured and certified values [14].

Inductively coupled plasma atomic emission spectroscopy was carried out at the Agriculture University, Plovdiv, Bulgaria using a Prodigy 7 spectrometer. About 0.5 g of the homogenized moss material was placed in Teflon vessels and treated with 7 ml concentrated NHO_3 and 2 ml H_2O_2 overnight. Full digestion of the moss material was achieved using a microwave digestion system. The digestion procedure was carried out in two steps: (1) ramp: temperature 180 °C, 10 min ramp time, power of 400 W and pressure 20 bar; (2) hold: temperature 180 °C, 20 min hold time, power of 400 W and pressure 20 bar. Digests were filtrated and quantitatively transferred to 25 ml calibrated flasks. Blank samples, triple replicates, and the standard reference materials (M2 and M3 [12], Finnish Forest Research Institute) were used for quality assurance for the three elements measured (Table 1).

Results and discussion

Concentrations of 34 elements in total were determined using instrumental epithermal neutron activation analysis (NAA) (Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Eu, Fe, Hf, I, K, La, Lu, Mg, Mn, Na, Nd, Ni, Rb, Sb, Sc, Se, Sr, Ta, Tb, Th, Ti, Tm, U, V, W, Yb, and Zn). Three additional elements (Cd, Cu, and Pb) were analyzed by means of inductively coupled plasma atomic emission spectroscopy (ICP-OES).

Summarized results (range and median values) of the determined elemental contents are presented in Table 2. These descriptive statistics were used for comparison of the results with data for the 2010/2011 moss survey in Bulgaria [7]. It was observed that the median values for V, Cr, Fe, Ni, Cu, and Zn remained similar between the two surveys. However, their respective maximal values decreased in

Table 1 Certified and measured values for the standard reference materials: 37 elements were determined using NAA and 3 additional elements were measured using ICP-OES*

	Certified values (mg kg^{-1})	Measured values (mg kg^{-1})	SRM		Certified values (mg kg^{-1})	Measured values (mg kg^{-1})	SRM
Al	64,400±773	64,432±1804	2710	Mn	246±8	246±12	1573a
As	136.2±3	135.5±2.7	1633b	Na	2010±30	2010±44	1633b
Ba	67.5±2	67.6±9.7	1632b	Nd	25±1.4	25±2.2	667
Br	67±8	67±5	443	Ni	128±9	128±10	667
Ca	50,500±909	50,559±3792	1573a	Pb*	3.33±0.25	3.56±0.12	M3
Cd*	0.106±0.005	0.12±0.01	M3	Rb	7.52±0.33	7.51±1.31	1632c
Ce	57±17	57±3	2710	Sb	1.96±0.04	1.96±0.05	443
Cl	1139±41	1140±101	1632c	Sc	8.7±2.61	8.7±0.19	2710
Co	23±1.3	23±1.3	667	Se	1.326±0.07	1.328±0.13	1632c
Cr	13.73±0.2	13.69±1.6	1632c	Sr	63.8±1.40	63.7±5.61	1632c
Cs	0.594±0.01	0.594±0.02	1632c	Ta	2.6±0.05	0.9±0.01	667
Cu*	3.76±0.23	4.02±0.16	M3	Tb	0.682±0.02	0.682±0.02	667
Eu	1±0.01	1±0.1	667	Th	1.4±0.03	1.4±0.04	1632c
Fe	7350±110	7354±346	1632c	Ti	2830±99	2832±535	2710
Hf	3.2±1	4.7±0.3	2710	Tm	0.326±0.03	0.326±0.05	667
I	1.84±0.03	1.84±0.33	1572	U	8.79±0.36	8.81±0.38	1633b
K	19,500±292.5	19,509±1132	1633b	V	23.72±0.52	23.70±1.45	1632c
La	27.8±1	28±1	667	W	93±28	93±28	2710
Lu	0.325±0.02	0.325±0.05	667	Yb	2.2±0.1	2.2±0.2	667
Mg	5800±302	5786±330	1572	Zn	6952±90	6953±125	2710

2015/2016, with the exception of V, which was unchanged. A decrease in both the median values and the range of the determined contents was observed for the elements As, Cd, and Pb. This trend of decreasing content was expected and can be explained by the shutdown of some industrial facilities (i.e. the Pb–Zn plant in Kardzhali), the implementation of better filtering technologies in coal-fuelled thermal power plants (at the Mini Maritsa Iztok complex), and improved state emission control [15].

