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BIOMONITORING OF HEAVY METAL DEPOSITION IN THE SOUTH URAL REGION: SOME PRELIMINARY RESULTS OBTAINED BY NUCLEAR AND RELATED TECHNIQUES

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Биомониторинг выпадений тяжелых металлов на Южном Урале: некоторые предварительные результаты, полученные с использованием ядерно-физических аналитических методов

Представлены результаты анализа мхов-биомониторов, используемых для изучения атмосферных выпадений тяжелых металлов в районе г. Магнитогорска, центра металлургической промышленности России. Образцы мха собраны в 30 км к северо-западу от Магнитогорского металлургического комбината и проанализированы методом эпитеплового нейтронного активационного анализа (ЭНАА). Всего были определены концентрации 38 элементов, включая Pd, Cd и Cu, определенных методом атомно-абсорбционной спектроскопии (ААС). Полученные результаты сравнивались с литературными данными для наиболее загрязненных регионов в Центральной и Северной Европе, а также с фоновыми значениями (Норвегия), полученными с помощью той же техники биомониторирования. Концентрация Sb в исследуемом районе оказалась самой высокой по сравнению с ранее опубликованными данными. Уровни Fe, Cr и V также оказались довольно высокими. При помощи сканирующего электронного микроскопа (SEM-XRF) исследовалась поверхность образцов мха. При увеличении в 3500-5000 раз были получены фотографии сферул железа и других аэрозольных частиц. Приведенные спектрограммы позволяют идентифицировать неорганическое и органическое происхождения этих образований.

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Biomonitoring of Heavy Metal Deposition in the South Ural Region: Some Preliminary Results Obtained by Nuclear and Related Techniques

The first results are reported from the analysis of feather mosses used to study heavy metal atmospheric deposition in the vicinity of Magnitogorsk, the center of the steel industry in Russia. Moss samples collected at sites 30 km to the north-west of the industry were analyzed by instrumental neutron activation analysis using epithermal neutrons (ENAA). Results for a total of 38 elements are reported, including Pb, Cd, and Cu determined by atomic absorption spectroscopy (AAS). The element concentrations in moss samples from this work are compared with relevant literature data for strongly polluted areas in Central and Northern Europe and background values from Norway obtained by the same biomonitoring technique. The concentrations of Sb in the examined area are the highest ever reported for mosses, and also levels of Fe, Cr, and V are found to be particularly high. A scanning electron microscope connected to an XRF analyzer (SEM-XRF) was used to examine the surface of the moss samples. Photographs of identified iron spherules along with other aerosol particles made at magnification of 3500 to 5000 times and corresponding XRF analyses verifying the nature of typical particles are presented.

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

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1. Introduction

The use of terrestrial mosses as biomonitors in large-scale, multi-element studies of heavy metal deposition from the atmosphere is a well-established technique in Europe.[1-3] The applicability of this method to monitoring the environmental situation around an iron smelter was demonstrated in a previous paper employing ENAA for the elemental determinations.[4] To the best of our knowledge however very few other studies have been carried out to estimate the environmental impact of particulate emissions from steel and iron smelters.

The region of the South Ural Mountains is ranked as the most severely polluted in all of Russia and probably is among of the most polluted areas in the world because of a high concentration of industrial enterprises of the former Soviet Union and the Russian Federation. As a result, the environment in the area has reached a state of deep ecological stress.[6,7] Chelyabinsk and Magnitogorsk are on the list of Russian cities characterized by the highest level of air pollution. Magnitogorsk, the «City of Steel», is located about 1500 km east of Moscow, near historically rich ore and energy deposits.

Following an international workshop in 1997 on Air Pollution in the Ural Mountains[8] a pilot project on a limited geographical scale was initiated in order to test the feasibility of the moss technique to study the regional air pollution situation in the south Ural region. Results from this study are presented here.

2. Experimental

Sampling

The selected sampling sites, situated in an area near around Lake Bannoe about 30 km north-west of Magnitogorsk, are shown in **Fig. 1**. The sampling was carried out according to a standard procedure described in detail elsewhere.[9] At each site around 10 subsamples were taken within a 50x50 m area and combined to one collective samples. The unwashed samples were air-dried at 30 °C and extraneous plant material was removed. The three youngest fully developed segments of *Hylocomium splendens* or the green part of *Pleurozium schreberi* or *Abietinella abietina* were taken for analysis. No further homogenization of samples was performed. Disposable polyethylene gloves were used during all handling of samples.

