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ATMOSPHERIC DEPOSITION STUDY IN THE AREA OF KARDZHALI LEAD-ZINC PLANT BASED ON MOSS ANALYSIS

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Изучение атмосферных выпадений в окрестности свинцово-цинкового комбината в г. Кырджали (Болгария) с использованием анализа мха

Впервые метод мхов-биомониторов был применен для оценки экологической ситуации в районе, находящемся под воздействием свинцово-цинкового комбината — одного из самых опасных предприятий в Болгарии. Летом и осенью 2011 г. было отобрано 77 образцов мха *Hypnum cupressiforme* в городе Кырджали. Концентрации 47 элементов были определены с помощью эпитеплового нейтронного активационного анализа (ЭНАА), атомно-абсорбционной спектрометрии (ААС) и атомно-эмиссионной спектрометрии с индуктивно-связанной плазмой (ИСП-АЭС). Для характеристики источников поступления элементов, определенных в пробах, был применен многомерный статистический анализ. Выделено четыре группы элементов. По сравнению с усредненными данными для территории, находящейся за пределами города, атмосферные выпадения элементов промышленного происхождения в Кырджали, где расположен металлургический комбинат, оказались гораздо выше. Средние уровни определенных концентраций большинства токсичных металлов (Pb, Zn, Cd, As, Cu, In, Sb) были чрезвычайно высоки в этой «горячей точке» по сравнению с усредненными данными по Болгарии, согласно Европейской программе по сбору мхов 2010–2011 гг. Были применены ГИС-технологии для создания карт распределения элементов, иллюстрирующих закономерности накопления элементов-загрязнителей в исследуемом районе. Полученные результаты вносят вклад в развитие экологических исследований в Болгарии и могут быть использованы для изучения и контроля технологических процессов на свинцово-цинковом комбинате в г. Кырджали.

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Hristozova G. et al. E18-2015-2

Atmospheric Deposition Study in the Area of Kardzhali Lead-Zinc Plant Based on Moss Analysis

For the first time the moss biomonitoring technique was used to assess the environmental situation in the area affected by the lead-zinc plant as one of the most hazardous enterprises in Bulgaria. 77 *Hypnum cupressiforme* moss samples were collected in the Kardzhali municipality in the summer and autumn of 2011. The concentrations of a total of 47 elements were determined by means of instrumental epithermal neutron activation analysis (ENAA), atomic absorption spectrometry (AAS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES). Multivariate statistics was applied to characterize the sources of elements detected in the samples. Four groups of elements were found. In comparison to the data averaged for the area outside of the town, the atmospheric deposition loads for the elements of industrial origin in Kardzhali, where the smelter chimney is located, were found to be much higher. Median levels of the measured concentrations of the most toxic metals (Pb, Zn, Cd, As, Cu, In, Sb) were extremely high in this hot spot when compared to the median Bulgarian cross-country data from the 2010–2011 European moss survey. GIS technology was used to produce element distribution maps illustrating deposition patterns of element pollutants in the study area. The results obtained contribute to the Bulgarian environmental research used to study and control the manufacturing processes of the lead-zinc plant in the town of Kardzhali.

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

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INTRODUCTION

Mosses have been used as biomonitors for assessment of heavy metal atmospheric deposition since the late 1960s [1]. This technique is an adequate method of air pollution evaluation due to negligible uptake from the moss substrate; nutrients are primarily obtained by means of dry and wet deposition. Certain morphological and physiological properties of the mosses (e.g., large cationic exchange properties within the cell wall, lack of advanced root system and cuticles) make them suitable biomonitors [2]. Several moss species are suitable for time-integrated assessment of present state environmental contamination due to the fact that annual growth increments can be easily separated for analysis. In addition, the abundance and large geographical distribution of mosses is advantageous and provides for an inexpensive and simple alternative to conventional bulk deposition analysis. Thus, a high density network of sampling sites is easily achieved. This allows for pollution distribution maps to be produced.

Large-scale monitoring using the moss technique was first introduced in Scandinavian countries four decades ago [3]. The Environmental Monitoring and Data Group in the Nordic countries extended an invitation to other European nations in the late 1980s and in 1990 the first European-scale survey was conducted [4]. The survey has been carried out at intervals of five years since. Standardized protocols and reference materials have been acknowledged. The species *Pleuzorium schreberi*, *Hylocomium splendens*, *Hypnum cupressiforme* and *Pseudoscleropodium purum* have been used in the monitoring programme to study temporal and spacial trends of deposition [5]. A decrease in the concentrations of all reported pollutants (arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, vanadium, and zinc) has been observed since the start of the survey. Generally, the highest concentrations were found in South-Eastern Europe [6].

The present study is focused on the area of the lead-zinc plant in Kardzhali, Bulgaria (Fig. 1). Based on State Energy and Water Regulatory Commission (SEWRC) data, it is a major source of pollution emissions that affect air quality and also have a direct effect on the health of the population [7].

