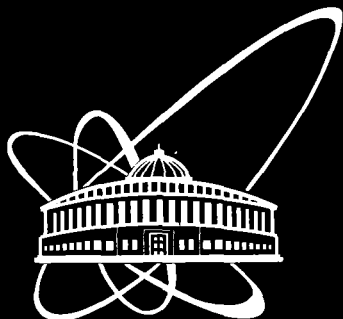




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A HEAVY METAL ATMOSPHERIC DEPOSITION STUDY IN THE SOUTH URAL MOUNTAINS

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Introduction

The Ural Mountains, the natural divide between Europe and Asia, is known for clustering of heavy industries which produce extremely high levels of air and water pollution. In fact the South Urals may be counted among the most polluted areas in the world, where human impact on the environment is largely irreversible. Two very important groups of pollutants emitted into the atmosphere in this region are heavy metals from various industrial plants and long-lived radionuclides from full-scale activities and accidents at the radiochemical “Mayak” Production Association (PA) [1-3].

Most researchers have focused their attention on radioactive contamination in this area. The knowledge on atmospheric emissions of heavy metals from mining and processing and other industries is so far limited to areas within and in the near vicinity of the main enterprises. Only recently general interest has been shown to their impact on the natural environment at a regional scale [4].

In regional trace element studies it is advantageous to determine as many elements as possible in order to better distinguish between different source categories. In the present work the moss biomonitoring technique and the combination of two analytical techniques – epithermal neutron activation analysis (ENAA) and flame atomic absorption spectrometry (AAS) – were applied to elucidate these problems. The use of terrestrial mosses as biomonitors is a well-established technique in Europe [5,6].

In addition the extent of surface soil contamination from atmospheric deposition was investigated on the basis of samples from the uppermost 3 cm of the undisturbed soil, in a similar way as previously done in Norway in studies related to the long-range atmospheric transport of heavy metals [7,8].

The objectives of the present study were:

- to determine the regional extent of pollution with specific metals
- to characterize the local pollution sources such as copper mining and processing industry in Karabash and other towns
- to compare the level of metal pollution produced by the copper industry in Karabash with that in similar copper basins in Poland and Serbia
- to characterize deposition patterns of Cu and As around Karabash
- to identify and characterize other problem areas and sources of heavy metal emissions in the north of the Chelyabinsk Region
- to compare the elemental composition of the surface soil with that of the moss in order to elucidate the soil contamination from air pollution.

The work described in this paper is a continuation of a previous study by the authors in the vicinity of the town of Magnitogorsk (South of the Chelyabinsk Region) [9].

Experimental

Sampling

The sampling network for the feather moss *Hylocomium splendens* and *Pleurozium schereberi* and surface soil is shown in Fig. 1. All sampling sites were placed at least 300 m away from main roads, villages and at least 100 m away from smaller roads and houses according to the guidelines described elsewhere [10].

Moss sampling

At each sampling site around 10 subsamples were taken within a 50m x 50m area and combined to one composite sample. The unwashed samples were air-dried at 30 °C and extraneous plant material was removed. The last three fully developed segments of each *Hylocomium* plant or the green part of *Pleurozium* were taken for analysis. No further homogenization of samples was performed. Disposable polyethylene gloves were used during all handling of samples.

Soil sampling

Surface soil was sampled by means of a steel corer with 10 cm internal diameter. After removal of the litter, the uppermost 3 cm of the soil profile was sampled. Ten subsamples from each site, taken within an area of about 10m x 10m, were joined to form a composite sample. The total amount of sample was about 2.5 liters. After sampling, the soil was dried and sieved (2 mm) before analysis.

Analysis

Soil and moss samples of about 0.1 and 0.3 g respectively 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 1 [11].

Table 1. Flux parameters of irradiation positions

Irradiation position	$\Phi_{th} \cdot 10^{12}, n \text{ cm}^{-2} \text{ s}^{-1}$ $E=0 \div 0.55 \text{ eV}$	$\Phi_{th} \cdot 10^{12}, n \text{ cm}^{-2} \text{ s}^{-1}$ $E=0.55 \div 10^5 \text{ eV}$	$\Phi_{th} \cdot 10^{12}, n \text{ cm}^{-2} \text{ s}^{-1}$ $E=10^5 \div 25 \cdot 10^6 \text{ eV}$
Ch1 (Cd-screened)	0.023	3.31	4.23
Ch2	1.23	2.96	4.10

The elements Sc, Cr, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Zr, Mo, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, 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 respectively.