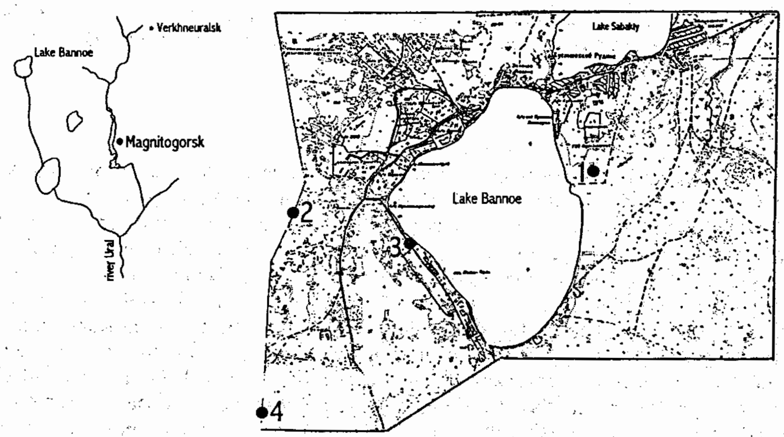


Fig.1. Location of study area and individual sampling points.

Analysis

Moss samples of about 0.3 g were heat-sealed in polyethylene foil bags for short-term irradiation and packed in aluminum cups for long-term irradiation in the pulsed fast reactor IBR-2 in Dubna. Neutron flux density characteristics and the temperature in the channel equipped with a pneumatic system are given in **Table I.**

Table I. Characteristics of the irradiation channels[10]

Irradiation site	$\phi_{th} \times 10^{12}$ (n/cm^2 s) E =0÷ 0.55 eV	$\phi_{epi} \times 10^{12}$ (n/cm^2 s) E=0.55÷10^5 eV	$\phi_{fast} \times 10^{12}$ (n/cm^2 s) E=0.1÷25 MeV	<E_{fast}> Mev E=0.1÷25 MeV	Temperature, °C
Ch1 Cd coat	0.023	3.31	4.32	0.88	70
Ch 2	1.23	2.96	4.10	0.92	60

The elements Sc, Cr, Fe, Co, Ni , Zn, As, Se, Br, Rb, Ag, Sb, Cs, Ba, La, Ce, Sm, Tb, Yb, Hf, Ta, W, Au, Th and U, were determined using channel 1 (Ch1). Samples were irradiated for 4 d. After 4-5 days of decay the samples were repacked and then measured twice for medium and long-lived isotopes twice respectively. Measuring time varied from 1 to 5 h. To determine the short-lived isotopes of Mg, Al, Cl, V, Mn, Cu, Al, In, and I, channel 2 (Ch2) was used. Samples were irradiated for 5 min and measured twice after 3-5 min and 20 min of decay for 5-8 and 20 min, respectively. To determine K and Na the same samples were re-irradiated for additional 30 min, and after 12-15 h of decay measured for 30 min.

Gamma spectra were measured using Ge(Li) detectors with a resolution of 2.5 keV for the ^{60}Co 1332.5 keV line, with an efficiency of about 6% relative to a 3×3′′ NaI detector for the same line. Data processing and element concentration determinations were performed using software developed in Dubna.[11] For long-term irradiation in Ch1 single comparators of Au (1 µg) and Zr (10 µg) were used. For short-term irradiation in Ch2 a comparator of Au (10 µg) was used.

Lead, cadmium and copper were determined by flame AAS at the Geological Institute of RAS, Moscow.

The accuracy of the analyses was checked using certified reference materials: bottom sediment SDM (International Atomic Energy Agency, Vienna) and Nordic moss DK-1.[12]

3. Results and discussion

Mean values and the ranges for a total of 38 elements determined in the present moss samples are presented in Table II. Literature data on mosses from nationwide surveys in Germany and Poland[1] and from the vicinity of an iron smelter in northern Norway[4] are shown for comparison, as well as typical background concentrations of the elements in question from previous studies.[13,14] It appears from this comparison that whereas heavy mertals such as Cu, Pb, and U show concentrations in the moss near background levels, the values of V, Cr, Fe, and As are rather high compared to the literature values and clearly indicate a significant contribution from the Magnitogorsk steel industries. In one particular case, *i.e.* for Sb, the present results (12-29 ppm) are far above any comparable values previously reported for mosses, and clearly indicate strong pollution with this element in the Magnitogorsk region. In that connection it may be noted that in a study of trace elements in human cancer *mammae* carried out in Magnitogorsk[15] the reported tissue concentrations of Sb were about 5 times higher than the normal level. Persons suffering from cancer had significantly higher levels than healthy persons.