The smelter, Lead-Zinc Complex (LZC) PLC, is situated in the industrial part of Kardzhali town, on the northern shore of the Studen Kladenets pond. It began operating in 1955, producing 5.000 tons of zinc and 7.000 tons of sulfuric acid annually. Lead and alloys production began in 1956, followed by zinc sulfate, bismuth, cadmium, sodium bisulfite, zinc alloys, lead-antimony alloys production as well as the processing of exhausted batteries, selenium and calcium-cadmium alloys used in the battery industry, and others [8]. The lead-zinc plant is famous for the production of nonferrous metals and is a major source of contamination. By the end of 2009 there had been multiple investment proposals and programs to increase production and efficiency, improve energy recovery and environmental conditions, and to replace the existing equipment. Nevertheless, due to delays in the implementation of new technology, the facility operation has inflicted environmental damage to the region with regular emissions of sulfur dioxide, heavy metals and other toxic elements (e.g., Pb, Zn, Cd, As, Sn), which are deposited from the air to the soil and water. The town of Kardzhali is considered to be one of the pollution hotspots in Bulgaria [9].

Within Kardzhali municipality pollutants have frequently been above the standards in place for atmospheric air quality in Bulgaria. The number of days with fog and calm weather predetermine the poor dispersion of local pollutants and therefore their increased concentration. Heat, light and moisture distribution are affected by the region's particularities of the relief, topography, altitude, inclination and wind rose [10].

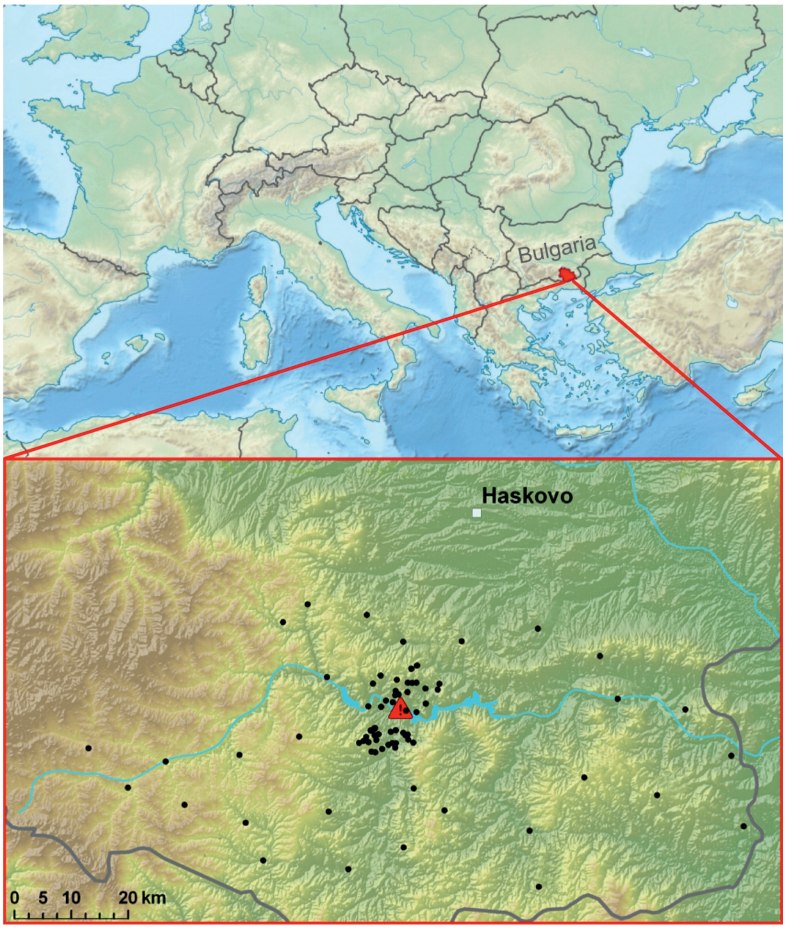

Fig. 1. Study area. Sampling sites marked by black dots, red exclamation sign identifies the position of the smelter chimney

The regulatory bodies for atmospheric air quality in Kardzhali municipality are the Ministry of Environment and Water, and Haskovo regional laboratory. Control data is obtained using an automated air quality monitoring station in Studen Kladenets, working since 2008. It registers the levels of several air quality indices: fine dust particles, SO_2, lead aerosols, As, Cd and polycyclic aromatic hydrocarbons. The data obtained is related to the operation of the Lead-Zinc Complex (LZC) and to the stock companies Gorubso–Kardzhali (tailings in particular), Bentonite and S&B Industrial Minerals [7]. The results were used to impose ecological measures, establish appropriate working and storage conditions, suggest improvements or replacements of old equipment and call for a temporary shutting down of the production processes, which took place in 2011 [11].

Subsequently, the reported values for Cd, Pb, and As, measured by the monitoring station in Studen Kladenets in 2012 did not exceed the average annual standard [7].

The objective of this study was to determine the concentration of elements in mosses obtained in an environmental hot spot and the surrounding area. The results were anticipated to be an expansion to the available data on a small number elements investigated by the State regulatory bodies. Multivariate statistics and GIS technology were used to classify data and to appoint possible sources of the element pollutants and their deposition patterns.

EXPERIMENTAL

Study Area. The moss species *Hypnum cupressiforme* was used as boimonitor to study an area of about 6000 km^2 located primarily on the territory of the Kardzhali municipality.

It spans 30 km to the North and South, and 55 km to the West and East from the smelter chimney.

A total of 77 moss samples were obtained in summer and autumn of 2011. The sampling strategy of the UNECE ICP Vegetation Programme on atmospheric deposition studies in Europe (United Nations Economic Commission for Europe, International Coopeative Programme on Effects of Air Pollution on Natural Vegetation and Crops) has been observed, with the exception of the recommended sampling network density. This was been altered due to the relatively small study area.