It should be noted that Cd, Cu, and Pb were the only three elements determined using the same analytical technique in both moss surveys (ICP-OES). Since NAA is a non-destructive method, the total amount of the element can be determined, whereas, in ICP-OES, possible refractory compounds present in the acid-digested samples may be omitted.

Table 2 also contains data from a region of Norway where the influence of local anthropogenic air pollution is considered minor [16]. This data was utilized as background values in previous surveys for different countries, including Bulgaria [17–19]. Local background values have not been determined to date. Generally, it is accepted that if the determined elemental content is greater than the respective background value by a factor of 5, then anthropogenic emissions are very likely the primary source of enrichment. Based on that assumption, it can be determined that the median values for the elements Al, As, Ce, Cr, Fe, La, Sc, Tb, Th, Ti, and U were rather high during the 2015/2016 campaign in Bulgaria. However, some of these elements are known to be conservative and of edaphic origin [20]. Taking into consideration the fact that soils in Bulgaria and in Norway are characterized by different mineral and moisture contents, five *Hypnum cupressiforme* Hedw. Samples were collected from the Strandzha Nature Park during the 2015/2016 campaign. Strandzha Nature Park has a larger area and a lower mean altitude than most of the nature parks in the country. This was an attempt to determine local background values, based entirely on location criteria (remote location relative to roads, houses, and quarries) and the protected status of the territory. The descriptive statistics (range and median values) were included in Table 2. Using these data for comparison, Ca was the only element characterized by a relatively high content, as it was greater than the Strandzha median value by a factor of 6. This confirmed that a statistical approach to the derivation of local background values should be preferred, and a review of the available data for the country is recommended.

The median values in Table 2 could be used to compare the results of the survey with data from neighbouring countries participating in the ICP Vegetation moss surveys. The median values reported during the 2010/2011 moss survey for Romania were roughly two times higher than the content determined during the 2015/2016 moss survey in Bulgaria [21]. The median content of elements determined in the Republic of North Macedonia for the 2015/2016 moss survey was similar to those in the present work, with the exception of Cd and Cr, whose content was higher in the Republic

Table 2 Content of elements in moss samples (mg kg^{-1}): range and median values for the two most recent surveys in Bulgaria: 2015/2016 and 2010/2011 [7]