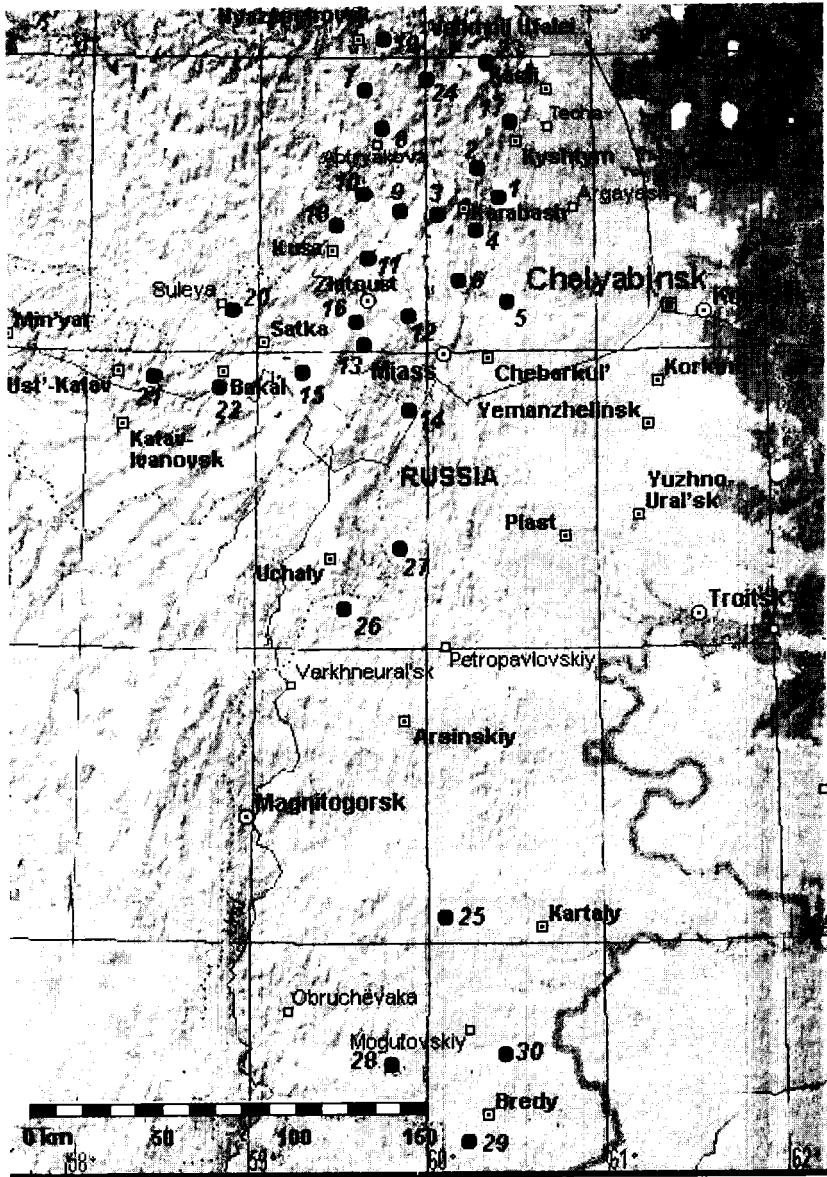


Fig. 1 The sampling network

Measuring time varied from 1 to 5 h. To determine the short-lived isotopes of Na, K, Mg, Al, Ca, Ti, V, and Mn, channel 2 (Ch2) was used. Samples were irradiated for 30-60 s (soil) or 180-300 s (moss) and measured twice after 3-5 min and 20 min of decay for 5-8 and 20 min, respectively.

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 $3\times 3''$ NaI detector for the same line. Data processing and element concentration determinations were performed using software developed in Dubna [12].

The certified reference materials Bottom sediment SDM (International Atomic Energy Agency, Vienna) and Danish moss DK-1 [13] were used for analytical quality control.

Copper, cadmium and lead were determined by flame atomic absorption spectrometry at the Geological Institute of RAS, Moscow.

Results and discussion

The median values and concentration ranges for the elements determined in soil and moss samples and local baseline levels of the Chelyabinsk Region, estimated from the values of samples 28-30 from a presumably clean region, are presented in Table 2. They are compared with corresponding data from other areas strongly affected by emissions from metal industries, studied by the authors in Poland [14 Grodzinska in press], Serbia [15 in press], and Norway [16].

From the comparison with baseline data it is apparent that many of the studied elements are generally enhanced in the moss: For Mg, V, Cr, Ni, and W the median value exceeds the local baseline by more than a factor of 3. Also for Al, Sc, Fe, Co, As, Sb, Cs, the heavy REE, Hf, and Ta the median is appreciably higher. For the soils on the other hand only Zn, As, and Sb appear to show distinctly higher median values than the baseline. Clearly the moss is a far better medium to express regional contamination from atmospheric deposition than the surface soil, as also concluded in a recent study by Fernandez and Carballeira [17]. It may also be noted that the baseline values from Ural are in most cases higher than the corresponding values from Norway.

When comparing the present moss data with those from other areas strongly affected by local air pollution from metal industries it appears that the general levels for elements such as V, Cr, Fe, Ni, As, and Sb are similar in the studied areas in Ural and Serbia but appreciably lower in Poland. In the case of Cu the pollution in the copper basins of Poland and Serbia appear to be significantly higher than in the corresponding area in Ural. However, the Karabash copper smelter was practically shut down in parts of the 1990s due to stagnation in the Russian economy, which may explain the apparently lower contamination in this area.

Multivariate statistics (VARIMAX rotated principal component analysis) was applied to the data set normalized to the local baseline value (sites 28-30) to identify and characterise different pollution sources. The factor scores were calculated and plotted (Figs.2 and 3) in order to determine the contribution of different sources source to each sample. Results of factor analyses of the soil and moss data are shown in Tables 3 and 4. The factors presented explain 82% and 86% of the total variance for moss and soil samples respectively.