From each site 5–10 subsamples were taken within a 1 × 1 km area and were combined on field. Random samples outside the sampling network were also collected. In the town of Kardzhali, sampling density was higher. The sampled area is presented in Fig. 1. Using GPS, longitude and latitude were noted for all sampling sites. All collected samples were put into plastic bags for storage and transportation to the analytical laboratories.

NAA. NAA was performed in the radioanalytical laboratory at the fast pulsed reactor IBR-2 of the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research (FLNP JINR), Dubna, Russia. In the laboratory the unwashed samples were air-dried to constant weight at 40 °C for 48 h, and extraneous plant material was removed. Samples were sorted so that only the green living part of the moss, approximately corresponding to a three-year growth, was subjected to analysis. Moss samples of about 0.3 g were packed in polyethylene foil bags for short-term irradiation and in aluminum cups for long-term irradiation [12].

Long-term irradiation was performed using a cadmium-screened irradiation channel with neutron flux density $\Phi_{\mathrm{epi.}} = 3.6 \cdot 10^{11}$ n/(cm$^2 \cdot$ s) to determine long-lived isotopes. Samples were irradiated for 5 days, repacked and then measured twice, after 4–6 days and 20 days of decay, respectively. The interval of measurement varied from 1 to 5 h. To determine the short lived isotopes (Cl, V, I, Mg, Al, and Mn), a conventional irradiation channel was used. Samples were irradiated for 3 min and measured twice, after 2–3 min and 9–10 min of decay. Data processing was carried out using software developed at FLNP JINR. Qualitative and quantitative analysis was conducted on the basis of certified reference materials and flux comparators.

Quality Control. Three certified reference materials were used to conduct quality control: (RM) Lichen 336 IAEA (International Atomic Energy Agency), SRM-1575 (Pine Needles) from the US National Institute of Standards and Technology, and moss DK-1, prepared for calibration of laboratories participating in 1990 moss survey in Northern Europe. The reference materials were packed together with the samples in each transport container. The reference material showing least deviation between measured and certified values of elemental content was chosen.

ICP-AES and AAS Analyses. ICP-AES and AAS were carried out at the Sts. Cyril and Methodius University, Skopje, Macedonia. Atomic emission spectrometer with inductively coupled plasma, ICP-AES (Varian, 715ES), was used for analyzing the content of Ag, Cd, Cu, Li, P, and Pb. ICP-Multielement standard solution IV (Merck) with concentration of 1000 mg L^{-1} was used for preparation of standard solutions. Mercury was determined by cold vapor AAS (Varian, SpectrAA 55B), using a continuous flow vapor generation accessory (Varian, VGA-76).

For ICP-AES and AAS analyses about 0.5 g of moss material was placed in Teflon vessel and treated with 7 ml of concentrated HNO_3 and 2 ml H_2O_2 overnight. The procedure was continued with full digestion of moss material in microwave digestion system (Mars, CEM, USA). Digestion 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 [13].

Quality Control. The QC/QA of the applied techniques was performed by standard addition method, and it was found that the recovery for the investigated elements ranges for ICP-AES from 98.5 to 101.2%, for ETAAS and CVAAS from 96.9 to 103.2%. The same methods were applied for the determination of the analyzed elements in certificated reference materials M2 and M3 (moss samples). The sensitivity in regard to the lower limit of detection was done. Optimization of instrumental condition for analyzed elements was previously done [14]. Beside standard addition method, blanks parallel to the decomposition of samples and preparation of sample solutions for analysis were analyzed. The loss of Hg was checked by standard additions. The same sample was decomposed with and without addition of Hg. The added content of Hg was recovered in the solution obtained after microwave digestion [15].

RESULTS AND DISCUSSION

Table 1 contains descriptive data (median, minimum and maximum) from the present analyses, corresponding Bulgarian data from the 2010 European moss survey, concentration values from a similar lead-zinc mine area in Macedonia (samples collected in 2012 and analysis performed using ICP-AES, ETAAS and CVAAS) [16], and comparison data from Norway (2007, utilizing ICP-MS) [20], where the influence of air pollution is considered minor.

The juxtaposition of the data clearly illustrates that for the vast majority of elements, concentrations in the Kardzhali Municipality are the highest. Exceptions from this observation are only the median and maximum values for Mg, which are the lowest, even in comparison with the Norwegian data [20]. The median values for Pb, Cd, Zn, and Al greatly exceed the averaged median in Bulgaria (by factors of about 16, 9, 8, and 13, respectively) and in the Macedonian lead-zinc mine (by factors of 5, 6, 5, and 6, respectively). When comparing the maximum values for the same elements, the situation is similarly unfavorable. The content of Na, Co, Ni and Cr in the Kardzhali mosses is considerably higher than in Macedonia [16].

It has to be noted that due to the methods applied, some differences in the results are anticipated. These arise from their different sensitivities and the fact that ICP-AES and AAS are both destructive methods based on acid digestion, so refractory compounds present in the samples cannot be analyzed. NAA is a non-destructive method where the whole amount of the elements is detected.

Multivariate statistics (factor analysis) was used to identify and characterize different pollution sources. The Varimax method was used for orthogonal rotation of variables standardized to zero mean and unit standard deviation [17]. The number of elements was reduced to four synthetic variables or factors. The results are presented in Table 2. Factor analysis with Varimax rotation is an approved approach when utilizing the moss biomonitoring technique. It is widely used for interpretation of the results of large arrays of environmental data [18].