	Bulgaria, 2015/2016; N = 115		Bulgaria, 2010/2011; N = 129		Strandzha Nature Park, 2015/2016; N = 5		Norwegian data	
	Median	Range	Median	Range	Median	Range	Median	Range
Al	2310	569–10,900	1245	402–8886	1037	546–1940	200	67–820
As	0.45	0.20–3.57	0.63	0.15–10.8	0.357	0.354–0.403	0.093	0.020–0.505
Ba	46	14.2–309			18.2	17.1–20.9	17.1	5.6–50.5
Br	2.8	1.2–9.4			2.55	2.21–5.21	4.5	1.4–20.3
Ca	6630	606–14,200			1130	944–1180	2820	1680–5490
Cd	0.10	0.02–1.56	0.21	0.043–7.75	0.04	0.02–0.1	–	–
Ce	2.4	0.5–29.2			1.87	1.46–2.05	0.342	0.095–4.61
Cl	78.8	16.6–861			74.9	71.5–390	–	–
Co	0.59	0.197–3.29			0.443	0.402–0.738	0.202	0.065–0.654
Cr	2.73	0.219–25	2.06	0.72–38.1	2.44	1.84–6.43	0.55	0.10–4.2
Cs	0.207	0.0716–1.8			0.143	0.11–0.26	0.072	0.016–0.88
Cu	7.36	3.2–46.88	7.01	2–270	6.84	6.56–7.00		–
Eu	0.07	0.009–0.92			0.047	0.035–0.069	–	–
Fe	1190	376–7240	1101	307–8546	948	723–1320	209	77–1370
Hf	0.16	0.04–1.44			0.105	0.083–0.121	–	–
I	1.28	0.48–2.99			1.51	1.43–2.2	2.5	0.6–41.7
K	5670	3250–14,200			5480	4700–6420	–	–
La	1.35	0.39–22.6			0.931	0.728–0.938	0.189	0.045–2.56
Lu	0.019	0.001–1.45			0.007	0.006–0.0164	–	–
Mg	2080	514–8550	1245	402–8886	1990	1230–3680	1730	940–2370
Mn	180	39–551			84	78–204	256	22–750
Na	225	79–1560			144	121–564		
Nd	1.3	0.2–24.1			0.85	0.79–0.99	–	–
Ni	2.1	0.45–13.5	2.06	0.72–38.1	1.75	1.42–2.98	1.14	0.12–6.6
Pb	10.72	3.72–102.8	8	1.69–333	9.68	9.16–15.08	–	–
Rb	7.38	2.24–50.7			4.94	4.05–5.64	7.7	1.3–51.5
Sb	0.11	0.04–0.51			0.088	0.061–0.099	0.033	0.004–0.240
Sc	0.41	0.10–3.13			0.32	0.26–0.52	0.052	0.009–0.220
Se	0.2	0.008–0.67			0.18	0.15–0.22	0.33	0.05–1.30
Sr	25	11.3–122			17.8	14.2–22.5	15.8	3.6–43.3
Ta	0.04	0.009–0.28			0.022	0.019–0.029	0.01	< 0.01–0.07
Tb	0.03	0.005–0.42			0.019	0.016–0.021	0.003	< 0.002–0.030
Th	0.39	0.09–2.8			0.227	0.186–0.241	0.033	0.004–0.240
Ti	143	46.4–764			105	99.3–174	23.5	12.4–66.4
Tm	0.014	0.002–0.21			0.010	0.006–0.011	–	–
U	0.12	0.03–3.2			0.067	0.059–0.074	0.015	0.001–0.138
V	3.89	1.3–22.7	3.07	0.96–22.4	2.7	2.47–5.79	0.92	0.39–5.1
W	0.1	0.02–1.44			0.058	0.047–0.061	0.127	0.009–1.23
Yb	0.1	0.03–1.08			0.055	0.036–0.055	–	–
Zn	28	9–101	22.2	8.22–286	17.8	17.2–19.4	26.5	7.9–173

Values for presumably unimpacted sites in Strandzha Nature Park collected in the 2015/2016 moss survey, N = 5. Norwegian data previously used as background values included [16]

of North Macedonia, and the values for Cu, Mg, and Pb, which were higher in Bulgaria [22]. The reported median content of all elements determined in mosses in Greece for the 2015/2016 moss survey was higher than the values shown in Table 2 [23]. The differences could be explained by dissimilarities in the inputs by both edaphic and anthropogenic sources in the countries [22].

The results of the two most recent moss surveys in Bulgaria could be compared further, using all available data points and not only the main descriptive statistics. The robust non-parametric Mann–Whitney U test was chosen, as the extreme values determined in the studies proved to be meaningful in the context of proximity to known sources of pollution emission [24]. Thus, the exclusion of outliers and extreme values from the datasets for the purposes of normalization was avoided. During the 2010/2011 moss survey in Bulgaria, the content of ten elements was determined. The summarized results from the U test are shown in Table 3. It was ascertained that the concentrations of the elements Al, As, Cd, Cr, V, Pb, and Zn in both moss surveys were significantly different ($p < 0.005$), even though the median values for Cr, V, Pb, and Zn were similar (Table 2). The test indicated that the medians for the concentrations of the elements Cu, Fe, and Ni in the two most recent moss surveys in Bulgaria were not significantly different ($p \geq 0.005$) and belong to the same distribution.

Principal component factor analysis was applied to identify the associations between the elements determined in the 2015/2016 survey based on their covariance (Table 4). Varimax rotation of the loadings was applied to aid data interpretation. Four factors were found, only one of which was interpreted as anthropogenic (Factor 3). 67% of the total variance in the dataset was explained by the factor analysis.

