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AIR POLLUTION STUDIES IN CENTRAL RUSSIA (TULA REGION) USING MOSS BIOMONITORING TECHNIQUE, NAA AND AAS

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INTRODUCTION

The conventional method to study atmospheric deposition of chemical pollutants, including heavy metals and other toxic elements, is precipitation analysis. An alternative method to measure integral heavy metal deposition is the use of terrestrial mosses growing in forests or other natural habitats as biomonitors. Mosses effectively accumulate the majority of heavy metals and other trace elements from air and precipitation. In addition, they do not have a root system and the contribution from sources other than atmospheric is thus negligible in most cases. Another advantage is that a given type of moss may grow in different climatic zones. Furthermore, it is easier to collect samples of moss than of precipitation.[1-3]

The moss biomonitoring technique has been used regularly for the last 20 years in Scandinavian countries for routine monitoring of the atmospheric deposition of trace elements over extended territories, and presently it is being adapted in an increasing number of European countries. In Russia the technique was until recently applied only in northwest Russia (Leningrad region, Karelia, Kola Peninsula).[4] At present, the moss biomonitoring technique is successfully used to study heavy metal atmospheric deposition in industrial areas of the Urals,[5] and work is in progress in other parts of Russia. We report here the first case of using this approach in Central Russia. It concerns the Tula region, which is situated in the centre of the East European Plain in Middle-Russia Hills where two natural zones meet: boreal forest (north) and forest-steppe (south) (latitude 53–55 degrees North and longitude 36–39 degrees East). The area of the territory is comparatively small (25 700 km^2) but it is densely populated. The Tula region is the home of 21 towns and 50 townships.

The Tula region has always been a well-developed industrial and farming area. A total of 473 units of the machine building, chemical, metallurgic, power generation, transportation and other industries as well as of agriculture operate in the Tula region. The industrial structure of the region is detailed in Table 1. The environment in the Tula region experiences a huge anthropogenic load due to operation of the plants.[6, 7]

Table 1. The industrial structure of the Tula region [6]

Industries	**in (%)**
Chemical and petrochemical	21.8
Power	20.3
Ferrous metallurgy	19.1
Machine building and metal working	15
Food	11.7
Construction materials	3.3
Fuel	2
Wood working and wood-pulp and paper	1.5
Light	1.4
Non-ferrous metallurgy	0.3

EXPERIMENTAL

Sampling

The sampling procedure was similar to that used in the European project «Atmospheric trace metal deposition in Northern Europe 1990, 1995, 2000».[4] The moss samples were collected during the summer-autumn of 1998-2000. The network of sampling includes 83 sites evenly distributed over the investigated territory (Fig. 1). The average distance between sites was 10–15 km. The sampling net was denser around industrial and urban territories where the distance between sites was less than 10 km. One sample was collected from an within an area of 50 × 50 m. The sampling site was chosen to be at a distance of over 300 m from highways or inhabited areas and not closer than 100 m from walking paths or separate buildings. Mosses were collected in the forest glades to exclude the canopy effect of trees. They were mainly collected on organic topsoils (plant litter substrate) or from the surface of decaying stumps to reduce soil-related effects. Each sample consisted of several sub-samples. Disposable polyethylene gloves were used during sampling and further handling of samples. The moss species *Brachythecium (salebrosum, rivulare* and *oedipodium)* and *Pleurozium schreberi* were found in the examined area. A preliminary comparative analysis of the species shows about equal concentrations of most elements in the different moss species.[8]

