# Atmospheric Deposition of Trace Elements in Central Russia: Tula Region Case Study. Comparison of Different Moss Species for Biomonitoring

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### **RUSSIAN FEDERATION**

*Abstract:* Using the method of passive moss biomonitoring air pollution of one of the major industrial regions of Central Russia - Tula region – was studied. A high content of a number of elements of anthropogenic origin V, Fe, Zn, As, Sm, Tb, Hf, W, Th, and U in the air compared to other regions of Russia and high content of As, Cd, Cr, Fe, V, Zn and Al compared to the CIS countries and Europe were revealed. The reason for such high level of anthropogenic air pollution in the region is the activity of enterprises of metallurgical, defense, engineering and chemical industries. Instrumental epithermal neutron activation analysis (ENAA) up to 42 elemental concentrations in moss samples collected in different natural zones of the investigated area (coniferous and deciduous forests, forest-steppe and steppe). It was shown that the ability to accumulate elements from wet and dry atmospheric deposition is similar to moss *Pleurozium schreberi* recommended by the UNECE ICP Vegetation Programme and for some studied moss species collected in Tula region *Abietinella abietina, Aulacomnium palustre, Climacium dendroides, Brachythecium rutabulum, Brachythecium salebrosum, Dicranum polysetum, Dicranum scoparium, Eurhynchium angustirete, Rhytidiadelphus subpinnatus, Orthotrichum speciosum, Oxyrrhynchium hians.* These species can be recommended for use in passive moss biomonitoring of atmospheric deposition of trace elements.

*Key-Words:* biomonitoring, epithermal neutron activation analysis, air pollution, trace elements, heavy metals, rare earth elements, species of moss bio-monitors

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### **1** Introduction

The idea of using terrestrial mosses for the analysis of atmospheric deposition of heavy metals has been proposed in the late 60-ies of the XX century by Ruhling and Tyler (1968) [25]. It is based on features of moss anatomic structure and physiology. The leaves of moss are composed of 1-3

layers of cells, they lack cuticles on the leaves preventing the penetration of pollutants, as well they have no roots and they readily absorb water and nutrients from wet and dry deposition by rhizoids.

Mosses effectively accumulate heavy metals and other compounds due to the large specific surface area and slow growth. As a passive biomonitor in most cases, they helps to identify the impact of pollutants at the ecosystem level. Ideas of moss monitoring in Europe have been developed by Rühling, Steinnes, Berg, Harmens et al. [1; 13-15; 17; 26-31; 36-39].

Since the 1970s, the Scandinavian countries, and in the last 20 years in the Western, Central and Eastern Europe passive briomonitoring receives support of targeted state grants and programs, it is held regularly every five years in the framework of the UN Convention on Long-Range Transboundary Air Pollution (LRTAP) [13, 16; 29-31]. Coordination of moss briomonitoring in Europe, Russia and Asia is carried out through the United Nations program (UNECE ICP Vegetation).

Based on the monitoring results, the atlases of atmospheric deposition of pollutants are edited and published, which allow estimating the cross-border transfer of elements, reveal sources of pollution and their impact on the environment, as well as to trace the retrospective distribution of elements in the atmosphere [13, 16, 18].

In Russia, conducting biomonitoring first started in the north-western regions: Leningrad Region, Kola Peninsula, Karelia [1]. Since the late 90-ies of the XX century briomonitoring carried out on the basis of the analytical complex of the Joint Institute for Nuclear Research for a number of central regions of Russia and South Ural: one-time study conducted in Tula Region [4, 6]; moss biomonitoring of Tver, Kostroma, part of the Moscow and Ivanovo regions [2, 3, 5, 8, 33, 40], as well as in Kaliningrad Region [19-21].

Since 2014 the coordination of ICP Vegetation has been transferred to the Joint Institute for Nuclear Research (Dubna, Moscow region) to M.V. Frontasyeva. Due to her efforts the following countries joint the moss biomonitoring programme in the Caucasus and Asia: Azerbaijan, Georgia, Kazakhstan, Mongolia, Vietnam and Moldova in the South-East and contribute to the moss survey in 2015-2016. In addition to atmospheric deposition of heavy metals, this method also allows evaluating the contamination with nitrogen, persistent organic pollutants (POPs) and radionuclides [15, 17].