Factor 1 was characterized by high loadings for crust elements [Na (0.66), Mg (0.81), Al (0.74), Sc (0.80), Ti (0.65), V (0.84) and Fe (0.82)], as well as marine aerosols [Cl (0.53), Br (0.53) and I (0.61)]. The sampling sites which contributed the most to the formation of this factor were located near the Black Sea coast and in sloped mountainous terrains, confirming the interpretation of the grouping of the elements. Factor 2 contained REEs, U (0.61), and Th (0.84)—typical crust components, indicating the presence of soil particles in the samples. No clear pattern was identified based on the location of the sampling sites with the highest scores. Factor 3 was characterized by As (0.75), Se (0.73), Sb (0.72), and Cu (0.74), all found in ores and coal ash. The highest scores for this factor were determined in sites near Cu–Ag mines and open tailings (Chelopech, Elatsite, Pirdop, and in the vicinity of Panagyurishte), and a coal-fired thermal power plant (Bobov Dol). A similar grouping of elements in one factor (namely As, Cu, Mo, Se, Sb, and Zn) was reported in a study conducted in Eastern Serbia between 2006 and 2009, and the factors scores related the source to the Bor copper mining and smelting complex [25]. Factor 4 had high loadings for K (0.67) and Ca (0.65), possibly characterizing a crustal component. The sampling sites with the highest factor loadings were located in forests. Results of similar studies employing this statistical procedure have been overviewed elsewhere [26].

To illustrate the spatial distribution of the elements reported to the ICP Vegetation programme, maps were constructed using ArcGIS/ArcMap. The spline interpolation method with tension was applied (Fig. 2). To avoid ambiguity related to concentration classifications and respective colouring, map legends from ICP Vegetation Thematic reports were referred, as they are derived from data submitted by all participants in the European-scale surveys [7].

Diagonal distribution patterns were observed for the elements Al, Cd, Fe, Ni, Sb, and V. In arid regions and during dry periods, the concentration of crustal elements such as Al, Cr, Fe, Ni, and V is biased, due to mineral particles (soil dust) released by erosion. The relatively high content of Al could be caused by application of NAA. However, as Sb and Cd are not as abundant in the Earth's crust, their patterns are usually considered as good indicators of anthropogenic pollution [7]. Indeed, the observed diagonal patterns could be explained by the location of mines, tailings, and a cement factory in the Northwest part of the studied area; a non-ferrous plant near Plovdiv (KCM Group) combined with resurgence of the industry in the region; as well as numerous quarries and several open tailings in Southeast Bulgaria.

Contaminated sites characterized by high concentrations of more than one element were depicted in the deposition maps. High concentrations of the elements Al, Cd, Fe, Ni, Pb, Sb, and Zn, all delineated in red colour, were determined in a moss sample in the vicinity of Bachkovo (to the south of Plovdiv in Fig. 2). This could be attributed to industrial accidents: the mine tailings in Lucky leaching metals in the rivers Yugovska and Chepelarska, as reported by the Regional Inspectorate of Environment and Water, as well as the producer of fertilizers and plant protection products "Agria" contaminating the Chepelarska River with Pb, Cu, Fe, and Mg, as reported in 2016 [27, 28].

Table 3 Mann-Whitney U test: the significance of the differences between the two most recent moss surveys in Bulgaria: 2010/2011 and 2015/2016 data

	Al	As	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn
2010/2011 Mean rank	47.42	35.51	77.51	56.14	62.32	64.03	71.04	57.34	56.66	56.65
2015/2016 Mean rank	75.08	52.49	44.99	66.36	60.18	58.47	51.46	65.16	65.85	65.85
U	3185.5	2515	4307.5	5313	6821.5	7239.5	5886.5	5606	5438.5	5438.5
Z	7.69	2.93	5.65	3.82	1.08	0.32	2.78	3.29	3.59	3.59
p	0.0000	0.003	0.0000	0.0001	0.279	0.747	0.0054	0.001	0.002	0.0003