GIS maps for elemental distribution based on the results of factor analysis were built using AcrGIS 9.3 (Factors 1, 2, 3 and 4 in Figs. 2–5, respectively). Factor scores illustrating the contributions of individual sampling sites to the relevant factor are shown graphically.

Factor 1. Rare earth elements Hf, Ta, U, and Th are soil indicators, typical for heavy crustal material, and partly reflect the contamination of moss samples with soil particles. The high loadings for Na (0.83), Mg (0.70), Al (0.85), Sc (0.69), and Ti (0.71) represent light crustal material (silicate rocks), V (0.63) and Fe (0.79) could be attributed to a basaltic component. K (0.84), Rb (0.81), Sr (0.77), Mo (0.66), Cs (0.77), Ba (0.81) are most likely of vegetation origin.

Table 1. Descriptive statistics of elements determined in mosses obtained in Kardzhali Municipality, Macedonian mine environ and data from moss surveys in Bulgaria and Norway (mg/kg)

Elements	Kardzhali Municipality (present study)		Macedonian Pb-Zn mine environ [16]		Bulgaria 2010 [6]		Norway [20]	
	Median	Range	Median	Range	Median	Range	Median	Range
Li[a]	1.49	0.51–8.06	1.1	0.31–3.9				
Na	1320	179–9710	41	20–890				
Mg	943	366–3740	3200	1700–4800			1730	940–2370
Al	16300	4120–76400	2500	680–13000	1245	402–8886	200	67–820
P[a]	988	405–1831	770	410–1500				
Cl	160	77.10–601						
K	7250	3650–30900	4600	2000–9800				
Ca	11400	5520–21700	6500	2900–14000			2820	1680–5490
Sc	2.25	0.12–13.00					0.052	0.009–0.220
Ti	672	170–3990					23.5	12.4–66.4
V	17.9	6.30–124	3.1	0.76–9.7	3.07	0.96–22.4	0.92	0.39–5.1
Cr	13.3	2.71–260	2.1	0.84–5.1	2.06	0.72–38.1	0.55	0.10–4.2
Mn	450	56–3380	160	43–550			256	22–750
Fe	5800	1250–32400	2500	820–18000	1101	307–8546	209	77–1370
Co	2.47	0.43–23.50	0.53	0.16–2.6			0.202	0.065–0.654
Ni	9.48	1.4–213	2.7	1.1–6.4	2.61	0.84–82.1	1.14	0.12–6.6
Cu[a]	13.69	7–126	7.2	3.6–57	7.01	2–270		
Zn	185	25–3750	36	11–460	22.2	8.22–286	26.5	7.9–173
As	2.83	0.48–22.40	2	0.56–13	0.63	0.15–10.8	0.093	0.020–0.505
Se	0.43	0.07–2.54					0.33	0.05–1.30
Br	6.42	1.66–19.50					4.5	1.4–20.3
Rb	24.8	6.93–229					7.7	1.3–51.5
Sr	71.2	19.50–527	17	7.2–36			15.8	3.6–43.3
Mo	0.49	0.12–1.78					0.135	0.065–0.70
Ag[a]	0.57	0.14–4.43						
Cd[a]	1.85	0.19–21.11	0.31	0.06–3.7	0.21	0.043–7.75		
In	0.05	0.0003–0.42						
Sb	2.07	0.14–46.50					0.033	0.004–0.240
I	2.18	0.90–7.71					2.5	0.6–41.7
Cs	1.32	0.19–8.81					0.072	0.016–0.88
Ba	164	35–1050	45	11–140			17.1	5.6–50.5
La	6.38	0.92–40.60					0.189	0.045–2.56
Ce	14.50	1.67–91.30					0.342	0.095–4.61
Nd	5.97	0.96–35.10						
Sm	1.14	0.20–7.47					0.33	0.05–1.34
Tb	0.15	0.03–0.94					0.003	$<$ 0.002–0.030
Dy	0.95	0.03–6.24						
Tm	0.11	0.02–0.63						
Yb	0.53	0.04–2.62						
Hf	0.93	0.21–7.62						
Ta	0.18	0.04–1.38					0.01	$<$ 0.01–0.07
W	0.47	0.10–3.43					0.127	0.009–1.23
Au	0.002	0.001–0.024						
Hg[b]	0.05	0.03–0.14	0.03	0.021–0.08				
Pb[a]	124.85	4.21–2168	24	0.14–450	8	1.69–333		
Th	2.70	0.24–21.60					0.033	0.004–0.240
U	0.60	0.10–5.22					0.015	0.001–0.138

[a] Determined by ICP-AES. [b] Determined by AAS

**Table 2. Matrix of rotated factor scores, Varimax normalized.
Four main source types identified. Characteristic elements marked in bold type**