## 2 Problem Formulation. Study area. Materials and methods.

The study area, Tula region is situated in the central part of the Eastern European Plain, it covers an area of 25.7 thousand square km. It borders in the north and north-east with Moscow, in the east with Ryazan region, in the south-east and south with Lipetsk region, in the south and south-west with

Oryol region, in the west and north-west with Kaluga region. The length of the territory from north to south is 200 km, from west to east is 190 km. The population is 1,513,600 people, 500,000 of which live in the territory of large industrial regional center - the city of Tula. Tula region is the second after Moscow and it is among the five most ecologically unfavorable regions of Russia, 10 times exceeding the amount of emissions to the atmosphere of the surrounding the Kaluga and Oryol regions. Regional environmental problems are caused, first of all, by clustering of 473 enterprises of chemical, metallurgy, defense, machine-building industry, fuel and energy and mining complex at a relatively small area, being the main sources of air pollution in the region.

According to a random Federal statistical observation in 2014 emissions of harmful substances by enterprises of Tula region amounted to 181.3 thousand tons. On average, it was 120 kg of harmful substances per capita per year. A total of 15129 stationary sources of emissions of air pollutants were encountered in the region in 2014. A bit more than half (52%) of emissions in the atmosphere of harmful substances are emissions produced by manufacturing industries, including metallurgical chemical enterprises: 32.8%, production companies: 6.3%. Only 74 % of environment pollutants are captured and neutralized every year. 32% of emissions are accounted for by the city of Tula and Novomoskovsky, Alexinsky, Shchekinsky, Efremovsky districts [24]. According to the number of harmful emissions into the atmosphere Tula is one of the 60 most polluted cities in Russia.

In our previous studies, geochemical anomalies were identified for heavy metal (HM) content in the air and soil for more than 30% of the city territory [11, 12]. Environmental pollution causes irreparable damage to the health of the population of the region, which is reflected in the growth rate of population mortality, rates for respiratory diseases, blood and blood-forming organs, tumors in children and adults, and congenital anomalies in children [23, 34].

Due to the severe environmental situation in the region it is necessary to conduct the regular monitoring studies. Previous study showed high content of V, Ni, As and Pb in atmospheric deposition of the region [4, 6].

In addition to the severe environmental situation, study area is characterized by a unique location at the crossroads of 3 natural zones: zone of mixed coniferous-deciduous forests in the north, deciduous in the central part and the forest-steppe zone, passing into steppe in the south of the region.

Since the standard techniques of passive briomonitoring includes a small number of recommended species found mainly in the zone of coniferous-deciduous forests, we had, in addition to carrying out monitoring using traditional moss species, a research task to determine the species of mosses, which can be used for passive briomonitoring in deciduous forests and foreststeppe regions of Russia and Asia.

To this end, we collected different species of moss in a number of sampling points to compare their bioaccumulation capacity.

### 2.1 Objects of investigation.

The objects of the study were 24 species of mosses collected in the northern, central and southern part of the region, among which recommended for biomonitoring species are Pleurozium schreberi and species that we used for comparison in terms of bioaccumulation of elements from atmospheric deposition: Dicranum polysetum, Dicranum scoparium, Drepanocladus polygamus, Drepanocladus aduncus, Anomodon longifolius, Aulacomnium palustre, Atrichum undulatum, Abietinella abietina. Cirriphyllum piliferum, Plagiomnium ellipticum, Climacium dendroides, Rhytidiadelphus triquetrus, Oxyrrhynchium hians, Eurhynchium angustirete, Cirriphyllum piliferum, *Rhytidiadelphus* subpinnatus, Orthotrichum speciosum, Plagiomnium undulatum, Polytrichum and Sphagnum species.

### 2.2. Sampling and sample preparation

Collection of moss samples was conducted in the summer-autumn season (June-September) 2014-2015, according to the standard technique [10]. The network included 82 sampling points. The average distance between points was 10-15 km. Sampling sites were chosen at a distance of at least 300 meters away from the roads and settlements, and no closer than 100 meters from the pedestrian roads. Sampling was conducted in disposable gloves to avoid contamination. Samples were transported in plastic bags, which were labeled according to the squares of the sampling, previously marked in the sampling map. Labels on the packages contained coordinates of sampling site, phytocenosis association, place of sampling (soil, deadwood, bark, etc.), distance to the nearest roads and settlements. The samples were not washed and grinded.

Moss was cleaned from extraneous materials (leaves, bark residues, soil, fallen pine needles and

other debris), and stored in paper bags. Green and greenish-brown moss segments corresponding to a three-year growth were used for analysis. The samples were dried at room temperature and brought to a constant weight at 40°C during 48 hours. Sample preparation was conducted in the laboratory using a spatula and tweezers of polymeric materials to prevent contamination with metals. Moss material was well mixed and 0.3 g of randomly chosen moss species was pressed and weighed. Then the pellets were packed into polythene bag to determine the short-lived isotopes and in the aluminum foil for the determination of long-lived isotopes.