Table 4 Factor analysis: matrix of the factor scores

Elements	Factor 1	Factor 2	Factor 3	Factor 4
Al	**0.74**	0.56	0.10	0.06
As	0.24	0.10	**0.75**	0.02
Ba	0.20	0.35	0.26	0.21
Br	0.53	− 0.04	0.01	0.09
Ca	− 0.07	0.04	0.11	**0.65**
Cd	− 0.15	0.11	0.40	0.22
Ce	0.58	**0.73**	0.11	− 0.14
Cl	0.53	− 0.27	− 0.20	0.42
Co	**0.64**	0.52	0.27	− 0.17
Cr	**0.65**	0.18	0.27	− 0.06
Cs	0.15	0.49	0.26	0.25
Cu	0.14	− 0.03	**0.74**	0.07
Eu	0.45	0.58	0.10	− 0.07
Fe	**0.82**	0.46	0.19	0.03
Hf	0.17	**0.75**	− 0.07	0.00
I	**0.61**	0.01	0.15	0.08
K	0.23	− 0.14	− 0.04	**0.67**
La	0.55	**0.77**	0.15	− 0.03
Lu	− 0.02	**0.70**	− 0.14	0.34
Mg	**0.81**	0.02	− 0.06	0.14
Mn	− 0.12	0.48	0.21	− 0.04
Na	**0.66**	0.33	− 0.10	0.23
Nd	**0.61**	**0.62**	0.01	− 0.05
Ni	**0.62**	0.26	0.29	− 0.19
Pb	− 0.19	0.20	0.47	0.23
Rb	− 0.01	0.24	0.06	0.50
Sb	0.17	0.09	**0.72**	0.10
Sc	**0.80**	0.41	0.09	− 0.08
Se	0.17	− 0.01	**0.73**	− 0.20
Sr	0.47	0.25	− 0.12	0.24
Ta	0.27	**0.83**	0.09	− 0.08
Tb	**0.61**	**0.72**	0.13	− 0.12
Th	0.29	**0.84**	− 0.02	0.08
Ti	**0.65**	**0.60**	0.13	− 0.08
Tm	0.41	**0.66**	0.24	− 0.17
U	0.10	**0.61**	− 0.11	0.32
V	**0.84**	0.39	0.15	− 0.03
W	0.16	0.58	0.35	0.04
Yb	0.04	0.55	0.11	0.17
Zn	**0.60**	0.05	0.21	0.44
Expl. var, %	22.77	17.41	14.16	13.07

Factor scores with values ≥ 0.6 were marked in bold

A possible explanation for the high concentrations of Al, Cr, Fe, Ni, Sb, and V determined in a sample near Karnobat (to the east of Sliven in Fig. 2) could be the oil depot and asphalt production base located around the town, or the unfavourable proximity of the collection site to railroad tracks.

The sampling sites near the border with Greece (the municipality of Kirkovo) were characterized by high content of Al, Cd, Cr, Fe, Ni, Sb, and V, and were located near newly built roads, quarries supplying building materials, and in proximity to new border checkpoints with Greece: Zlatograd-Thermes and Makaza–Nymfaia, inaugurated in 2010 and 2013, respectively. The elements Sb and V are attributed to road transportation emissions (road dust, brake and tire wear) [7]. The moss survey results from Greece confirm that the content of the elements Al, As, Cr, Fe, Ni, V, and Zn was high near the borders with Bulgaria. The presence of serpentinites near the border between both countries could explain the elevated content of Cr and Ni [23, 29]. Since the moss samples from Karnobat (oil depot, asphalt base, railroad tracks) were characterized by a similar group of elements, it could be hypothesized that they are characteristic of fuel combustion (especially Ni and V) and road surfacing with asphalt concrete.

Aluminium In the absence of local anthropogenic pollution emissions, the element Al is considered an indicator of windblown soil particles because of its high crustal abundance and low solubility and bioavailability [30–32]. The distribution patterns for Al content in mosses may indicate a strong contribution of wind re-suspension [18]. Typical anthropogenic sources are cement plants, mining, agriculture, coal combustion, and the ferrous industry [33]. The patterns determined in the 2015/2016 moss survey depict the effects of natural and anthropogenic sources. High Al content was ascertained in samples from the Upper Thracian Plain (an agricultural region). The highest concentration of Al was determined in samples collected in the vicinity of the cement factory Zlatna Panega. Delineated in read in Fig. 2 are also the sampling sites near the towns of Plovdiv (an industrial canter in the Upper Thracian Plain, there is a non-ferrous smelter in the region), Bachkovo (likely affected by leaching of mine tailings and the production of fertilizers), Sliven (a coal-fired thermal power plant, textile and machine-building industries), Karnobat (oil depot, asphalt production base), and near the border with Greece (construction of roads and exploitation of two new border checkpoints).