Table 2. Radionuclides, energies of γ -lines used for calculations, element concentrations (ppm) in Ural samples and in some other relevant areas used for comparison

Element	Radio-nuclide used	E_{γ} , measured (keV)	Ural soil		Ural moss		Poland (Copper Basin) moss [14]		Serbia moss [15]		Norway (back-ground) moss [16]		Background (Ural moss)	Background (Ural soil)
			median	range	median	range	median	range	median	range	median	range		
Na	^{23}Na	2753.6	6194	1893-23870	337	174-1051	152	74-302	694	178-2440			214	6550
Mg	^{24}Mg	1014.4	18805	10000-49510	5535	1697-15400	1694	800-6480	2780	1100-8130	1543	645-3680	1860	22600
Al	^{27}Al	1778.9	22000	14400-31800	2905	942-7000	815	237-2590	6800	1280-22090	350	97-10970	1280	22900
Cl	^{35}Cl	2766.8			242	58-871	226	123-537	256	105-1030			249	
K	^{41}K	1524.7	10044	1610-20890	6170	3011-11220	5000	515-8708	5090	2710-11750			8400	12400
Ca	^{40}Ca	3084.4	7110	2417-25430	4142	2680-13800	2230	1190-12800	7720	2890-18120	3120	1380-22500	4300	5760
Sc	^{46}Sc	889.2	9.5	1.4-24	0.485	0.1-1.45	0.15	0.03-0.63	1.31	0.27-4.13			0.22	8.2
Ti	^{48}Ti	320.0	523	208-1264					71	11-297	31	10-414		590
V	^{51}V	1434.1	68	30-160	9.4	3.06-22	2.5	1.14-8.13	11	2.85-39	1.35	0.28-22.6	3.25	67
Cr	^{52}Cr	310.1	79	15-313	9.5	1.51-194	1.43	0.80-3.16	6.51	1.14-22	0.69	0.058-2.59	2.26	69
Mn	^{55}Mn	1810.7	2339	975-3971	325	111-1402	222	70-896	217	30-2340	333	28-5420	239	1543
Fe	^{56}Fe	1291.6	24720	3327-54840	1511	335-7438	357	147-845	3110	720-9230	362	99-11220	847	22850
Co	^{60}Co	1332.4	15.7	5.9-51	0.62	0.14-1.95	0.26	0.11-1.48	8.24	1.42-39	0.17	0.014-2.6	0.37	11.9
Ni	^{60}Ni	810.8	47	4.1-503	6.2	0.42-94	1.83	0.09-3.55	6.73	1.96-26	1.1	0.057-72.1	0.50	31
Cu					13.5	3.4-200	20	7.3-2040	94	6.31-3140	4.2	1.7-52.7	16	
Zn	^{67}Zn	1116.0	105	14-817	49	15-304	45	3.1-110	44	14-415	32	9.7-461	52	65
As	^{76}As	559.1	17.9	3.4-211	1.45	0.37-9.7	0.61	0.25-6.04	3.35	0.46-61	0.135	0.0023-2.63	0.51	9.6
Se	^{78}Se	264.7	0.74	0.2-5.4	0.17	0.02-0.8	0.33	0.22-0.77	0.39	0.046-10			0.12	0.73
Br	^{81}Br	776.5			6.1	2.82-25	1.38	0.89-2.85	5.75	1.83-18			3.5	
Rb	^{87}Rb	1876.6	56	11-166	9.3	2.76-21	22.4	2.0-45.5	13	3-47	9.9	1.2-50.7	7.1	69
Sr	^{87}Sr	514.0	126	18-421			12.4	0.69-339	22	6.8-95	11.5	2.0-74.2		101
Zr	^{90}Zr	756.7	678	331-1185										760
Mo	^{99}Mo	140.5	3.71	0.78-11.6			0.29	0.05-2.42	0.85	0.12-23	0.108	0.0087-2.42		2.76
Ag	^{109}Ag	657.7			0.059	0.013-0.474	0.09	0.04-1.7	0.078	0.012-1.5	0.021	0.0017-0.27	0.033	
Cd					0.300	0.06-1.2			<0.4	<0.4-6.5	0.087	0.001-2.65	0.209	

Table 2. (continued)

