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A study on the environmental situation in the area of the Kardzhali lead-zinc plant using the moss technique, neutron activation analysis, atomic absorption spectrometry, and GIS technology

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The results of a study on atmospheric deposition of trace elements using the moss biomonitoring technique in the area of the lead-zinc plant in Kardzhali are reported. This plant is the main source of lead, cadmium, zinc and sulphur oxide contamination. Various moss types were used to study atmospheric deposition of trace elements in 54 sampling sites. The concentrations of the following elements Na, Mg, Al, Cl, K, Sc, Ca, Cr, Ti, V, Mn, Ni, Fe, Co, Zn, Se, As, Br, Rb, Sr, Mo, In, Sb, I, Cs, Ba, La, Ce, Sm, Tb, Dy, Hf, Ta, W, Au, U, Th were determined by means of instrumental epithermal neutron activation analysis (ENAA) at the IBR-2 reactor of FLNP JINR, Dubna. Multivariate statistics was applied to characterize the pollution sources. GIS technology allowed apportioning the deposition patterns of element pollutants in the study area. The present investigation is a continuation of the environmental surveys in Bulgaria used to regulate the Bulgarian industries.

Keywords*: atmospheric deposition of trace elements, moss biomonitoring, lead-zinc plant, neutron activation analysis*

INTRODUCTION

The use of terrestrial mosses as biomonitors in large-scale multielement studies of heavy metal deposition from the atmosphere is a well-established technique in Europe. The present study is part of the UN European Cooperative Programme „Atmospheric Heavy Metal Deposition in Europe" aimed at investigating the long-range transboundary air pollution in Europe at 5-year intervals [1].

This paper presents results from the moss survey in 2011 around the Kardzhali lead-zinc plant (LZP) known for its non-ferrous metal deposits. According to the Ministry of Environment and Water, Kardzhali is one of the ecological "hot spots" in Bulgaria.

The manufacturing process in Kardzhali is a major source of contamination with significant amounts of heavy metals and other toxic elements (*e.g.* Pb, Zn, Cd, As, Sn) in the soil, water and air. These inflict environmental damage to the region of research interest. Due to the constant circulation of chemical elements in nature, contaminants such as trace metals and their compounds are effectively deposited onto mosses after being released into the air.

Since mosses have no root system, the soil has insignificant influence on the concentration of trace metals found in them.

EXPERIMENTAL

Study Area

Figure 1 shows allocation of the sampling area in the map of Bulgaria. The study area of about 110 km^2 is located around LZP Kardzhali. It spans 6 km to the North and South and 5 km to the West and East from the plant's chimney.

Fig. 1. Study area.

About 6% of the world zinc deposits and about 3% of the lead deposits are located in Bulgaria. 75% of the lead-zinc ore is located in the Rhodope Mountains and over 70% of the total available ore

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is mined. Annually, LZP Kardzhali produces 27,200 tons of zinc, 30,000 tons of lead and 45,000 tons of sulfuric acid. After a project to increase lead production in the plant was accepted, the annual production will rise up to 60,000 tons by 2014 [2].

Surveys in the area of Kardzhali, particularly in the last few years, show increased trace metals content in the soil and the plants, including mosses, as a consequence of mining polymetallic ores, flotation and heavy metal production. The approximate size of the land affected by aerogenic lead contamination with higher than the admissible concentrations is about 40,000 da of virgin soil and about 18,000 da of arable lands [3].

Sampling

A total of 77 moss samples, of which *Hypnum cupressiforme* was the dominant type, were collected according to the sampling strategy of the UNECE ICP Vegetation Programme on atmospheric deposition studies in Europe [1]. For each site 5-10 subsamples were taken within a 50 X 50 m area and were combined in the field.

Sample Preparation

The unwashed samples were air-dried to constant weight at 40 °C for 48 h, and extraneous plant material was removed. The whole living part corresponding approximately to three years growth of the moss was subjected to analysis. Therefore, the results from the survey represent the average deposition situation over the period 2008-2010 for the elements retained in the moss. Moss samples of about 0.3 g in weight were packed in polyethylene foil bags for short-term irradiation to determine short-lived isotopes, and in aluminum cups for long-term irradiation for determination of long-lived isotopes.