Variables	Factor 1	Factor 2	Factor 3	Factor 4
Li	0.52	–0.10	0.39	–0.15
Na	**0.83**	0.12	0.16	–0.10
Mg	**0.70**	–0.13	0.48	0.15
Al	**0.85**	–0.13	0.27	0.04
P	0.03	0.15	–0.09	0.59
Cl	0.02	0.13	–0.28	**0.60**
K	**0.84**	0.19	–0.14	0.19
Ca	0.28	–0.06	–0.06	0.35
Sc	**0.69**	–0.15	0.35	–0.05
Ti	**0.71**	–0.19	0.43	–0.13
V	**0.63**	–0.09	**0.48**	–0.20
Cr	0.13	0.07	**0.84**	0.09
Mn	0.23	–0.18	0.21	0.47
Fe	**0.79**	–0.05	0.44	–0.10
Co	0.46	0.02	**0.79**	0.03
Ni	0.08	0.08	**0.85**	0.09
Cu	0.03	**0.90**	–0.12	–0.07
Zn	0.05	**0.94**	–0.02	0.05
As	0.19	**0.68**	0.53	0.22
Se	–0.03	**0.80**	0.07	0.16
Br	–0.08	0.27	0.29	**0.73**
Rb	**0.81**	0.14	–0.11	0.32
Sr	**0.77**	0.03	–0.22	0.03
Mo	**0.66**	0.42	0.13	0.23
Ag	0.04	**0.96**	0.00	–0.05
Cd	0.08	**0.97**	–0.04	0.05
In	0.17	**0.89**	0.06	0.06
Sb	0.06	**0.96**	–0.08	0.02
I	0.03	0.05	0.35	**0.77**
Cs	**0.77**	0.09	–0.1	0.30
Ba	**0.81**	0.03	0.05	0.05
La	**0.89**	0.12	0.21	0.02
Ce	**0.92**	0.14	0.20	0.05
Nd	**0.77**	0.30	0.09	0.04
Sm	**0.93**	0.04	0.18	0.02
Tb	**0.89**	0.08	0.25	–0.03
Dy	**0.81**	–0.06	0.31	–0.03
Tm	**0.62**	0.11	0.54	–0.03
Yb	**0.89**	0.06	0.23	0.05
Hf	**0.90**	0.09	0.16	–0.04
Ta	**0.88**	0.05	–0.03	0.24
W	**0.78**	0.10	0.07	0.18
Au	0.07	**0.63**	0.15	0.11
Hg	0.12	**0.70**	–0.07	0.45
Pb	0.06	**0.98**	–0.03	–0.05
Th	**0.93**	0.15	–0.01	0.13
U	**0.90**	0.23	–0.01	0.13
Explained variance, %	*17.9*	*8.96*	*4.71*	*3.05*