Element	Radio-nuclide used	E _γ measured (keV)	Ural soil		Ural moss		Poland (Copper Basin) moss		Serbia moss		Norway (back-ground) moss		Background (Ural moss)	Background (Ural soil)
			median	range	median	range	median	range	median	range	median	range		
Sb	¹²⁵ Sb	1691.0	1.70	0.48-3.6	0.245	0.08-3.46	0.25	0.16-0.79	0.52	0.13-7	0.056	0.001-0.46	0.112	0.874
Cs	¹³⁷ Cs	795.8	2.15	0.62-6.9	0.205	0.03-0.61	0.416	0.16-1.3	0.76	0.11-18.2	0.129	0.01-2.06	0.129	3.1
Ba	¹³⁷ Ba	496.8	423	65-1033	37	6.25-125	10.3	5.5-79.2	39	13-130	19.2	4.3-217	31	405
La	¹⁴⁰ La	1596.5	21	3.1-68	1.41	0.51-5.22	0.5	0.14-1.61	4.66	1.09-13	0.28	0.049-9	0.93	25
Ce	¹⁴⁰ Ce	145.4	61	16-177	2.96	0.53-11.7	1.1	0.24-3.74	9.2	1.84-28	0.54	0.098-17.6	1.9	64
Nd	¹⁴⁷ Nd	531.0	18	8-182					2.81	0.37-8	0.22	0.032-7.8		17
Sm	¹⁵³ Sm	103.2	3.5	0.5-8	0.29	0.087-1.05							0.108	3.64
Eu	¹⁵³ Eu	1407.5	1.01	0.088-12.3					0.08	0.02-0.48	0.010	<0.0003-0.24		0.715
Gd	¹⁵³ Gd	103.3	32	8-76										28
Tb	¹⁶⁰ Tb	879.4	0.46	0.09-0.911	0.032	0.004-0.171	0.01	0.003-0.09	0.11	0.02-0.36	0.005	<0.0001-0.16	0.013	0.434
Dy	¹⁶² Dy	94.7	4.07	<3-7.26										4.7
Yb	¹⁶⁹ Yb	198.0	1.50	0.302-3.01	0.079	0.005-0.545							0.047	1.43
Hf	¹⁸⁰ Hf	482.0	4.5	1.76-7.7	0.186	0.023-1.778	0.09	0.01-0.58	0.78	0.15-2.6	0.006	0.001-0.16	0.107	4.63
Ta	¹⁸² Ta	1221.4	0.71	0.14-1.663	0.029	0.004-0.097	0.02	0.004-0.13	0.11	0.024-0.29	<0.0005	<0.0005-0.14	0.013	0.736
W	¹⁸⁷ W	685.7	1.29	0.46-14.4	0.24	0.048-1.27	0.19	0.02-0.67	1.34	0.19-3.3	0.04	0.002-0.89	0.077	1.091
Au	¹⁹⁸ Au	411.8	0.0049	0.00045-0.1	0.006	0.002-0.086			0.0041	0.0003-0.09			0.006	0.0061
Pb					7.4	2.3-24								
Th	²³¹ Pa	312.0	5.8	1.76-32	0.255	0.05-1.72	0.13	0.08-0.45	0.82	0.18-2.4	0.054	<0.0002-1.7	0.156	6.4
U	²³⁸ Np	228.2	1.58	0.442-4.52	0.165	0.06-0.73	0.08	0.02-0.99	0.32	0.08-1.03	0.017	<0.0004-0.37	0.356	1.67

The factor analysis shows three distinct components in both cases. Factor 1 has high loadings for typical crustal elements –Al, Ca, Sc, Cr, Fe, REE's. Factor 2 (moss) and Factor 3 (soil) have high loadings for Cu, Zn, As, Ag, Cd, Sb at sites 1-4 (cfr. Figs.2 and 3) and are related to emissions from the Karabash copper smelter. Factor 6 (moss) and Factor 4 (soil) with high loadings for Co and Ni at site 23 are associated with a production plant for Co and Ni in the town Ufalei. The rest of the factors appear to be more difficult to explain.