Analysis

Neutron activation analysis (NAA) was performed in the radioanalytical laboratory at the pulsed fast reactor IBR-2 of the Frank Laboratory of Neutron Physics, JINR, Dubna, Russia [4].

Long-lived isotopes were determined using epithermal neutrons in cadmium-screened irradiation channel with neutron flux density Φ_{epi}.= 3.6×10^{11} n/(cm$^2\times$s). Samples were irradiated for 5 d, re-packed and then measured twice after 4–6 and 20 d of decay, respectively. Measuring time varied from 1 to 5 h. To determine the short lived isotopes (Cl, V, I, Mg, Al, and Mn) conventional irradiation channel was used. Samples were irradiated for 3 min and measured twice after 2–3 min and the second one for 20 min after 9–10 min of decay.

The concentration of the environmentally meaningful element Pb cannot be determined by INAA, and Cu and Cd are difficult for determination at low concentration levels. These elements will therefore be determined by atomic absorption spectrometry (AAS) at the Sts. Cyril and Methodius University, Skopje, Macedonia in the nearest future.

RESULTS AND DISCUSSION

At the time of writing, 54 samples were analyzed. The results of the descriptive statistical analysis of the elemental concentrations determined in the moss samples (min, max, mean and median) are given in Table 1 along with data for the neighboring Macedonia[5].

For comparison, the corresponding values for the Norwegian moss data representing territories with minor influence from air pollution[6] are given in the same table.

Multivariate statistics (factor analysis) was used to identify and characterize different pollution sources. The results of factor analysis are presented in Table 2.

Values of the four factors are given in Table 2.

Factor 1 has particularly high values of K, Rb, Sr, Mo, Cs, Ba, typically found in plants and of rare earth elements (REEs), Hf, Ta, U, and Th, which are soil indicators. Most of these elements are typical of heavy crustal material, and they partly reflect the contamination of moss samples with soil particles.

Factor 2 has high factor loadings particularly for Na, Mg, Al, Sc, Ti, which are typical light crustal material (silicic rocks), as well as for V, Fe, and Co, which could be attributed to a basaltic component.

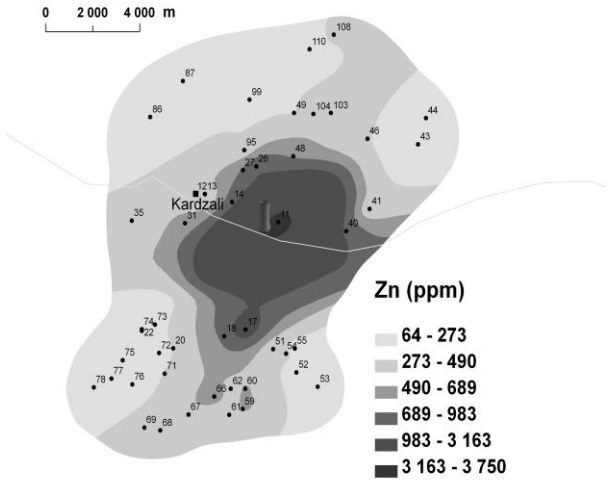

Fig. 2. The geographical distribution map of Zn relevant to factor 3.

Factor 3 has high loadings for Zn, Se, As, In, Sb, Au associated with the Kardzhali LZP. This group of elements correlates very well with metal contamination of surface soils around the lead and zinc smelter in the Republic of Macedonia [7] .

Factor 3 is illustrated by the distribution map for Zn (Figure 2) as the main polluting elements of ZLP in Kardzhali with the maximal concentrations of Zn exceeding the normal (unpolluted values, taken from the Norwegian data), by the order of 10-100. The highest concentrations of Zn are observed in sampling points 11, 14, 18, and 17 and 40. The town of Kardzhali is experiencing tremendous impact of elements, associated with lead-zinc ores. To construct this map the program ArcGIS 9.3 with geostatistical analysis was used.