### 2.3. Analysis

Instrumental epithermal neutron activation analysis was carried out at pulsed fast reactor IBR-2 of the Frank Laboratory of Neutron Physics, JINR, Dubna, Russia. Characteristics of neutron flux density in the two irradiation channels equipped with the pneumatic system and registration of gamma spectra can be found elsewhere [9].

A total of 42 elements were determined. To determine elements with short lived isotopes (Cl, V, I, Mg, Al, and Mn) samples were irradiated for 3 min and measured for 20 min. To determine elements with long lived isotopes: Na, Sc, Cr, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Zr, Mo, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Hf, Ta, W, Th, and U, the cadmium-screened channel 1 was used. Samples were irradiated for 4 days, re-packed, and measured twice using HP germanium detectors after 4 and 20 days of decay, respectively. The NAA data determination processing and of element concentrations were performed using software developed in FLNP JINR [22].

The quality control of ENAA results was provided by using certified reference matertials: 1570a (*Spinach* Leaves) and 1575a (*Pine* Needles). The experimentally measured contents were in good agreement with the recommended values.

The uncertainties in elemental determinations of Na, K, Cl, As, Sr, Fe, Pb were in the range of 5-10%; and uncertainty for V, Ni, Cu, Se, Mo, Cd, Sb was 30%.

To evidence any association of chemical elements as well as to decrease the number of variables for the obtained data, Factor Analysis (FA) was use. Multivariate statistical analysis was performed using Stat-SoftTM Statistica 9.

## **3** Problem Solution

Table 1 presents data of ENAA of 41 elements in mosses biomonitors of Tula region in retrospective. The data reflect the improvement of the ecological situation in the region with regard to the content in the air of some heavy metals: Mn, Zn, and V. This is may be due to a production decrease at one of metallurgical enterprises "Vanadium-Tula" allocated in the city of Tula. However, in atmospheric air increase the concentration of such elements as Fe (till 30% of average values), Cr and Co (till 40-43%), As and Cd (till 37%), Sr and Sm (till 22%) was observed. The increase of anthropogenic impact on the environment of the region can be attributed to several factors: the increase in production at enterprises of ferrous metallurgy, metal processing and defense industries, ore processing, an increase in the share of vehicle pollution and increasing the pace of development of agricultural production. As a consequence increased erosion and reduction of the area occupied by natural ecosystems which is a barrier against the spread of pollutants and natural filter take place. Also we don't exclude transboundary transfer of these elements through the south-west winds from the Ukraine (HM and rare earth elements as the results of mining and processing of coal as well as of military actions).

ENAA results of moss samples collected in Tula region showed that the region is characterized by high level of pollution in comparison with the countries of CIS and Europe, and in comparison with other studied regions of Russia (Tab. 2, 3).

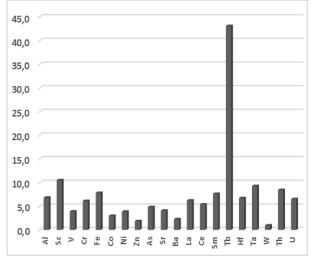


Fig.1 Coefficients of accumulation of elements in mosses of Tula region compare with background values

Table 1	l
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Comparative elemental content in moss from moss surveys in 2000 and 2015