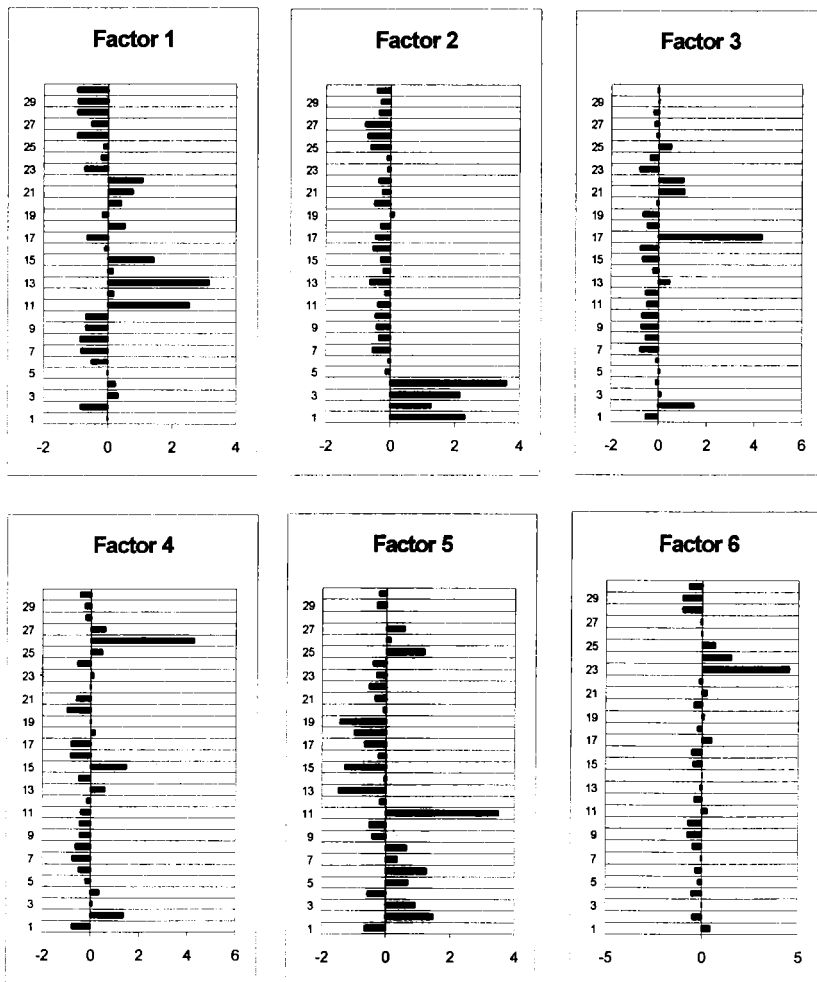


Fig. 2 Plots of factor scores for moss samples

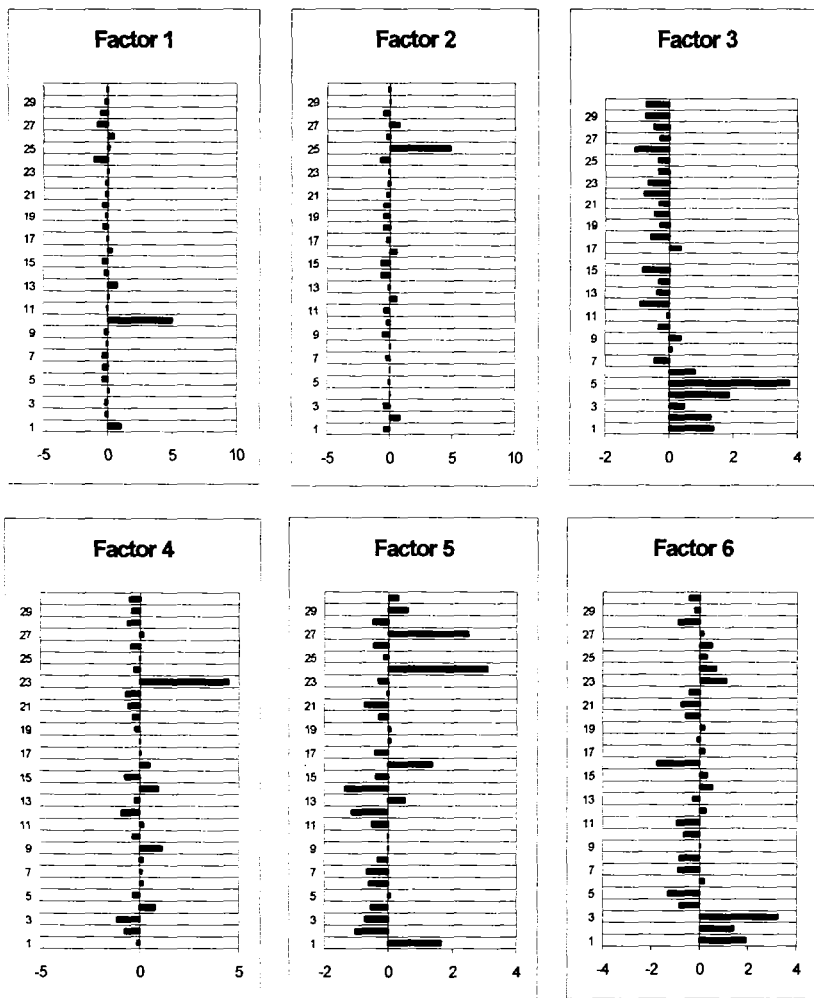


Fig. 3 Plots of factor scores for soil samples

The results obtained for Cu and As allow one to examine their concentration gradients from the Karabash copper smelter. It is clearly seen from Fig.4 that the pollution patterns are quite local and the levels of Cu and As approach the background value at 30-40 km distance from the smelter.

Factors	1	2	3	4	5	6
% of variance	23	21	16	9.3	6.8	6.5
Na	0.22	0.31	0.79	0.13	0.22	0.07
Mg	0.84	0.10	0.04	0.05	-0.12	-0.11
Al	0.59	0.29	0.65	-0.15	0.04	0.13
Cl	0.41	0.63	-0.11	0.09	-0.39	-0.19
K	-0.44	0.61	0.07	0.36	0.11	-0.19
Ca	0.82	0.11	0.06	0.14	0.22	-0.03
Sc	0.65	0.33	0.43	0.00	0.40	0.10
V	0.72	0.17	0.33	-0.18	0.19	0.21
Cr	0.59	0.00	-0.09	-0.06	0.64	0.04
Mn	0.20	-0.11	-0.03	0.83	-0.03	0.11
Fe	0.77	0.15	0.21	0.04	0.50	0.07
Co	0.41	-0.07	0.05	0.39	0.42	0.60
Ni	-0.01	0.10	-0.12	-0.02	-0.06	0.95
Cu	0.02	0.96	0.03	0.00	-0.02	-0.03
Zn	0.09	0.97	0.05	0.01	0.07	-0.04
As	0.05	0.95	0.10	0.05	0.05	0.19
Se	-0.14	0.27	0.42	0.16	0.07	0.76
Br	0.06	0.05	0.06	0.90	0.08	0.15
Rb	0.34	-0.13	0.33	0.11	0.76	-0.02
Ag	0.07	0.89	0.03	0.01	-0.04	0.03
Cd	0.06	0.86	-0.12	-0.10	-0.19	0.34
Sb	-0.02	0.96	0.21	0.04	0.06	0.05
Cs	0.48	0.14	0.54	0.04	0.10	0.08
Ba	0.49	0.04	0.22	0.48	0.11	-0.07
La	0.65	-0.10	0.76	0.14	0.15	0.05
Ce	0.56	-0.03	0.67	0.24	0.18	-0.01
Sm	0.74	-0.06	0.62	-0.08	-0.02	0.07
Tb	0.84	0.08	0.30	0.09	0.14	-0.02
Yb	0.92	-0.11	0.22	0.11	-0.04	-0.01
Hf	0.33	0.58	0.04	0.02	0.09	0.07
Ta	0.53	0.48	0.37	0.24	0.34	-0.05
W	-0.12	0.46	0.19	0.49	0.45	0.10
Au	-0.08	0.12	-0.02	0.83	-0.03	-0.08
Th	0.24	0.04	0.93	-0.01	0.08	0.07
U	-0.04	-0.03	0.85	-0.02	-0.05	-0.11