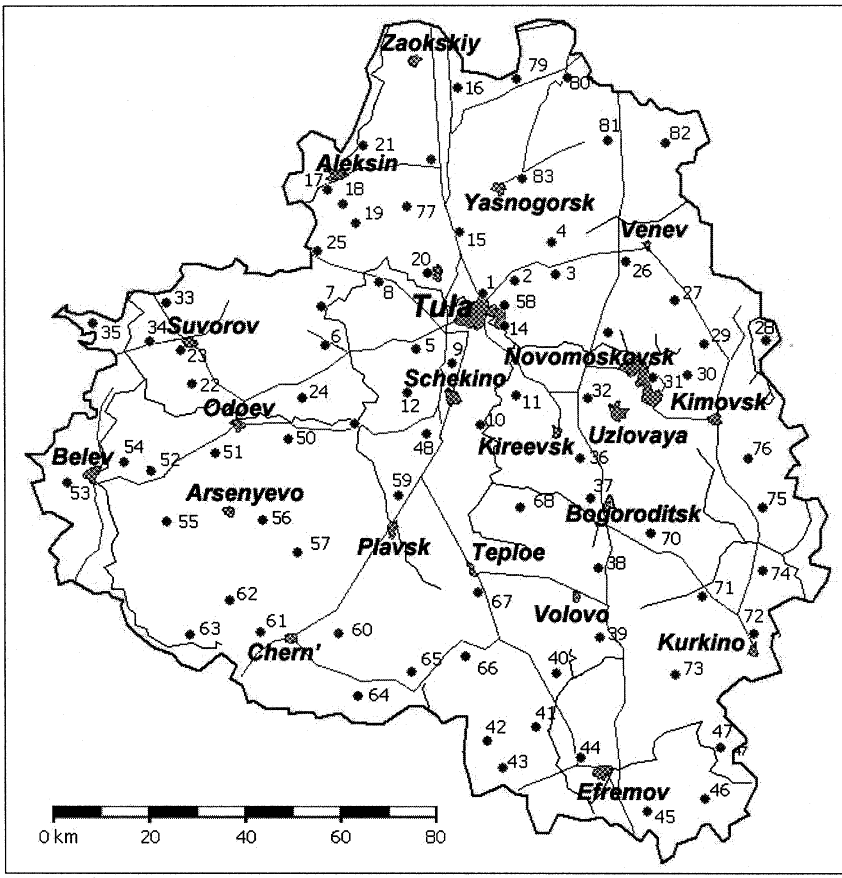

Fig 1. Tula region. Sampling network

Sample preparation

In the laboratory the samples were cleaned from extraneous plant materials and dried to constant weight at 30°–40° for 48 hours. The samples were not washed and not homogenized. Green and green-brown moss shoots were subjected to analysis for the deposition over three years as they correspond to an approximately three-year period of moss growth.

Analysis

The concentration of elements in the moss samples was determined by a combined method of instrumental neutron activation analysis (NAA) and atomic absorption spectrometry (AAS). To carry out NAA investigations, moss samples of about 0.3 g were heat-sealed in polyethylene foil bags and packed in aluminum cups for short and long irradiation, respectively. NAA was performed at the IBR-2 reactor in the Frank Laboratory of Neutron Physics. The analytical procedures and the basic characteristics of the employed pneumatic system are described in detail elsewhere.[9] Two types of analysis were done. One is a short irradiation of 3–5 min to analyze for short-lived isotopes (Al, Ca, Cl, I, Mg, Mn, and V). After a decay-period of 5 to 7 min the irradiated samples were measured twice, first for 3–5 and then for 10–15 min. A long-irradiation of 4–5 days was used to analyze for long-lived radionuclides. After irradiation the samples were re-packed and measured twice, first in 4–5 days for 40–50 min to determine As, Br, K, La, Na, Mo, Sm, U, and W and in 20 days for 2.5–3 hours to determine Ba, Ce, Co, Cr, Cs, Fe, Hf, Ni, Rb, Sb, Sc, Sr, Ta, Tb, Th, Yb, and Zn. The gamma spectra of the samples were measured with a Ge-Li detector with a resolution of 2.5–3 keV for the ^{60}Co 1332 keV line. A HPGe detector with a resolution of 1.9 keV for the ^{60}Co 1332 keV line was also used. The processing of the data and determination of the concentrations of elements were performed using certified reference materials and flux comparators with the help of the software developed in FLNP, JINR.[10]

To determine Cd, Cu and Pb, moss samples of 1.0–1.3 g were digested with 20 ml of concentrated nitric acid in a sample bottle on a hot plate at 80°–85° for 18–20 hours. After being cooled to room temperature, the samples were filtered and demineralized water was added to a total volume of 50 ml. Analysis for Cd, Cu and Pb was carried out by flame atomic absorption spectrometry on a Perkin-Elmer Analyst-600 spectrometer in the Norwegian University of Science and Technology, Trondheim, Norway. All calibration standards and blanks matched the nitric acid concentration of the samples.