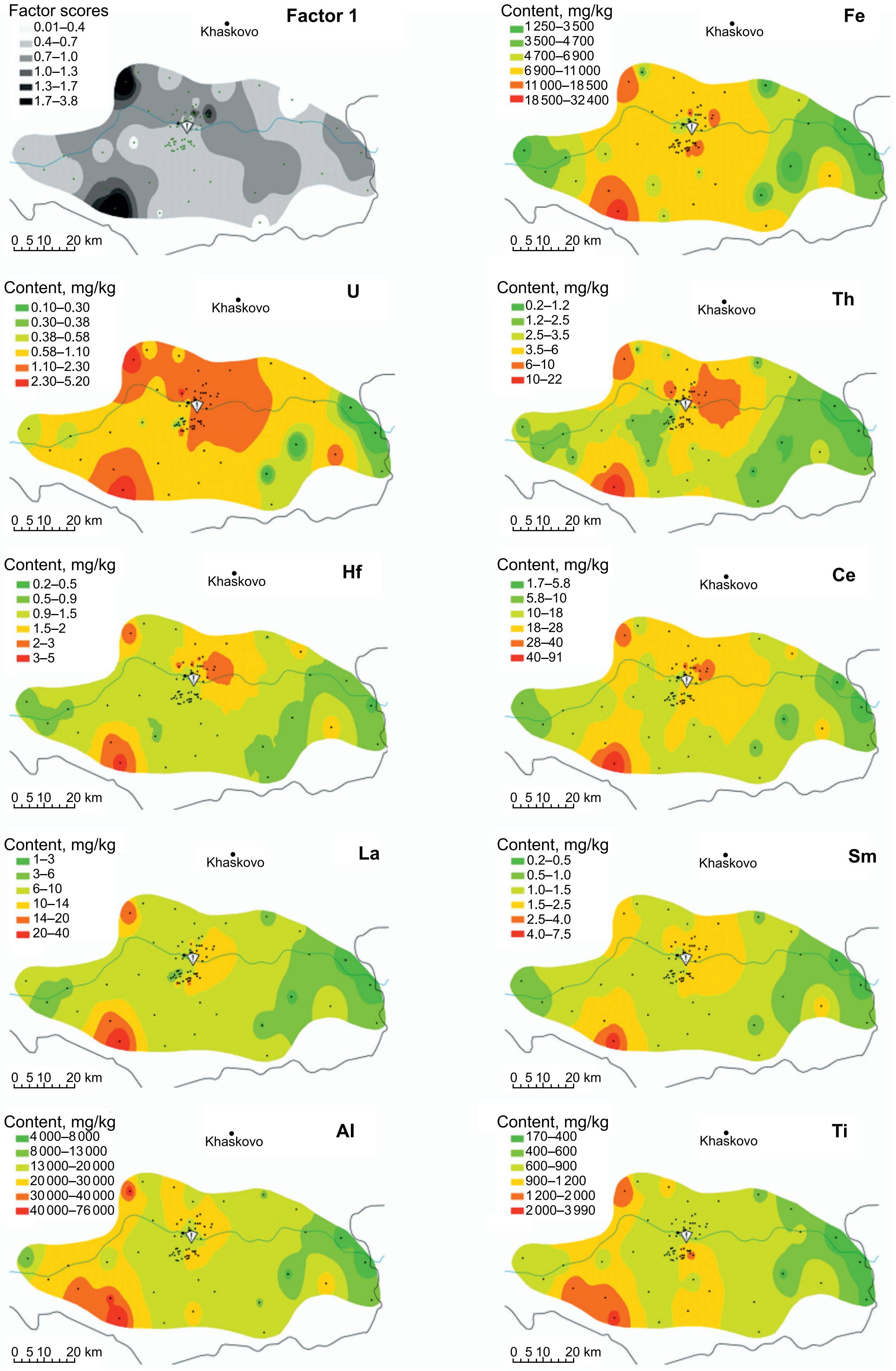

Fig. 2. Spatial distribution of Factor 1 scores and atmospheric deposition patterns for Fe, U, Th, Hf, Ce, La, Sm, Al, and Ti

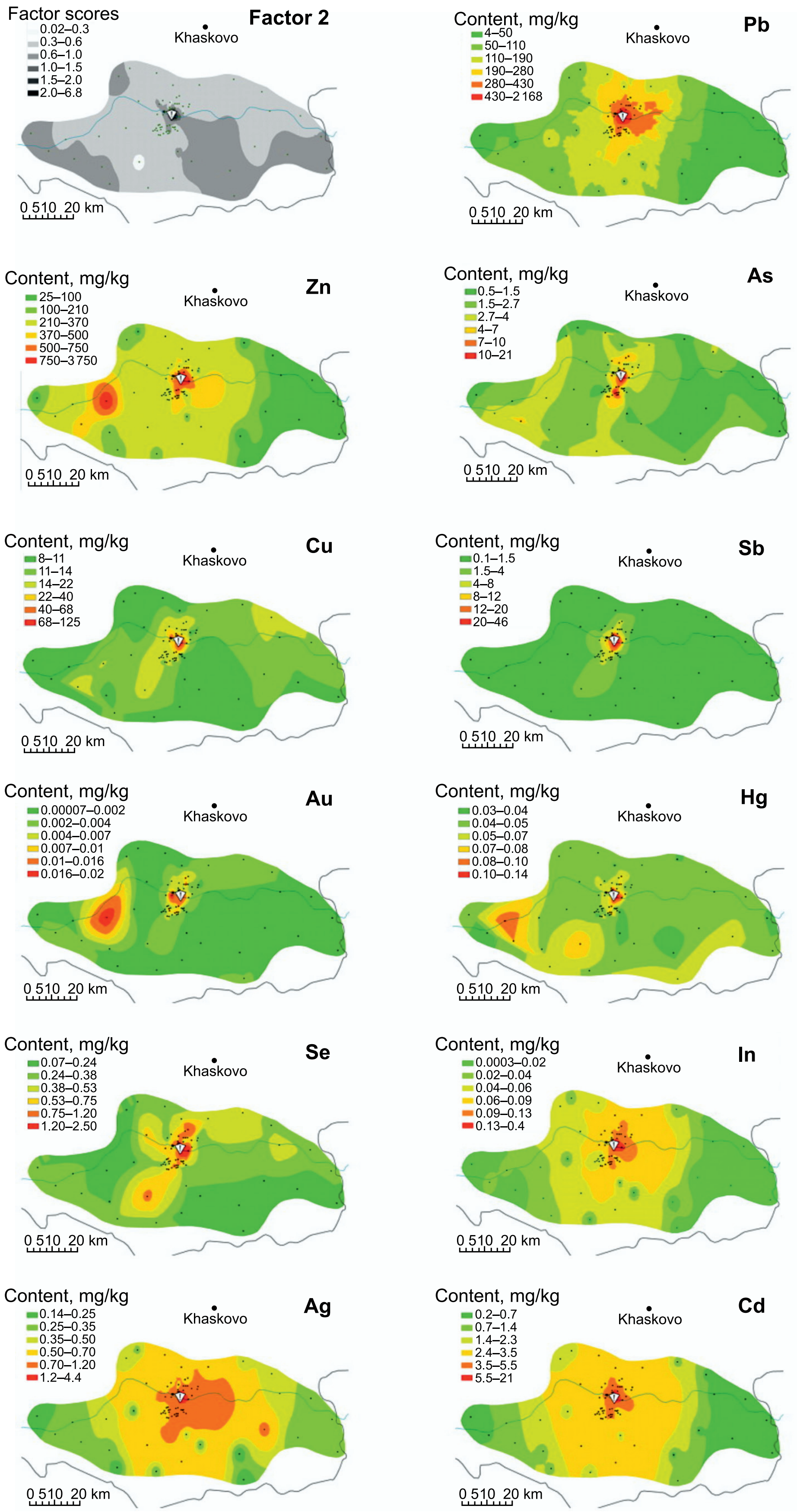

Fig. 3. Spatial distribution of Factor 2 scores and atmospheric deposition patterns for Pb, Zn, As, Cu, Sb, Au, Hg, Se, In, Ag, and Cd

Factor 2. The high loadings for Cu (0.90), Zn (0.94), As (0.68), Se (0.80), Ag (0.96), Cd (0.97), In (0.89), Sb (0.96), Au (0.63), Hg (0.70), and Pb (0.98) in this factor characterize the Kardzhali LZP productions.