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

Table 3. The results of FA for Urals moss

Factors	1	2	3	4	5	6
% of variance	42	12	10	8.6	6.6	5.8
Na	0.82	0.18	0.11	0.07	0.13	0.42
Mg	0.35	0.34	-0.08	0.67	0.32	0.14
Al	0.66	0.26	-0.03	-0.05	0.58	0.19
K	0.04	0.59	-0.46	-0.21	-0.02	-0.19
Ca	0.77	-0.17	0.18	0.23	0.18	0.22
Sc	0.89	-0.15	0.16	0.28	0.18	0.01
Ti	0.29	0.09	-0.22	0.10	0.85	0.00
V	0.47	-0.11	0.05	0.32	0.69	-0.10
Cr	0.63	-0.23	0.15	0.67	-0.06	-0.15
Mn	-0.33	0.42	0.09	0.15	-0.07	0.53
Fe	0.92	-0.14	0.14	0.28	0.12	-0.02
Co	0.29	-0.13	0.12	0.79	0.25	-0.15
Ni	0.28	-0.16	0.09	0.91	-0.11	0.06
Zn	0.19	-0.07	0.92	-0.03	-0.09	0.13
As	0.00	-0.05	0.88	0.12	-0.05	0.10
Se	-0.03	0.80	0.41	-0.09	0.14	0.28
Rb	0.95	0.16	0.01	0.14	0.06	-0.06
Sr	0.91	0.04	0.20	0.18	0.02	0.24
Zr	0.80	-0.12	-0.16	-0.01	0.28	-0.22
Mo	0.63	0.02	0.51	0.19	-0.01	-0.32
Sb	-0.01	-0.15	0.44	-0.19	0.00	0.66
Cs	0.38	0.65	-0.16	-0.06	0.22	-0.34
Ba	0.93	0.19	0.19	0.06	-0.05	0.15
La	0.60	0.51	-0.10	0.12	0.00	-0.41
Ce	0.74	0.50	-0.12	0.08	0.12	-0.31
Nd	0.12	0.92	-0.14	-0.04	0.05	-0.02
Sm	0.90	0.06	0.01	0.22	0.17	-0.24
Eu	0.13	-0.18	0.36	0.22	-0.31	0.30
Gd	0.95	0.13	0.14	0.14	0.04	-0.13
Tb	0.90	-0.10	0.04	0.20	0.26	-0.23
Yb	0.92	-0.06	0.05	0.17	0.24	-0.19
Hf	0.93	0.29	-0.02	0.15	0.04	-0.06
Ta	0.89	0.27	0.04	0.18	0.16	-0.19
W	0.61	0.14	-0.27	-0.09	0.40	-0.15
Au	0.97	0.02	0.04	0.11	0.09	0.02
Th	0.00	0.95	-0.03	-0.06	-0.07	0.07
U	0.12	0.02	0.88	0.04	-0.07	0.02

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

Table 4. The results of FA for Urals soils

The surface soil concentrations of As, Zn and Ni, the main elements associated with the copper and nickel industries, were plotted against moss data from the same sites (unfortunately Cu was not determined in the soils). As shown in Fig. 5, high correlations are evident for As, Zn and Ni ($R = 0.94$, $R = 0.88$, and $R = 0.85$, respectively), supporting the assumption that the surface soils contaminated with these elements from atmospheric deposition.

A brief discussion of some elements often associated with air pollution is presented in the following, based mainly on the moss data:

V: In the present material is mainly associated with a typical crust component (Factor 1). The highest values in moss however were observed at sites 11 and 13 in the vicinity of the industrial towns Kusa and Zlatoust.