In order to better distinguish between contribution from air pollution and a crustal component from windblown soil particles enrichment factors (EF = $(X/Sc)_{moss}/(X/Sc)_{crust}$) were calculated[16] and plotted in **Fig. 2.** Typical crustal components such as Al, REE, Th, etc. show EF values near unity, whereas values appreciably above that level indicates that the element in question is either enriched in the moss by active biological processes (K, Ca,) or stems from atmospheric deposition. It may be noted that V and Fe, in spite of their high concentrations in the moss, are enriched only a factor of 2-3 over the expected crustal contribution, whereas other heavy metals such as Cr, Zn, As, Se, Ag, Cd, Sb, and Au are enriched 10 times or more, clearly indicating that these elements represent a regional pollution problem.

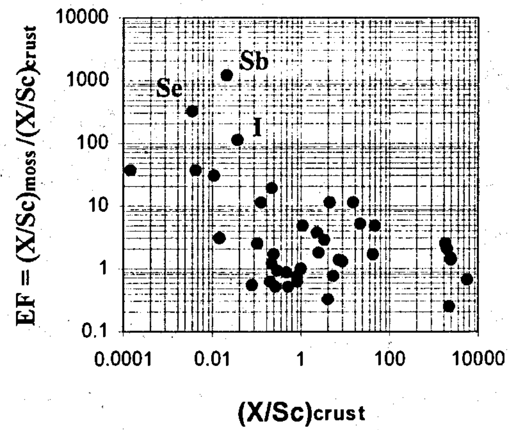
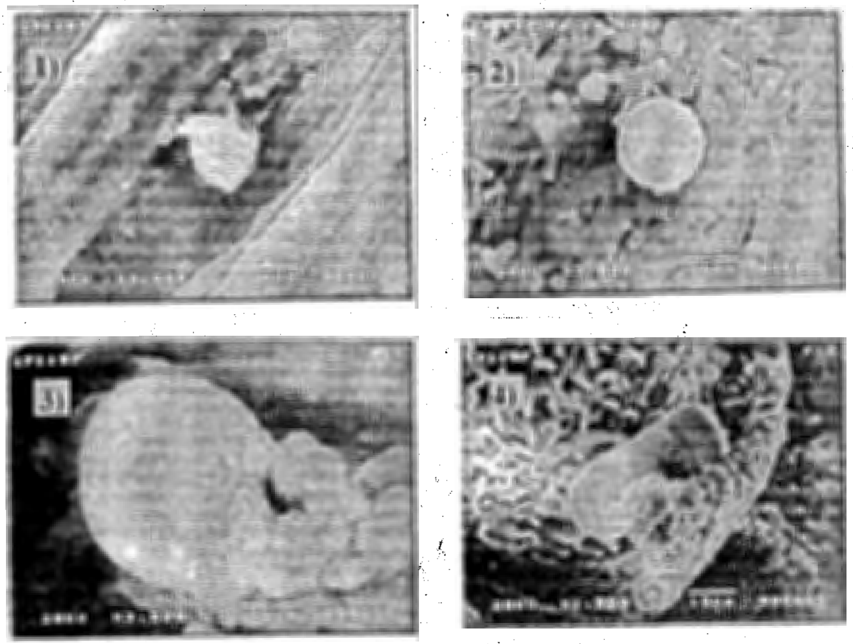


Fig. 2. Enrichment factors of elements studied (Turekian, Model A).