I	moss surveys in 2000 and 2015					
(	2000	[4, 6]		2015		
( <b>n&gt;90</b> )	mean	medi ana	range	mean	$Md \pm \sigma$	
Na	409	373	72-1780	436	295±52	
Mg	2425	2200	1320- 10800	3429	2720±407	
Al	3600	2700	434- 25400	4566	2560±542	
Cl	650	540	68-2510	499	345±59	
K	10500	$\begin{array}{c} 1000 \\ 0 \end{array}$	5300- 23200	1303 4	13000±1547	
Ca	6100	5600	2000- 16100	7520	7350±892	
Fe	2200	1660	293- 20100	3186	1860±378	
Mn	300	240	62-608	210	185±25	
Zn	54	52	19-120	52	49±6	
Ti	-	-	47-1770	363	188±43	
Ba	46	41	9-171	60	<b>46</b> ±7	
Sc	0.57	0.4	0.08-4.38	0.90	0.49±0.07	
V	8	6	0.71-72	8.8	4.5±1.04	
Cr	5	4	0.6-47.8	8.9	5.8±1.1	
Ni	3.7	3.2	0.64-12.7	3.9	3.2±0.4	
Со	0.63	0.5	0.16-5.34	1.1	0.68±0.13	
As	0.5	0.4	0.13-4.92	0.8	0.46±0.09	
Br	3.1	2.9	1.4-18	3.8	3.2±0.5	
Rb	14.3	13	3-39	12	10.4±1.4	
Sr Cd	26.5	25	8-110	33	29±4	
Cd I	<b>0.32</b> 1.5	<b>0.3</b> 1.5	<b>0.14-1.77</b> 0.18-16.2	<b>0.5</b> 1.4	0.38±0.06 0.99±0.16	
La	2.6	2	0.18-10.2	3.1	0.99±0.10 1.7±0.4	
	2.0		0.42-27.5			
	16					
Ce	4.6	3.8		6.4	3.6±0.8	
Nd	4.6 -	-	0.35-10.9	3.3	2.1±0.4	
Nd Zr	4.6 - -	- -	0.35-10.9 2-119	3.3 31	2.1±0.4 15±4	
Nd Zr Se	- - -		0.35-10.9 2-119 0.03-0.51	3.3 31 0.18	2.1±0.4 15±4 0.16±0.02	
Nd Zr Se Mo	- - 0.43	- - 0.36	0.35-10.9 2-119 0.03-0.51 0.08-0.91	3.3 31 0.18 0.24	2.1±0.4 15±4 0.16±0.02 0.18±0.03	
Nd Zr Se Mo Sb	- - 0.43 0.15	- - 0.36 0.13	0.35-10.9 2-119 0.03-0.51 0.08-0.91 0.02-1.51	3.3 31 0.18 0.24 0.17	2.1±0.4 15±4 0.16±0.02 0.18±0.03 0.13±0.02	
Nd Zr Se Mo	- - 0.43	- - 0.36	0.35-10.9 2-119 0.03-0.51 0.08-0.91	3.3 31 0.18 0.24	2.1±0.4 15±4 0.16±0.02 0.18±0.03	
Nd Zr Se Mo Sb Cs	- - 0.43 0.15 0.25	- - 0.36 0.13 0.21	0.35-10.9 2-119 0.03-0.51 0.08-0.91 0.02-1.51 0.05-1.56	3.3   31   0.18   0.24   0.17   0.34	2.1±0.4 15±4 0.16±0.02 0.18±0.03 0.13±0.02 0.20±0.04	
Nd Zr Se Mo Sb Cs Sm	- - 0.43 0.15 0.25	- - 0.36 0.13 0.21	0.35-10.9 2-119 0.03-0.51 0.08-0.91 0.02-1.51 0.05-1.56 <b>0.02-2.13</b>	3.3   31   0.18   0.24   0.17   0.34	2.1±0.4 15±4 0.16±0.02 0.18±0.03 0.13±0.02 0.20±0.04 <b>0.33</b> ±0.06	
Nd Zr Se Mo Sb Cs Sm Eu	- - 0.43 0.15 0.25	- - 0.36 0.13 0.21	0.35-10.9 2-119 0.03-0.51 0.08-0.91 0.02-1.51 0.05-1.56 <b>0.02-2.13</b> 0.04-0.56	3.3   31   0.18   0.24   0.17   0.34   0.50   0.144	2.1±0.4 15±4 0.16±0.02 0.18±0.03 0.13±0.02 0.20±0.04 <b>0.33</b> ±0.06 0.09±0.02	
Nd Zr Se Mo Sb Cs Sm Eu Gd	- 0.43 0.15 0.25 0.39 -	- 0.36 0.13 0.21 0.29 -	0.35-10.9 2-119 0.03-0.51 0.08-0.91 0.02-1.51 0.05-1.56 <b>0.02-2.13</b> 0.04-0.56 0.01-4.08 0.006-	3.3   31   0.18   0.24   0.17   0.34   0.50   0.144   0.46	2.1±0.4 15±4 0.16±0.02 0.18±0.03 0.13±0.02 0.20±0.04 <b>0.33</b> ±0.06 0.09±0.02 0.19±0.05	