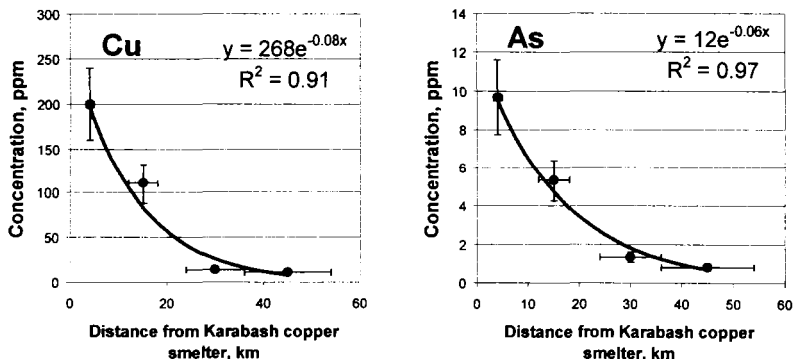


Fig. 4 Gradient of Cu, As (moss samples)

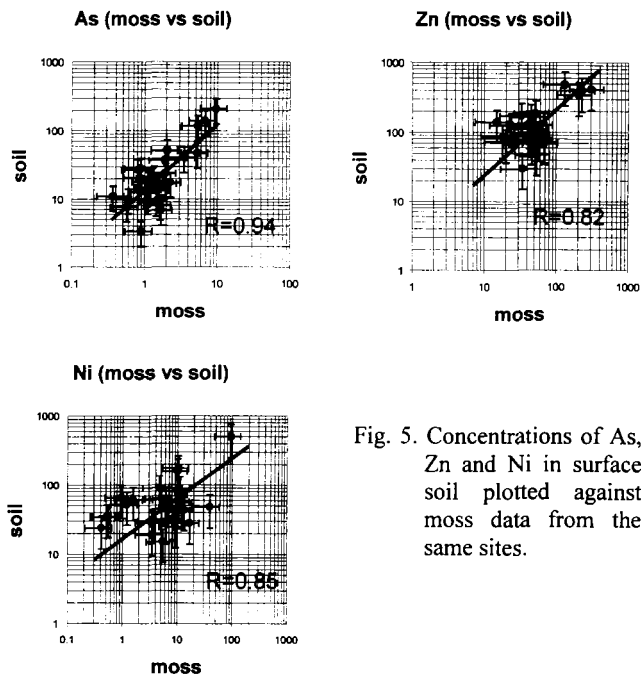


Fig. 5. Concentrations of As, Zn and Ni in surface soil plotted against moss data from the same sites.

Cr: the highest concentrations of Cr were found out at the site 11 in moss and at the sites 11, 18, 23 in soil samples. Site 23 is affected by the activity of the Ufalei metal industry.

Fe: Fe is mainly associated with the crustal component (Factor 1) but the maximum Fe concentration is observed at site 11.

Ni: High concentrations of Ni in both moss and soil samples are observed at site 23, associated with the Ufalei industry.

Cu: Pollution by Cu is observed at sites 1-4 only, related to the Karabash copper smelter.

Zn: High concentrations of Zn are observed in the vicinity of the Karabash copper smelter (sites 1-4) and at site 18 near the industrial town Kyshtym.

As: The highest As levels are observed at sites 1-4 (Karabash), followed by sites 23-24 (presumably Ufalei).

Sb: Like in the case of Cu, pollution by Sb is observed only in the vicinity of the Karabash copper smelter.

Table 5. Total pollution coefficients Z_c (for Cr, Fe, Co, Ni, V, Zn, As, Se, Sb, Ba) for the Urals moss and soil. For moss Cu is included also.

Sampling site	Z_c (moss)	Z_c (soil)
1	64	47
2	49	24
3	87	51
4	88	39
5	39	46
6	24	10
7	21	7
8	12	8
9	0.42	50
10	-0.92	6
11	130	7
12	19	2
13	43	3
14	33	11
15	35	0
16	14	9
17	37	14
18	23	4
19	24	3
20	22	1
21	40	2
22	33	1
23	211	27
24	94	7
25	29	5
26	15	-6
27	15	4
28	-1.3	-1
29	1.1	1
30	0.22	0.04

The total pollution coefficient Z_c [18] was calculated for all sampling sites (Table 5) to identify the most heavy metal polluted areas:

$$Z_c = \sum K_c - (n-1) \text{ where}$$

where $K_c = X/X_{\text{background}}$ (pollutant concentration divided by baseline level) and n is the number of pollutants considered. The following pollutants were selected: V, Cr, Fe, Co, Ni, Zn, As, Se, Sb, and Ba.

Table 5 shows that most high Z_c values are related to the above mentioned industrial areas in the South Ural region: sites 1, 2, 3, 4 – Karabash; site 23 – Ufalei; site 11 – Zlatoust; site 17 – Kyshtym.

In order to better distinguish between contribution from air pollution and from a crustal component associated with windblown soil particles enrichment factors ($EF = (X/Sc)_{\text{moss}} / (X/Sc)_{\text{soil}}$) were calculated from the moss data and plotted in Fig. 6. Typical crustal elements such as Sc, REE, Th, etc. show EF values near unity, whereas values appreciably above that level indicate that the element in question is either enriched in the moss by active biological processes (K, Ca)

in stems from atmospheric deposition. Cr, Zn, As, Se, Ag, Cd, Sb, and Au are significantly enriched in the moss, clearly indicating that these elements represent a regional pollution problem.