Quality control and Quality assurance

The QC and QA of NAA results were ensured by carrying out a concurrent analysis of the standard reference materials Lichen 336 IAEA (International Atomic Energy Agency) and NORD DK-1 (moss reference sample) prepared for doing the calibration in the laboratories participating in the corresponding 1990 Nordic survey.[11] The standard reference materials SRM-1575 (pine needles) from the US NIST (National Institute of Standards and Technology) were also used.

RESULTS AND DISCUSSION

Table 2 shows minimum, maximum and mean element concentrations and median values for 36 elements detected in moss samples from 83 sites in the Tula region. The local background levels for most of the elements were calculated as an average of values from the 3 sites showing the lowest concentrations. For comparison Table 2 in its last column shows the background concentrations from the Moss survey 2000 in Norway.[12] It is seen from Table 2 that the concentration of some elements is several times larger than the local background level, *e.g.,* the concentrations of V, Cr, Fe, W, As, Th, U are 25–40 times higher than the local background. This is possibly due to local pollution sources in the Tula region. On the other hand, the concentrations of Mn, Ni, Cu, Zn and Pb are only 3–8 times higher than the local background, and may be the result of general territorial pollution caused by local sources and long-range transport from external sources. For example, a 4 times difference between the maximum and background concentration value of Pb in mosses from the Tula region (the mean value is 8.7 mg/kg) is assumed to be due to local contamination caused by a developed network of highways in the region.

Table 2. Element concentrations (*mg/kg*) in mosses collected from Tula region

Element	Range	Mean	Median	Local background	Norway
Na	142-1100	409	373	150	
Mg	790-9860	2455	2200	940	1543
Al	400-31200	3600	2700	585	350
Cl	113-3800	650	540	215	
K	4860-18450	10500	10000	5550	
Ca	1550-13600	6100	5600	2325	3120
Sc	0.09-3.50	0.57	0.44	0.09	
V	1.4-63	8	6	1.6	1.35
Cr	0.6-28	5	4	0.7	0.69
Mn	35-820	300	240	150	333
Fe	350-19700	2200	1660	400	362
Co	0.14-2.66	0.63	0.52	0.20	0.17
Ni	0.7-11.7	3.7	3.2	1.4	1.1
Cu*	4-36	9	8	4.5	4.2
Zn	16-105	54	52	24	32
As	0.11-3.0	0.5	0.4	0.1	0.135
Br	0.8-13	3.1	2.9	1.0	
Rb	3.2-36.4	14.3	12.8	8.5	9.9
Sr	7.2-59	26.5	25	10	11.5
Mo	0.12-1.2	0.43	0.36	0.16	0.108
Cd*	0.04-1.22	0.32	0.28	0.12	0.087
Sb	0.05-0.70	0.15	0.13	0.06	0.056
I	0.4-5.2	1.5	1.45	0.5	
Cs	0.06-1.07	0.25	0.21	0.08	0.129
Ba	10-145	46	41	16	19.2
La	0.4-13.2	2.6	2.0	0.5	0.28
Ce	0.6-27.0	4.6	3.8	0.7	0.54
Sm	0.05-1.98	0.39	0.29	0.06	0.042
Tb	0.007-0.317	0.052	0.042	0.007	0.005
Yb	0.02-0.75	0.15	0.11	0.02	0.013
Hf	0.08-5.70	0.82	0.64	0.12	0.006
Ta	0.008-0.960	0.078	0.058	0.011	<0.0005
W	0.02-2.12	0.16	0.13	0.04	0.04
Pb*	3.8-18.6	8.7	8.2	5.0	2.7
Th	0.09-4.93	0.65	0.49	0.10	0.054
U	0.04-1.38	0.20	0.15	0.04	0.017

* determined by AAS

Factor analysis

Factor analysis is a multivariate statistical technique commonly used in environmental studies to deduce source from data set. This approach is widely used in analysis of atmospheric deposition.[13, 14] From a matrix of correlation or covariance, factor analysis generates a few underlying «factors» that describe group of variables. In environmental studies, each factor is generally treated as a source. The 8 factors presented in Table 3 explain 86.3% of the total variance in the data set. The factor loadings and the geographical distribution of the factor scores are given in Figs. 2 and 3.

From the knowledge of the element composition of each factor and values of factor loadings, the major sources may be identified.