Arsenic This element is a marker of coal combustion. It should be noted that on the Balkans, arsenic is naturally present at relatively high concentrations because of ore deposits and mineral belts [34]. The distribution map illustrated that high content was determined in sampling sites near the towns of Pernik (a coal-fired thermal power plant ‘Republika’, waste incineration, ferrous industry and opencast mining of brown and bituminous coal), Chelopech, Zlatitsa, Elatsite, and Pirdop (all of them located near Cu–Ag mines and tailings), Stara Zagora (to the north of the Maritsa-Iztok mining and energy complex: a large

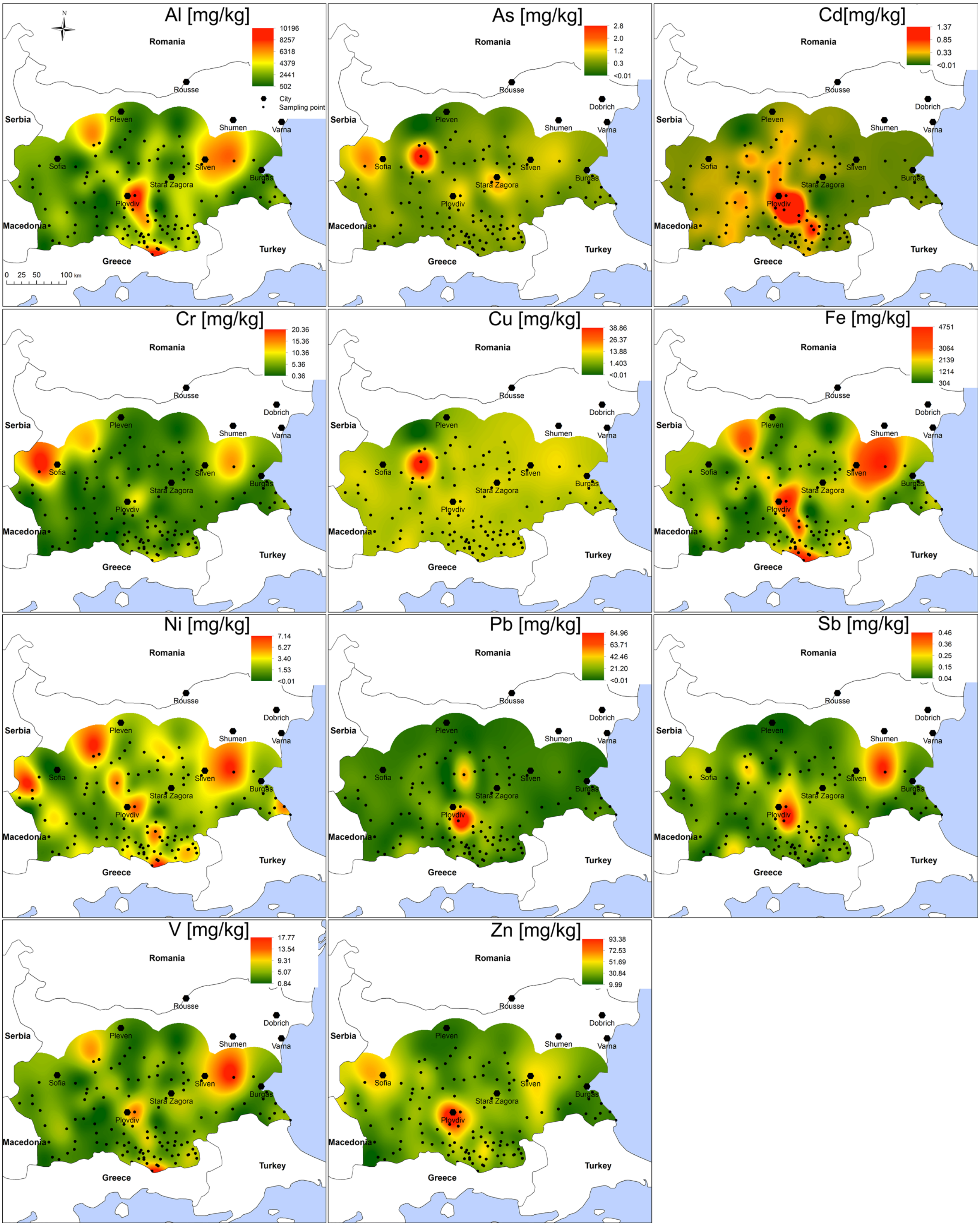

Fig. 2 Atmospheric deposition patterns for element pollutants investigated by the ICP vegetation programme: Al, As, Cd, Cr, Cu, Fe, Ni, Pb, Sb, V, and Zn. Thematic reports were referred for concentration classification and map legends

lignite coal basin with coal mines, enrichment plants, and a cluster of three coal-fired thermal power stations), Plovdiv, and Karnobat.

Cadmium High content was present in samples collected near Plovdiv (the KCM non-ferrous smelter), Haskovo and Kardzhali (tailings, polymetallic ores and a non-ferrous smelter shutdown in 2011 [35]), Zlatitsa (Cu–Au mines), Lovech (machine factories and an iron foundry), Gotse Delchev (lignite coal mines), and near new border checkpoints with Greece.

Chromium and nickel It was observed previously that the elements Cr and Ni had corresponding distribution patterns in Bulgaria. This was attributed to crude oil and coal combustion, steel production, as well as the presence of serpentinites in the Rhodope Mountains [23, 34, 36, 37]. Known anthropogenic sources of Ni include oil combustion, Ni mining and smelting, refining, steel production, fossil fuel combustion, wood combustion, waste incineration and road traffic [36]. Based on the maps in Fig. 2, the patterns of the two elements matched in the 2015/2016 survey, even though the degree of the impact differed. According to the ICP Vegetation classification used for the construction of maps, the Ni content was high in numerous sites, whereas the deposition map for Cr revealed only 5 heavily impacted