This group of elements is also found in the investigation of surface soils around a lead and zinc smelter in the Republic of Macedonia [19].

For this factor, the highest factor score is observed on the sampling site closest to the smelter chimney.

When inspecting the data obtained on the territory of the town of Kardzhali, where the sampling network has the highest density, and comparing it with the averaged values determined for the exterior sites, disparities were observed. There is a significant difference between the obtained maximum, minimum and median values for the concentrations of the elements Cu, Zn, Ag, Cd, In, Sb, and Pb in and outside the town. For Pb, the maximum determined concentration in the territory of the town exceeds the maximum concentration measured in the vicinity by a factor of 55. Minimum and median values in Kardzhali exceed the corresponding values in the suburban area by a factor of 4.

Sb content in the town has a maximum value 23 times higher than in the suburbs. The median value is higher by a factor of 10 and the minimum — by a factor of 3.

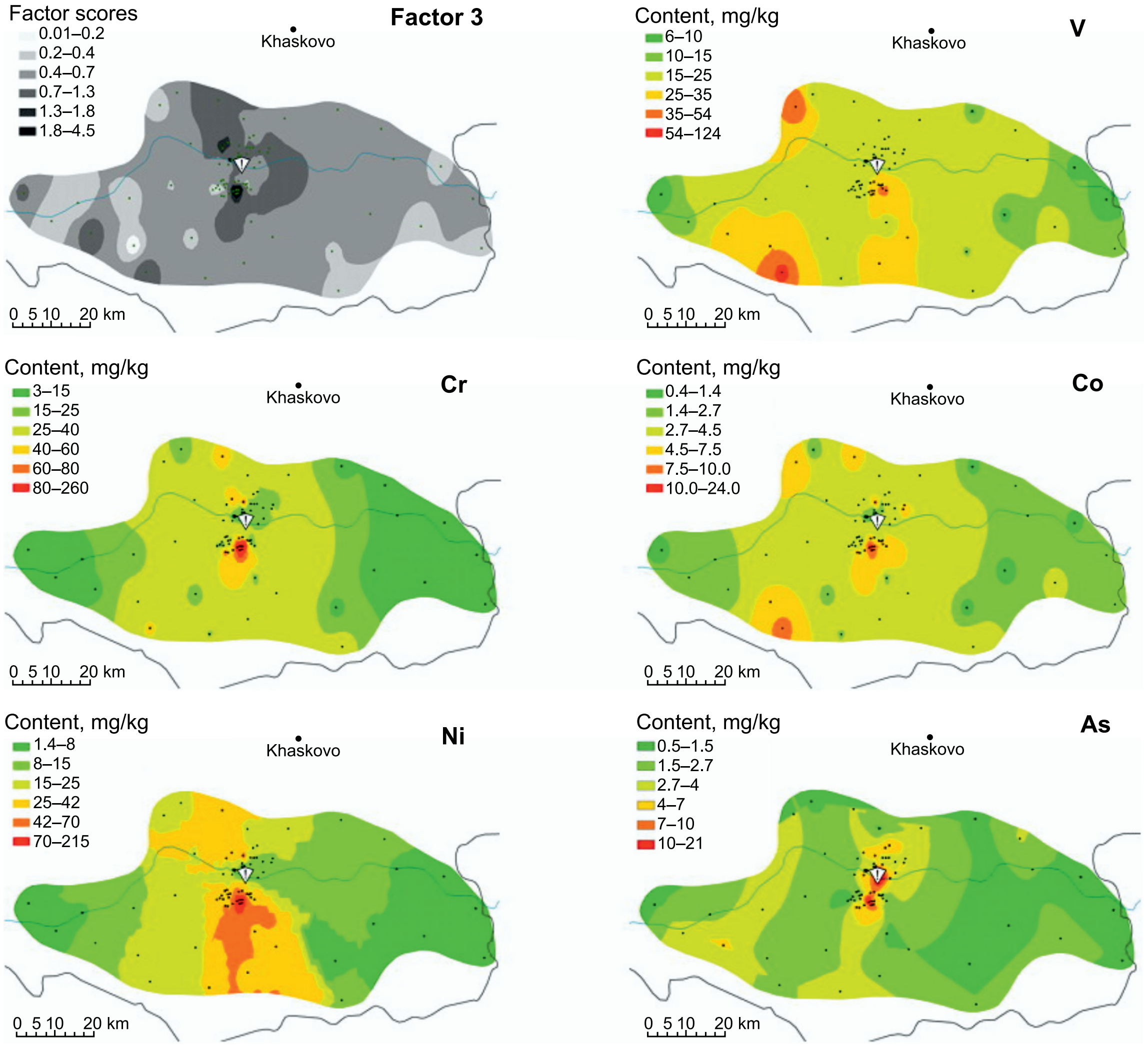

Fig. 4. Spatial distribution of Factor 3 scores and atmospheric deposition patterns for V, Cr, Co, Ni, and As

The maximum obtained In concentration from the town exceeds the corresponding value from the extra urban area by a factor of 144. The minimum and median values are higher on the territory of the town by a factor of 2 and 3, respectively.