Table 3. Explained variance for the eight factors

	Factor							
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
% of Variance	47.1	14.3	6.5	5.2	4.2	3.7	3.1	2.3
Cumulative %	47.1	61.4	67.9	73.1	77.3	80.9	84.0	86.3

Extraction Method: Principal Component Analysis
Rotation Method: Varimax with Kaiser Normalization
Rotation converged in 8 iterations

Below is the interpretation of 8 factors in the sequence of their appearance in Table 3:

Factor 1 is responsible for 47.1% of total variance and is characterized by the presence of Mg, Al, Sc, Cr, Co, As, Cs, La, Ce, Sm, Tb, Yb, Hf, Ta, Th and U, all typical crustal elements. Moreover, the geographical distribution of Factor 1 resembles the geographical distribution of the individual elements in mosses, especially As, Th and U (Fig 4). Coal mining and refining plants are operating in the east of the Tula region. A high content of .As, U, Th is characteristic of brown coal. In the west of the Tula region a large thermal power plant operating on brown coal is located. Factor 1 reflects the impact of the earth crust, coal mining, refining and coal combustion industries.

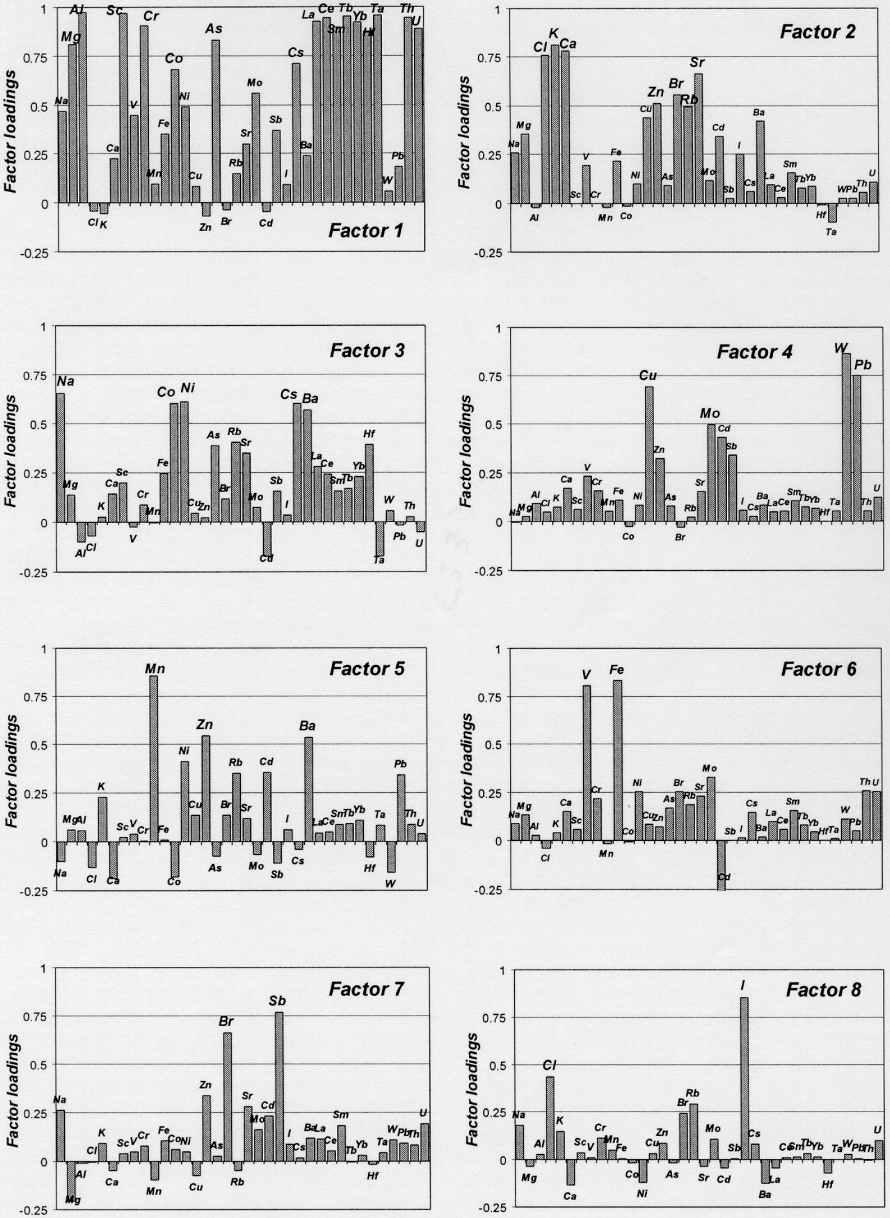

Fig 2. Factor loadings

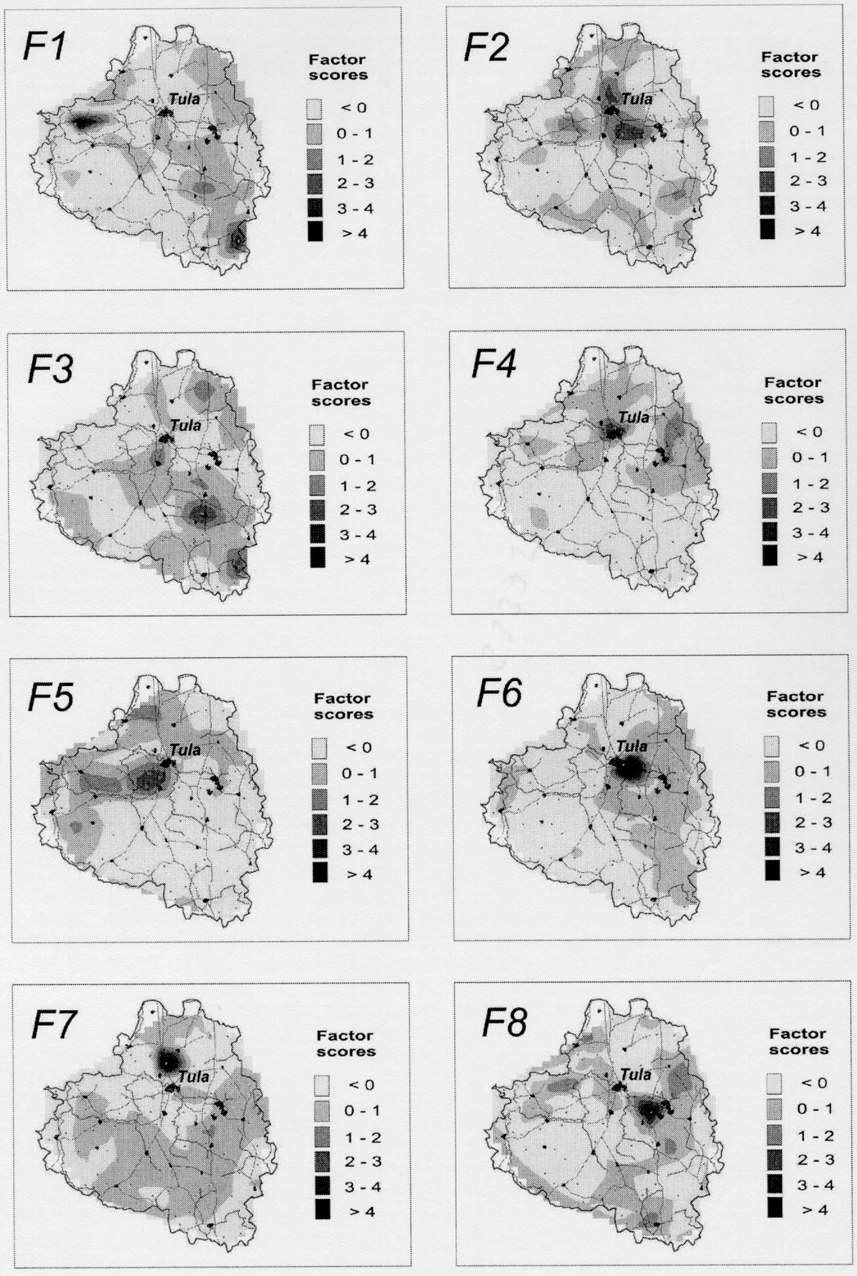

Fig 3. Geographical distribution of the factor scores
(GIS-INTEGRO was used to generate the maps)

Factor 2 includes Cl, K, Ca, Zn, Br, Rb and Sr and explains 14.3% of total variance. The factor loading is from 0.50 to 0.81. The factor probably reflects the natural content of elements in the feather moss. There is no correspondence between the factor scores and the geographical distribution of individual elements.

Factor 3 includes mainly Na, Co, Ni, Cs and Ba. This factor explains 6.5% of total variance and may be related to anthropogenic sources in neighbouring regions. One of them is in the Moscow region and another is in the Lipetsk region. Metallurgical plants in the Tula region could be the source of these elements as well.