Factor 4 seems to be a mixture of two factors: high values of Cr, Ni, Co, and As indicate the presence of industrial pollution. High values for Br and I usually considered as "marine" elements, given the lack of elements such as Na and Cl in this factor, suggest heavy fuel oils used in the smelting process at the LZP plant as a source of pollution.

Table 1. Comparison of the results obtained with Macedonia and Norway, mg/kg

Elements	Bulgaria, LZP		Macedonia [5]		Norway [6]	
	median	range	median	range	median	range
Na	1525	179-8190	419	118-8673	–	–
Mg	1006.5	366-3730	2377	674-7421	1730	940-2370
Al	17400	4120-53800	3736	825-17600	200	67-820
Cl	162	78.6-601	149	43-693	–	–
K	7585	3650- 30900	8615	2861-18190	–	–
Ca	11450	5520- 21700	5593	1207-23640	2820	1680-5490
Sc	2.415	0.12- 13-	0.81	0.12-6.79	0.052	0.009-0.220
Ti	716	170- 3990	163	12-1365	23.5	12.4-66.4
V	20	6.3- 124	6.9	1.79-43	0.92	0.39-5.1
Cr	14.4	2.71- 260	7.47	2.33-122	0.55	0.10-4.2
Mn	424	56- 1700	186	37-1475	256	22-750
Fe	6440	1250- 32400	2458	424-17380	209	77-1370
Co	2.64	0.43- 23.5-	1.09	0.24-13.6	0.202	0.065-0.654
Ni	10.7	1-213	2.4	0.09-24	1.14	0.12-6.6
Zn	269	28.8-3750	39	14-203	26.5	7.9-173
As	3.18	0.479-22.4	0.80	0.12-8.0	0.093	0.020-0.505
Se	0.54	0.1-2.54	0.18	0.013-0.61	0.33	0.05-1.30
Br	6.65	1.66-19.5	2.16	0.06-7.7	4.5	1.4-20.3
Rb	31.5	6.93-229	10.9	5-47	7.7	1.3-51.5
Sr	81.2	19.7-527	31	11.8-136	15.8	3.6-43.3
Mo	0.54	0.121-1.78	0.19	0.03-1.12	0.135	0.065-0.70
In	0.074	0.014-0.424	–	–	–	–
Sb	3.93	0.162-46.5	0.2	0.039-1.4	0.033	0.004-0.240
I	2.26	0.90-4.87	1.18	0.36-2.8	2.5	0.6-41.7
Cs	1.46	0.19-8.81	0.39	0.097-1.7	0.072	0.016-0.88
Ba	165.5	35.2-847	54	14-256	17.1	5.6-50.5
La	6.93	0.924-227.2	2.32	0.50-22	0.189	0.045-2.56
Ce	17.35	1.67-52	5.60	0.83-42	0.342	0.095-4.61
Sm	1.27	0.199-3.82	0.46	0.07-3.4	0.33	0.05-1.34
Tb	0.174	0.026-0.476	0.06	0.01-0.56	0.003	<0.002-0.030
Dy	1.09	0.218-3.55				
Hf	1.04	0.25-7.62	0.26	0.05-3.8	–	–
Ta	0.22	0.04-1.48	0.09	0.013-0.79	0.01–	<0.01-0.07
W	0.55	0.107-2.15	1.21	0.25-3.9	0.127	0.009-1.23
Au	0.004	0.00107-0.0235	0.0061	0.001-0.034	–	–
Th	3.215	0.244-19	0.67	0.12-7.6	0.033	0.004-0.240
U	0.856	0.102-5.22	0.21	0.03-1.45	0.015	0.001-0.138

Table 2. Factor analysis of NAA data on moss samples collected in the vicinity of Kardzhali LZP (Varimax normalized)