Nd Zr Se Mo Sb Cs Sm Eu Gd Tb	- 0.43 0.15 0.25 0.39 -	- 0.36 0.13 0.21 0.29 -	0.35-10.9 2-119 0.03-0.51 0.08-0.91 0.02-1.51 0.05-1.56 <b>0.02-2.13</b> 0.04-0.56 0.01-4.08 0.006- 0.314 0.005-	3.3   31   0.18   0.24   0.17   0.34   0.50   0.144   0.46   0.081	2.1±0.4 15±4 0.16±0.02 0.18±0.03 0.13±0.02 0.20±0.04 <b>0.33</b> ±0.06 0.09±0.02 0.19±0.05 0.04±0.01	
Nd Zr Se Mo Sb Cs Sm Eu Gd Tb Tm	- - 0.43 0.15 0.25 0.39 - - 0.052 -	- - 0.36 0.13 0.21 <b>0.29</b> - - 0.042 -	0.35-10.9 2-119 0.03-0.51 0.08-0.91 0.02-1.51 0.05-1.56 <b>0.02-2.13</b> 0.04-0.56 0.01-4.08 0.006- 0.314 0.005- 0.355 <b>0.05-1.34</b> 0.05-3.71	3.3     31     0.18     0.24     0.17     0.34     0.50     0.144     0.46     0.081     0.065	2.1±0.4 15±4 0.16±0.02 0.18±0.03 0.13±0.02 0.20±0.04 <b>0.33</b> ±0.06 0.09±0.02 0.19±0.05 0.04±0.01 <b>0.046±0.008</b>	
Nd Zr Se Mo Sb Cs Sm Eu Gd Tb Tm Yb	- 0.43 0.15 0.25 0.39 - 0.052 - 0.15	- - 0.36 0.13 0.21 <b>0.29</b> - - 0.042 - <b>0.11</b>	0.35-10.9 2-119 0.03-0.51 0.08-0.91 0.02-1.51 0.05-1.56 0.02-2.13 0.04-0.56 0.01-4.08 0.006- 0.314 0.005- 0.355 0.05-1.34	3.3   31   0.18   0.24   0.17   0.34   0.50   0.144   0.46   0.081   0.065   0.34	2.1±0.4 15±4 0.16±0.02 0.18±0.03 0.13±0.02 0.20±0.04 <b>0.33</b> ±0.06 0.09±0.02 0.19±0.05 0.04±0.01 <b>0.046±0.008</b> <b>0.20±0.04</b>	
Nd Zr Se Mo Sb Cs Sm Eu Gd Tb Tb Tm Yb Hf	- 0.43 0.15 0.25 0.39 - 0.052 - 0.15 0.82	- 0.36 0.13 0.21 <b>0.29</b> - - 0.042 - <b>0.11</b> 0.64	0.35-10.9 2-119 0.03-0.51 0.08-0.91 0.02-1.51 0.05-1.56 <b>0.02-2.13</b> 0.04-0.56 0.01-4.08 0.006- 0.314 0.005- 0.355 <b>0.05-1.34</b> 0.05-3.71 0.009-	3.3   31   0.18   0.24   0.17   0.34 <b>0.50</b> 0.144   0.46   0.081   0.065 <b>0.34</b> 0.91	2.1±0.4 15±4 0.16±0.02 0.18±0.03 0.13±0.02 0.20±0.04 <b>0.33</b> ±0.06 0.09±0.02 0.19±0.05 0.04±0.01 <b>0.046±0.008</b> <b>0.20±0.04</b> 0.46±0.11	
NdZrSeMoSbCsSmEuGdTbTmYbHfTa	- 0.43 0.15 0.25 0.39 - 0.052 - 0.15 0.82 0.078	- 0.36 0.13 0.21 <b>0.29</b> - - 0.042 - <b>0.11</b> 0.64 0.058	0.35-10.9 2-119 0.03-0.51 0.08-0.91 0.02-1.51 0.05-1.56 <b>0.02-2.13</b> 0.04-0.56 0.01-4.08 0.006- 0.314 0.005- 0.355 <b>0.05-1.34</b> 0.05-3.71 0.009- 0.363	3.3   31   0.18   0.24   0.17   0.34   0.50   0.144   0.46   0.081   0.065   0.34   0.91   0.087	2.1±0.4 15±4 0.16±0.02 0.18±0.03 0.13±0.02 0.20±0.04 <b>0.33</b> ±0.06 0.09±0.02 0.19±0.05 0.04±0.01 <b>0.046±0.008</b> <b>0.20±0.04</b> 0.46±0.11 0.05±0.01	