Cu, Mo, W, and Pb are the main constituents of **Factor 4**. Their loadings in the factor are 0.69, 0.50, 0.86 and 0.75, respectively. Factor 4 explains 5.2% of total variance. The map of the factor scores is similar to that of the above elements in mosses. The factor components originate from heavily populated industrial areas in the Tula Region around the cities of Tula, Novomoskovsk and Suvorov.

Three major elements in **Factor 5** are Mn, Zn and Ba. Factor 5 explains 4.2% of total variance. The map of the factor scores shows maximum values to the southwest of Tula. Factor 5 possibly reflects the impact from metallurgical plants.

The characteristic elements of **Factor 6** are V and Fe with factor loadings of 0.81 and 0.83, respectively. Other elements in the factor have a loading of less than 0.25. Factor 6 explains 3.7% of total variance. The correlation coefficient between V and Fe is 0.92 for the given data set. The isopleths of the factor scores also resembles the distribution maps of relevant elements (Fig. 4). It is evident that ferrovanadium production at one of the metallurgical plants is a dominant source of V and Fe in the Tula region.

A pilot element in **Factor 7** is Sb with a factor loading of 0.77. Br also has a fairly high factor loading (0.66). Factor 7 bears 3.1% of total variance. The geographical distribution of the factor indicates the existence of a point source of Sb pollution to the north of Tula.