sites. A high content of both Cr and Ni was determined in the samples collected near Karnobat (oil depot and an asphalt base), Pernik (a coal-fired thermal power plant, waste incineration, ferrous industry and opencast mining of coal), Zlatna Panega (cement factory), Elatsite (Cu–Au mines and tailings), and to the east of Plovdiv (industrial and agricultural centre). Samples with high Ni content were collected near Kyustendil (coal mines), Blagoevgrad, Starosel, Ahtopol, as well as near the borders with Greece, possibly because of traffic-related pollution and fuel combustion.

Copper The highest Cu content, 48 mg kg^{-1}, was determined in a moss sample located 6 km to the east of the Elatsite copper mine. The overall colour of the deposition map for this element (Fig. 2) illustrates that Cu content is relatively high in Bulgaria as compared to other participants in the ICP Vegetation programme.

Iron This element is present at high content in the Earth's crust. Natural sources of airborne dust particles containing Fe are related to weathering of rocks and wind erosion in regions with sparse vegetation. Anthropogenic sources include mining, steel and iron industry, coal extraction and combustion, as well as traffic [38]. The moss samples collected in the vicinity of Zlatna Panega (cement factory) were determined to have the highest content, followed by samples near the towns of Sliven (a coal-fired thermal power plant, textile and machine-building industries), Karnobat (oil depot, asphalt production base), Plovdiv (agricultural and industrial center), Starosel, Bachkovo, as well as in the municipalities near the border with Greece.

Lead In previous moss surveys, samples collected in Bulgaria had the highest reported Pb content among all ICP Vegetation participants (both median and maximal values) [29]. After the shutdown of the Kardzhali Pb–Zn plant in 2011, the highest Pb content in the 2015/2016 moss campaign was determined in samples near Bachkovo (contamination likely due to tailings leak accidents and wastewater discharges from fertilizer production processes), and in the vicinity of Iganovo, where an explosion in an ordnance plant (VMZ Sopot) took place in 2015 [39].