Cd content in Kardzhali has a maximum value 13 times higher than the corresponding value for the vicinity. Minimum and median values are both 3 times higher in the town than outside of its territory.

The maximum determined Ag concentration from mosses obtained in Kardzhali is 4 times higher than the Ag concentration in the extra urban area. The minimum and median values are higher in the town by a factor of 3.

In the town, the maximum determined concentration for Zn is 7 times higher than the corresponding content outside of the town. The minimum and median values are higher in Kardzhali by a factor of 3 and 4, respectively.

The maximum and median values for the measured Cu content in the urban area are higher than the corresponding values determined in the suburbs by a factor of 3. The minimum value is 4 times higher in Kardzhali than in the extra urban area.

Factor 3. Contamination from metallurgical industry is associated with the high values for V (0.48), Cr (0.84), Co (0.79), and Ni (0.85) in this factor. The studied area is rich in ore deposits and is characterized by extensive mining activities which took place in the past but have dwindled nowadays. The elemental deposition maps indicate such sites in the south-west and south-east of the plant (Fig. 4). The highest factor loadings for this factor are found in sampling sites located nearby an open quarry used for the production of building materials such as sand, rubble, and cement. The quarry is used for extraction of perlite, betonite (Na-Ca type), zeolite, marble, gneiss, tuff, limestone, and obsidian.

Factor 4. The combination of high values for Cl (0.60), Br (0.73), and I (0.77) in one factor usually suggests a “marine” contribution to the air pollutants. The climate on the territory of the municipality is Continental-Mediterranean [21] and is not influenced strongly by the proximity to the Back Sea. The north-south direction of the wind rose and the seasonal impact on the atmospheric circulation by the Aegean Sea agree with the marine interpretation.

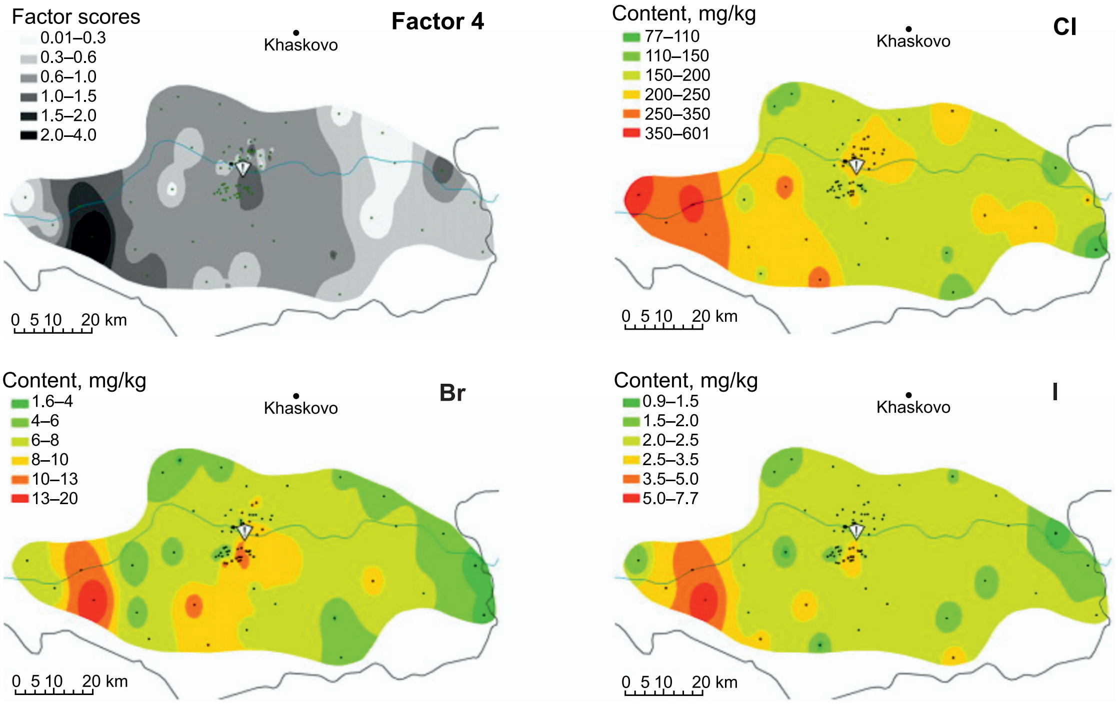

Fig. 5. Spatial distribution of Factor 4 scores and atmospheric deposition patterns for Cl, Br, and I

CONCLUSIONS

Besides the well-known hazardous contaminants Pb, Zn, and Cd (first group of toxicity), elements posing a risk to the human health like Se, Ti, Cr, Cu, Ni, Al, As, Hg, and Mo (first, second and third groups of toxicity) were determined. The anthropogenic association of elements including Ag, As, Au, Cd, Cu, Hg, In, Pb, Sb, Se, and Zn presents typical group of elements in Pb-Zn concentrates processed in the smelter plants as well in the produced metals. Therefore similar distribution patterns of element-pollutants for any lead-zinc plant may be expected taking into consideration the peculiarities of the landscape and productive capacity of the Pb-Zn plant. The data obtained, used in conjunction with the results from the state monitoring programs, could provide for a better estimation of health and environmental risk, and risk-management decisions. Moss biomonitoring surveys could be of great use as they provide a cost-effective and efficient means for a time-integrated assessment of the environmental situation and evaluation of anthropogenic changes.

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