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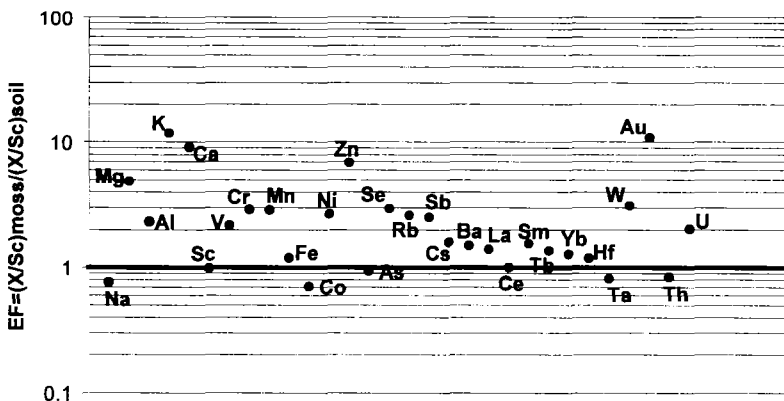


Fig. 6 Enrichment factors of elements in moss with respect to soil

Conclusion

For the first time the moss biomonitoring technique was applied to study heavy metals atmospheric deposition on a regional scale in the heavily industrialized South Urals. Epithermal neutron activation analysis appeared to be a convenient analytical technique for assessing the environmental situation in the concerned area as far as heavy metal pollution is concerned. Comparison with corresponding results from areas with similar industries in Poland (Copper Basin) and Serbia (Bor) indicated that the northern part of Chelyabinsk Region is among the most polluted areas in Europe for elements such as V, Cr, Fe, Ni, As and Sb. Factor analyses applied to the experimental set of data allowed to identify and characterize two main pollution sources in the examined area: the Karabash copper smelter (Cu, Zn, As, Ag, Cd, and Sb) and the Verkhni Ufalei production plant for Ni and Co. The Cu and As deposition was mainly limited to an area

within a distance of about 30-40 km from the Karabash copper smelter. The total pollution coefficients calculated for all sampling sites revealed the highest antropogenic loadings in the areas surrounding Karabash, Kusa, and Zlatoust.

High correlations for As, Zn, and Ni between moss and soil samples collected at the same sites evidence significant surface soil contamination with these elements from atmospheric deposition.

As follows from enrichment factors relative to mean crustal values, calculated in order to distinguish contributions from windblown soil particles from those derived from air pollution, elements such as Cr, Zn, As, Se, Ag, Cd, Sb, and Au are significantly enriched in the moss, clearly indicating the anthropogenic origin of these elements.

The results from the present work could profitably be used in future studies looking at correlations with geographically distributed public health data.

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Образцы мхов *Hylocomium splendens* и *Pleurozium schreberi*, собранные летом 1998 г., использовались для изучения глобальных атмосферных выпадений тяжелых металлов на севере Челябинской области (Южный Урал), которая является самым загрязненным промышленным районом Российской Федерации. Образцы почв и мхов были собраны одновременно в 30 точках для изучения накопления тяжелых металлов и для исследования корреляции элементов в образцах мхов и поверхностном слое почв для учета вклада почвенных компонентов в атмосферные выпадения. Применение метода эпитеплового нейтронного активационного анализа (ЭНАА) позволило определить концентрации 38 элементов (Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Zr, Mo, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Yb, Hf, Ta, W, Au, Th, U) в образцах почв и концентрации 33 элементов (Na, Mg, Al, Cl, K, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Rb, Ag, Sb, Cs, Ba, La, Ce, Sm, Tb, Yb, Hf, Ta, W, Au, Th, U) в образцах мхов. Элементы Cu, Cd и Pb, содержащиеся во мхах, были определены методом атомно-абсорбционной спектроскопии (ААС). Результаты сравнивались с данными, полученными для медных бассейнов Польши и Сербии, а также с данными фоновых значений по Норвегии. Многомерный статистический анализ этих данных (выделение главных компонентов с использованием вращения «VARIMAX») позволил установить и охарактеризовать различные источники загрязнения в исследуемом регионе. Для выявления наиболее загрязненных мест были рассчитаны суммарные показатели загрязнения аномальных уровней по отношению к фоновым значениям для каждой точки пробоотбора.

Работа выполнена в Лаборатории нейтронной физики им. И. М. Франка ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна, 2002

Samples of the mosses *Hylocomium splendens* and *Pleurozium schreberi*, collected in the summer of 1998, were used to study the atmospheric deposition of heavy metals and other toxic elements in the Chelyabinsk Region situated in the South Ural, one of the most heavily polluted industrial areas of the Russian Federation. Samples of natural soils were collected simultaneously with moss at the same 30 sites in order to investigate surface accumulation of heavy metals and to examine the correlation of elements in moss and soil samples in order to separate contributions from atmospheric deposition and from soil minerals. A total of 38 elements (Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Zr, Mo, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Yb, Hf, Ta, W, Au, Th, U) in soil and 33 elements (Na, Mg, Al, Cl, K, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Rb, Ag, Sb, Cs, Ba, La, Ce, Sm, Tb, Yb, Hf, Ta, W, Au, Th, U) in mosses were determined by epithermal neutron activation analysis. The elements Cu, Cd and Pb (in moss samples only) were obtained by atomic absorption spectrometry. The element concentrations were compared to those for copper basins in Poland and Serbia as well as to baseline concentrations in Norway. VARIMAX rotated principal component analysis was used to identify and characterise different pollution sources and to point out the most polluted areas.

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

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