In addition to the ENAA a study of particulate matter and aerosol particles captured on the moss surface was carried out using scanning electron microscope and XRF analysis (SEM-XRF). Photographs of particles (spherules) on the surface of moss samples (**Fig. 3**) and corresponding spectrograms (**Fig. 4**) were obtained. An iron particle containing a certain amount of Mg on the surface of moss *Hylocomium splendens* is seen in **Fig. 1.1** (magnification 5000). It corresponds to the spectrogram in **Fig. 4.1** showing distinct Fe and Mg peaks. A spherule of pure iron (**Fig. 1.2**, magnification 3500) captured by the moss *Pleurozium schreberi* (note the spelling) is documented by the spectrogram shown in **Fig. 4.2. Fig. 3.3** (magnification 3500) shows a large Al-Fe cluster particle with apparent impurities of Zn, Cu and Ti as follows from the spectrogram in **Fig. 4.3.** A living object - a diatomic alga having a SiO_2 skeleton and soft tissue inside - is shown in **Fig. 4.4** (magnification 1500); corresponding spectrogram is shown in **Fig. 4.4. Fig. 3.5** shows a moss segment at different magnifications, 150 and 750, respectively. The presence of Au, Zn, Cu peaks in all spectra is explained by the specific conditions used in the X-ray analysis: Au is due to spattering, Zn and Cu are from a brass table used for sample examination.



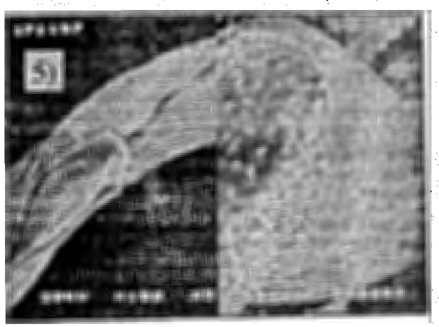


Fig. 3. SEM photographs of different mosses and particles captured by them.

1 - Fe particle with Mg impurity
2 - Spherule of pure iron
3 - Al-Fe cluster particle with impurities of Zn, Cu, and Ti
4 - Diatomic alga
5 - Segment of *Pleurozium schereberi* moss at different magnifications

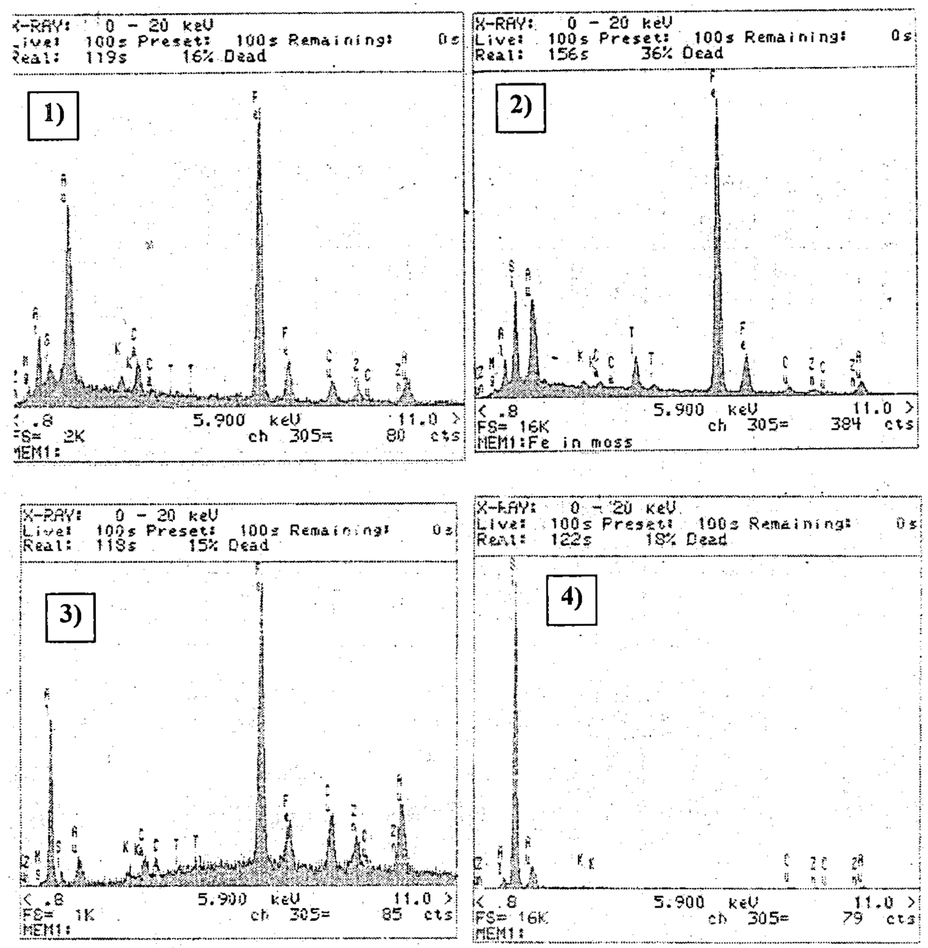


Fig. 4. X-ray spectrograms of particles captured by moss. Each spectrogram corresponds to the photograph with the same number.