In comparison with other regions of Russia, revealed a high content of V, Fe, Co, As, Sr, La, Ce, Tb, Hf, Ta, Th, U and Sm in moss-biomonitors was revealed (Tab. 2).

Table 2

#### Comparison of atmospheric deposition of elements in different regions of Russia based on moss analysis, (mediana) mg/kg

		Mosc		-		
	Tula region	ow region [40]	Tver region [5]	Ivano vo [2, 3]	Kostr oma	Udmu rtia
Na	295	240	263	190	487	260
Mg	2720	1963	6045	2530	3040	-
Al	2560	813	374	884	1880	1140
Cl	345	182	1174	161	13500	143
K	13000	10765	34268	9750	11850	9600
Ca	7350	3496	22545	3565	6060	4100
Sc	0.49	0.161	0.047	0.286	0.298	0.2
V	4.45	2.32	1.14	2.42	5.21	2.6
Cr	5.80	3.09	0.95	2.32	5.93	6.2
Mn	185	405	836	706	33650	210
Fe	1860	843	237	635	1270	890
Со	0.68	0.31	0.23	0.45	0.823	0.4
Ni	3.19	2.39	0.82	3.96	5.21	4.7
Zn	49.0	51.2	26.4	48.1	44.3	42
As	0.46	0.19	0.09	0.57	0.42	0.3
Se	0.16	0.17	0.10	0.25	0.13	0.12
Br	3.2	1.7	1.6	4.0	7.4	1.8
Rb	10.4	16.9	25.4	15.2	14.7	5.3
Sr	29.0	17.2	7.1	24.4	22.3	22
Мо	0.18	0.37	0.39	0.11	-	0.5
Cd	0.38	-	0.22	0.43	0.07	-
Sb	0.13	0.22	0.08	0.19	0.12	0.12
Cs	0.20	0.16	0.14	0.15	0.17	0.12
Ba	46.0	47.6	20.1	86.6	59.8	58
La	1.72	0.67	0.28	0.61	2.13	0.6
Ce	3.60	2.12	0.67	1.05	2.84	1
Sm	0.33	0.12	0.04	0.15	0.24	0.08
Tb	0.041	0.013	0.001	0.016	0.023	0.01
Hf	0.460	0.148	0.068	0.121	0.313	0.200
Та	0.055	0.029	0.006	0.027	-	0.020
W	0.140	0.347	0.146	0.202	0.363	0.400
Th	0.530	0.189	0.063	0.156	0.341	0.100
U	0.160	0.077	0.025	0.073	0.143	0.060

The coefficients of elemental concentrations in mosses were calculated in relation to the background values (Fig. 1). A relatively pristine area of the Tver region was chosen as a background zone [40]. The model developed by Fernandes and Carballeira was used to assess the level of contamination [7].

Table 3

#### Comparison of atmospheric pollution of Tula region with different countries [14, 18], (mean) mg/kg

(mean) mg/kg							
Element μg/g	v	Cr	Fe	Ni	Zn	As	Cd
Tula region RF	8.8	8.9	3186	3.9	53	0.76	0.49
Russia	2.3	3.6	679	2.7	40	0.23	0.24
Belarus	1.3	1.2	394	1.3	31	0.15	0.21
Ukraine	2.1	1.9	450	1.7	36	0.22	0.32
Austria	1.0	1.1	300	1.0	29	0.18	0.18
Belgium	4.5	4.5	967	4.0	77	0.68	0.49
Bolgaria	3.9	2.4	1399	3.0	28		0.31
Croatia	3.1	2.8	991	2.7	29	0.37	0.28
Czech Republic	1.5	1.2	409	1.4	33	0.29	0.23
Denmark	2.5	0.8	401	0.9	17	0.08	0.06
Estonia	1.0	0.7	177	0.7	28		0.16
Finland	1.2	0.9	186	1.5	32	0.11	0.14
France	2.4	2.0	713	2.2	28	0.37	0.11
Macedonia	6.4	6.8	2239	5.8	36	0.68	0.29
Germany	1.1	2.4	328	1.2	47	0.16	0.21
Iceland	-	3.3	-	3.2	21	0.11	0.05
Italy	2.9	3.4	1038	2.9	33	0.46	0.12
Latvia	1.3	0.8	188	0.8	40	0.11	0.24
Lithuania	1.2	1.0	183	1.0	18	0.16	0.13
Norway	1.4	0.6	273	1.2	31	0.12	0.09
Poland	2.6	2.7	775	2.6	64	0.9	0.25
Serbia	5.8	6.4	2267	4.4	29	1.41	0.26
Slovakia	3.3	2.4	840	3.9	49	0.86	0.5
Slovenia	3.4	2.1	943	2.8	39	0.43	0.33
Spain	1.5	6.5	352	3.7	37	0.18	0.08
Sweden	0.9	0.6	117	0.6	31	0.07	0.14
Switzerlan d	0.7	1.2	261	1.6	31	0.15	0.15
Turkey	6.3	4.4	1709	4.0	28	1.71	0.3
Great Britain	1.2	0.8	-	0.8	20	0.12	0.09