Variables	Factor 1	Factor 2	Factor 3	Factor 4
Na	0.48	**0.65**	0.25	-0.06
Mg	0.37	**0.73**	-0.03	0.29
Al	**0.55**	**0.71**	-0.03	0.05
Cl	0.34	-0.38	0.23	0.03
K	**0.86**	0.24	0.23	-0.06
Sc	0.30	**0.64**	-0.11	0.18
Ca	0.46	-0.09	-0.04	0.14
Cr	-0.02	0.34	-0.02	**0.84**
Ti	0.14	**0.91**	-0.05	0.06
V	-0.01	**0.91**	0.05	0.07
Mn	0.33	0.45	-0.06	0.11
Ni	-0.04	0.34	-0.03	**0.84**
Fe	0.45	**0.69**	0.01	0.28
Co	0.11	**0.57**	0.01	**0.72**
Zn	0.07	-0.03	**0.96**	-0.04
Se	-0.02	-0.12	**0.82**	0.08
As	0.15	0.21	**0.65**	**0.57**
Br	0.10	-0.14	0.36	**0.59**
Rb	**0.89**	0.12	0.12	0.06
Sr	**0.72**	0.23	0.01	-0.23
Mo	**0.62**	0.24	0.49	0.20
In	0.15	0.03	**0.89**	0.07
Sb	0.07	-0.08	**0.95**	-0.10
I	0.29	-0.09	0.16	**0.73**
Cs	**0.92**	0.055	-0.01	0.15
Ba	**0.62**	0.53	0.18	-0.05
La	**0.67**	0.49	0.18	0.19
Ce	**0.75**	0.48	0.17	0.20
Sm	**0.74**	0.52	0.09	0.15
Tb	**0.64**	**0.61**	0.07	0.16
Dy	0.47	**0.69**	-0.05	0.08
Hf	**0.81**	0.41	0.08	0.037
Ta	**0.92**	0.24	-0.02	0.08
W	**0.82**	0.23	0.08	0.23
Au	0.13	0.05	**0.64**	0.18
U	**0.81**	0.29	0.28	0.01
Th	**0.91**	0.26	0.14	0.05
Expl. Var	*11.1*	*7.5*	*5.0*	*3,7*

CONCLUSIONS

As evident from the median values in Table 1, it is clear that the study area around the Kardzhali LZP is considerably polluted compared to previously obtained data for the other areas of Bulgaria [8].

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ИЗСЛЕДВАНЕ НА СЪСТОЯНИЕТО НА ОКОЛНАТА СРЕДА В РАЙОНА НА ОЛОВНО-ЦИНКОВ ЗАВОД КРАЙ КЪРДЖАЛИ ЧРЕЗ ИЗПОЛЗВАНЕ НА МЪХОВА ТЕХНИКА, НЕУТРОНЕН АКТИВАЦИОНЕН АНАЛИЗ, АТОМНО-АБСОРБЦИОННА СПЕКТРОМЕТРИЯ И ГИС ТЕХНОЛОГИИ

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(Резюме)

Представени са резултатите от изследванията на атмосферното замърсяване с тежки метали с помощта на биомониторинг на мъхове в района на оловно – цинковия комбинат в Кърджали. Този комбинат е основен източник на замърсяване с олово, кадмий, цинк и серен диоксид. За изучаване на атмосферното замърсяване бяха събрани проби от мъхове от 54 точки. Определени са концентрациите на следните елементи Na, Mg, Al, Cl, K, Sc, Ca, Cr, Ti, V, Mn, Ni. Fe, Co, Zn, Se, As, Br, Rb, Sr, Mo, In, Sb, I, Cs, Ba, La, Ce, Sm, Tb, Dy, Hf, Ta, W, Au, U, Th с помощта на инструментален епитермичен неутронен активационен анализ (ЕНАА) при реактор ИБР – 2 в лабораторията по неутронна физика на ОИЯИ, Дубна. За характеризиране на различните източници на замърсяване е използван многофакторен анализ. С помощта на GIS технологии са построени карти на разпределението на замърсяванията с различни елементи в изучавания район. Представените резултати са продължение на изследванията на околната среда в България, които се използват за регулиране на българската индустрия.