Table 1. Element concentrations (*ppm*) in moss near Magnitogorsk and in some other relevant areas used for comparison

Element	Ural moss		Mo (Norway)[4]		Germany[1]		Poland[1]		Norway background levels**
	Mean	Range	Mean	Range	Mean	Range	Range	Mean	Mean
Na	443	304-765	294	93-635					200
Mg	2520	1708-3814	1861	556-4230					1200
Al	2807	1443-4505	1244	243-3100					350
Cl	129	44-363	294	50-1110					200
K	3343	2642-4975	3845	1930-7160					3000
Ca	3532	2030-5227	2871	1450-6740					1500
Sc	0.75	0.52-0.97	0.41	0.06-1.41					0.06
V	7.3	6.8-9.1	5.72	1.05-31.0	3.11	0.5-13.6	4.8	1.7-16.8	2.0
Cr	7.17	4.63-9.57	11.7	0.5-50	2.11	0.49-11.8	2.54	0.97-7.98	1.5
Mn	171	88-337	384	89-1460					200
Fe	2708	2155-3420	12280	700-72100	720	153-4560	1500	386-6830	400
Co	0.36	0.24-0.46	0.61	0.06-2.2					0.3
Ni	3.7	2.8-4.6	1.69	<0.5-6.96	2.61	0.56-11.6	2.49	1.03-6.29	1.6
Cu	6.6*	5-9	12.3	2.9-29.0	9.49	4.12-25.5	10.4	4.9-28.6	5.2
Zn	39	30-52	99	31-397	55.2	23.7-163	66.4	33.0-463	36
As	1.02	0.63-1.32	0.62	0.06-2.20	0.39	0.12-2.09	N.D.		0.3
Se	0.91	0.64-1.10	0.47	0.21-1.17					0.25
Br	3.07	1.80-4.70	6.94	3.6-12.2					5
Rb	8.5	4.5-11.4	17.2	6.7-46.2					10
Ag	0.119	0.011-0.280	0.059	<0.03-0.16					0.04
Cd	0.25*	0.18-0.31			0.34	0.13-0.87	0.59	0.19-5.20	0.13
In	0.032	0.012-0.067							-
Sb	18.95	12.4-29.4	0.250	<0.05-0.76					0.09
I	3.0	2.2-3.9	2.26	<1.0-4.3					2
Cs	0.23	0.17-0.28	0.37	<0.05-1.03					0.18
Ba	54.2	32.3-80.2	33.1	12-83					24
La	0.98	0.69-1.47	0.69	<0.10-2.87					0.3
Ce	3.1	2.4-4.4							-
Sm	0.2	0.14-0.28	0.33	0.05-1.34					0.06
Tb	*0.033	0.024-0.047	0.019	<0.005-0.067					0.015
Yb	0.103	0.070-0.130	0.069	<0.010-0.230					0.03
Hf	0.19	0.06-0.33	0.179	<0.04-0.71					0.05
Ta	0.289	0.27-1.08	0.043	<0.003-0.180					0.005
W	0.2	0.1-0.3	1.71	<0.6-6.4					-
Au	0.004	0.001-0.007	0.0002	<0.0001-0.010					-
Pb*	4.0	2.8-4.5			14.6	5.1-80.5	30.0	8.0-269.0	3
Th	0.47	0.33-0.62	0.267	0.04-1.10					0.08
U	0.08	0.06-0.12	0.143	<0.03-0.51					0.05

* - results obtained by AAS

** - typical values observed in *Hylocomium splendens* in areas little affected by air pollution [13-14]

4. Conclusions

The results of the present pilot study clearly show the need for more work to assess the heavy metal pollution situation in the South Ural region. It also shows the feasibility of nuclear and related techniques in the investigation of these matters. This study is now being followed up by analysis of moss samples collected according to a regular network covering an area of the whole Chelyabinsk Region in order to better assess the magnitude of the problem.

5. Acknowledgements

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