The level of contamination determined as <1 is "no pollution", 1-2 is "possible contamination"; 2-3.5 is "slight pollution"; 3.5-8 is "average pollution", 8-27 is "high pollution". Air pollution of Tula region with HM and metalloids, as well as rare earth elements can be classified as slight: Co, Ni, Ba; average: Al, V, Cr, Ni, As, Sr, La, Ce, Sm, Hf, U; strong: Fe, Tb, Ta, Th (Fig. 1).

Comparison of the data with the values for the European countries represented in the atlas of atmospheric deposition (Tab. 3) shows a high level of content in the ambient air of the region of such heavy metals and metalloids as:

V: values 2 times higher than the average for Russia and 6.8 above the Republic of Belarus, in 1.4-9 times higher than European Union countries;

**Cr**: value 2.5 times higher than the Russian average, in 7.4 above the Republic of Belarus, in 1.3-9 times higher than in Europe;

**Fe**: value 4.7 times higher than the Russian average, 8 times higher than for the Republic of Belarus mosses, in 1.4-12 times above the European Union countries;

**Zn**: value 32% exceed the Russian average, 42% of the Belarus Republic and 1.3-3 times higher than in Europe;

**As**: value 3.3 times higher than the Russian average, 5 times higher than the Republic of Belarus and 1.2-7 times higher than in Europe;

**Cd**: values 2 times higher than the average for Russia and Republic of Belarus, in the 1.5-10 times higher than in European countries.

Results of the factor analysis revealed four factors (tab 4.):

**Factor 1**: *Na*, *Mg*, *Al*, *Sc*, *Ti*, *Cr*, *Ni*, *Co*, *As*, *Rb*, *Zr*, *Ba*, *Cs*, *La*, *Ce*, *Nd*, *Sm*, *Eu*, *Tb*, *Yb*, *Hf*, *Ta*, *Th*, *U* associate with soils, industrial pollution of soil and weathering processes.

**Factor 2**: *V*, *Fe*, *Zn*, *Se*, *Mo* - can be attributed to technogenic industrial pollution.

Factor 3: *Ca*, *Cl*, *Br* associate with physiological activity of mosses.

**Factor 4**: *Sb*, *Tm*, *W* associate with the extraction and processing of ores.

Comparison of the ability of different moss species collected in the phytocenosis of different natural zones of the region to accumulate trace elements from atmospheric deposition revealed that part of analyzed moss species is characterized by a low accumulative capacity.

Among them: *Plagionnium undulatum* (Hedw.) T.J. Kop: accumulates 2-2.5 times less V, Mn, Ni, Sb, Mo than the recommended species; 2.5-4 times -Fe, Co, Cs; 3-7 times less the rare earth elements. This may be due to the peculiarities of its morphological structure, by water elution of elements, as it is growing in in wetland habitats and marshes. *Cirriphyllum piliferum* (Hedw.) is also not suitable for passive biomonitoring of atmospheric deposition. It accumulates 6-8 times less V, 3.5-4 times less Fe, Co, Cs, 3 times less As and Mo, 2 times less Sb; at 40-50% smaller Zn, Cd, Sr; up to 5 times less the rare earth elements than the recommended species. Such species as *Atrichum undulatum* (Hedw.) P. Beauv. D can be used for passive moss biomonitoring of atmospheric pollution most of trace and rare earth elements, but have poor accumulative capacity for such elements as V (values are below up to 30%) and Mn (accumulate up to 3 times less than recommended species).

*Plagiomnium ellipticum* (Brid.) T.J. Kop. can be used for biomonitoring, but we do not recommend to collect it in wetland biocenosis. *Plagiomnium ellipticum* growing on wetland accumulate 3-4 times less Cl, 4 times less V, 1.5-2 times less Fe, Cu and As than *Sphagnum* mosses.