Antimony Due to the low content of Sb in the Earth's crust, this element is considered a good indicator of anthropogenic pollution and a traffic tracer. The results of the 2015/2016 moss survey show that high Sb content was present in samples collected near Plovdiv (agricultural and industrial center, proximity to a non-ferrous smelter), Bachkovo (industrial accidents in the region), Karnobat (asphalt base and an oil depot), Chelopech (opencast mining and tailings), Pernik (waste incineration, coal mining and a coal thermal power plant) and Gotse Delchev (lignite coal mines).

Vanadium Vanadium and nickel are present at high concentrations in crude oil, therefore the common interpretation for vanadium deposition is fuel combustion. Besides oil-fired plants, refineries, and industrial boilers, other known anthropogenic sources of V are coal mining and burning, mine tailings, vehicular traffic and certain fertilizers [40]. High V content was determined in moss samples collected near Karnobat (oil depot), Zlatna Panega (a large cement factory), Plovdiv (agricultural and industrial centre, proximity to a non-ferrous smelter), Sliven (industrial centre, thermal power plant), and near the border with Greece.

Zinc According to an ICP Vegetation report, the median values for the content of Zn in mosses from Bulgaria are among the lowest ones reported in Europe [7]. Local "hotspots" were previously determined in proximity to Pb–Zn smelters and mines [8]. The patterns observed for the element Zn in the 2015/2016 moss survey differed to those for Pb, except in the vicinity of Plovdiv, which is explained by the non-ferrous plant "KCM 2000". High concentrations were determined in samples collected near Sofia (urban dust, vehicular pollution), Pernik (coal mining, coal-fired thermal power plant), Bobovdol (coal-fired thermal power plant), Sliven (industrial center, a coal power plant), Bachkovo (industrial accidents in the region). In a moss survey conducted in Kosovo, high content of Zn was similarly determined in samples collected close to thermal power stations [41].

Conclusions

The moss technique allowed for a detailed study of the atmospheric depositions of metals and metalloids in Bulgaria, including their spatial and temporal trends. During the most recent 2015/2016 moss survey, a sampling network of 115 sites was achieved and the content of 34 elements was determined using instrumental neutron activation analysis (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Zn, As, Se, Br, Rb, Sr, Sb, I, Ba, Cs, La, Ce, Nd, Eu, Tb, Tm, Yb, Lu, Hf, Ta, W, Th, U). Inductively coupled plasma optical emission spectroscopy (ICP-OES) was employed as a complementary analytical technique to measure the content of the elements Cd, Cu, and Pb. The data on rare earth elements aided the interpretation of the performed factor analysis, as they are considered markers for edaphic sources. Of the four synthetic factors determined in the dataset, one was purely anthropogenic (As, Cu, Se, and Sb) and associated with coal combustion and copper ore mining. Sampling sites located near Cu–Ag mines, coal mines, and coal-fired power stations contributed the most to the formation of this factor. Non-parametric *U* tests were performed to compare the results with the available data on 10 elements from the preceding moss survey in Bulgaria. It was shown that the content of Al, As, Cd, Cr, Cu, Pb, V, and Zn differed significantly between the two surveys, even though the reported Cr, V, Pb, and Zn median values appeared very similar. This hinted at changes in the pollution emission sources or emission rates between the surveys. Element deposition maps illustrated the spatial patterns for pollutants investigated by the ICP Vegetation programme. It was observed that after the shutdown of the Kurdzhali lead–zinc plant, the environmental situation in the region vastly improved but is still affected by tailings and quarries. Road construction and increased traffic at the newest border crossing points with Greece were associated with increased content of Al, Cr, Fe, Ni and V in the moss samples. These findings were in agreement with data from a similar study conducted in Greece, reporting that the content of the elements Cr, Fe, Ni, V, and Zn is high close to the Bulgarian borders and has increased since the preceding 2010/2011 moss survey.

Acknowledgements The research was part of the JINR Topical plan for international cooperation 03-4-1104-2011/2016. The authors gratefully acknowledge the grant of the Plenipotentiary of Bulgaria at JINR, Order 31 of 23.01.2015, p. 15.

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