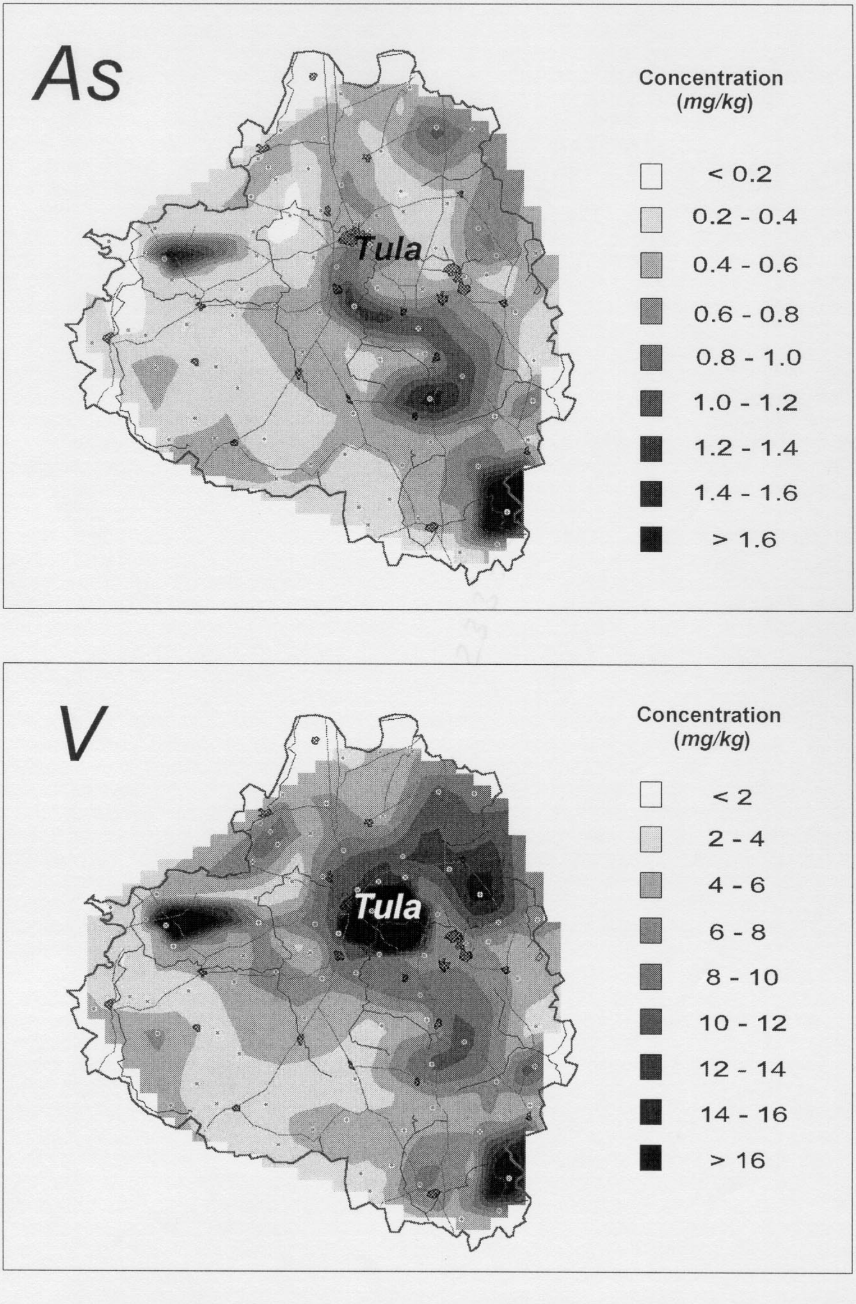

Fig 4. Distribution maps of arsenic and vanadium in Tula region

Finally, **factor 8** explains 2.3% of total variance. The dominating elements in the factor are the halogens Cl and I. The factor scores are the highest in the area of clusters of chemical plants near the cities of Novomoskovsk, Uzlovaya, Efremov, Aleksin and Schekino. Thus the sources of Cl and I deposition may be production of chlorine and organic compounds.

CONCLUSION

The investigated elements can be classified by their main sources through factor analysis of moss data as follows:

- natural sources, such as windblown topsoil dust and cation exchange on the surface of the moss tissue (Cl, K, Ca, Zn, Br, Rb, Sr)
- Obvious anthropogenic sources: coal-mining and coal refining industries (As, U, Th, rare-earth elements), ferrovanadium industry (Fe, V), chlorine and organic production (Cl, I), other industries, urban territories (Co, Ni, Ba, Cs, Mn, Zn, Cu, Pb, Mo, W)
- a not identified point source of Sb.

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Ермакова Е. В., Фронтасьева М. В., Стейнес Э. E14-2002-137
Изучение воздушных загрязнений в Центральной России (Тульская область) с помощью метода мхов-биомониторов НАА и ААС

Впервые метод мхов-биомониторов был применен для оценки воздушных загрязнений в Центральной России на территории Тульской области. Образцы мхов собирались в 83 точках в соответствии с правилами пробоотбора европейских проектов по биомониторингу атмосферных выпадений элементов. Применение НАА позволило определить 33 элемента (Na, Mg, Al, Cl, K, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Zn, As, Br, Rb, Sr, Mo, Sb, I, Cs, Ba, La, Ce, Sm, Tb, Yb, Hf, Ta, W, Th, U) в широком диапазоне концентраций — от 10000 мг/кг для K до 0,001 мг/кг для Tb и Ta. Концентрации элементов Cu, Cd и Pb были определены методом пламенной атомной абсорбции. Применение факторного анализа позволило определить естественное и антропогенное происхождение отдельных элементов во мхах, а также выявить основные источники загрязнения в Тульской области. Построены карты географического распределения восьми факторов. Примеры распределения концентрации отдельных элементов также приводятся в работе.

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

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Ermakova E. V., Frontasyeva M. V., Steinnes E. E14-2002-137
Air Pollution Studies in Central Russia (Tula Region) Using Moss Biomonitoring Technique, NAA and AAS

For the first time the moss biomonitoring technique has been applied to air pollution monitoring in Central Russia (Tula Region). Moss samples were collected from 83 sites in accordance with the sampling strategy of European projects on biomonitoring of atmospheric deposition. Neutron activation analysis (NAA) at the IBR-2 reactor has made it possible to determine the concentration of 33 elements (Na, Mg, Al, Cl, K, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Zn, As, Br, Rb, Sr, Mo, Sb, I, Cs, Ba, La, Ce, Sm, Tb, Yb, Hf, Ta, W, Th, U) over a large concentration range (from 10000 mg/kg for K to 0.001 mg/kg for Tb and Ta). In addition to NAA, flame AAS (atomic absorption spectrometry) was applied to determine the concentration of Cd, Cu and Pb. Factor analysis was applied to determine possible sources of elements detected in the investigated mosses. Eight factors were identified. The geographical distribution of factor scores is presented. The interpretation of the factor analysis findings points to natural as well as anthropogenic origin of trace element deposition in the Tula mosses. The obtained data are used to construct element distribution maps over the investigated territory. Examples of such maps are shown in the paper.

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

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