From the studied moss species have good capability and close to the accumulative recommended for biomonitoring of atmospheric deposition of trace elements species are such moss species as: Abietinella abietina (Hedw.) M. Fleisch., Aulacomnium palustre (Hedw.) Schwägr, Brachythecium rutabulum (Hedw.) Bruch et al., Brachythecium salebrosum (F. Weber & D. Mohr) Bruch et al., Climacium dendroides (Hedw.) F. Weber & D. Mohr, Dicranum polysetum Sw., Hedw., Dicranum scoparium Eurhynchium angustirete (Broth.) T.J. Kop., Rhytidiadelphus subpinnatus (Lind.) T.J. Kop., Orthotrichum speciosum Nees, Oxyrrhynchium hians (Hedw.) Loeske. These species can be recommended for use for passive biomonitoring in a moderatelycontinental zone of Russia, Europe and Asia.

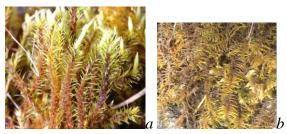


Fig. 2. Aulacomnium palustre (a) [41]; Abietinella abietina (b) [42]; Dicranum polysetum (c) [44]; Dicranum scoparium [45]





Fig.3. Brachythecium rutabulum



Fig. 4. Brachythecium salebrosum



Fig. 5. Rhytidiadelphus subpinnatus



Fig. 6. Climacium dendroides



Fig. 7 Eurhynchium angustirete



Fig. 8. Orthotrichum speciosum



Fig. 9. Oxyrrhynchium hians

	Factor 1	Factor 2	Factor 3	Factor 4
Na	0.89	0.16	0.26	0.11
Mg	0.85	0.31	0.18	-0.04
Al	0.91	0.28	0.00	0.04
Cl	0.14	-0.06	0.86	-0.20
K	0.27	-0.17	0.28	-0.49
Ca	0.19	0.32	0.62	0.22
Sc	0.97	0.21	0.03	0.05
Ti	0.94	0.21	-0.05	-0.03
V	0.41	0.77	-0.10	0.30
Cr	0.78	0.53	0.04	0.10
Mn	0.58	0.34	-0.28	-0.15
Fe	0.54	0.69	-0.06	0.22
Ni	0.87	0.37	-0.02	0.10
Со	0.93	0.26	0.05	0.08
Zn	0.12	0.70	0.15	-0.08
As	0.84	0.20	0.14	0.10
Se	0.06	0.86	-0.04	0.27
Br	0.06	0.38	0.79	-0.15
Rb	0.82	0.23	0.23	-0.09
Sr	0.68	0.37	0.16	0.17
Zr	0.96	0.06	-0.09	-0.01
Мо	0.34	0.67	0.16	0.28
Cd	0.26	-0.01	-0.29	-0.28
Sb	0.12	0.51	0.03	0.73
Ι	0.37	0.56	0.08	0.07
Ba	0.92	0.12	-0.10	0.11
Cs	0.92	0.30	0.03	0.08
La	0.97	0.19	-0.01	0.07
Ce	0.97	0.18	-0.01	0.07
Nd	0.94	0.16	-0.04	0.21
Sm	0.96	0.19	0.01	0.04
Eu	0.89	0.16	0.03	0.20
Gd	0.67	-0.02	0.06	0.51
Tb	0.98	0.14	-0.03	0.04
Tm	0.50	-0.02	0.03	0.71
Yb	0.95	0.20	-0.04	0.03
Hf	0.96	0.05	-0.09	0.00
Та	0.98	0.17	-0.02	0.04
W	0.20	0.39	0.06	0.76
Au	-0.23	-0.14	0.41	0.11
Th	0.97	0.17	-0.02	0.11
U	0.87	0.31	-0.02	0.18
Expl.Var	22.847	5.352	2.470	2.883
Prp.Totl	0.544	0.127	0.059	0.069

Table 4 Factor analysis of INAA data on moss samples from Tula region (2015)

## 4 Conclusion

The study of atmospheric pollution by passive biomonitoring in the industrial region of central Russia - Tula region revealed a tendency to increased pollution with such elements as: Fe, Cr, Co, As, Cd, Sr, and Sm in the past 10 years. Compared to the other regions of Russia the air of Tula region is contaminated with such elements as: V, Fe, Co, As, Sr, La, Ce, Tb, Hf, Ta, Th, U, and Sm. These are the elements of technogenic origin, associated with the activity of the metallurgical, metalworking, defense, coal mining enterprises in the region. These elements can be transferred by air masses to neighboring areas. Compared with data of passive moss biomonitoring for the Republic of Belarus and the EU, as well as the for the UK, the air of Tula region contains 1.5-7 times more V, Cr, Fe, Zn, As, Cd, that may be a cause of cancer, chronic cardiovascular and respiratory system diseases in adults and children, as well as the cause of weakening the immune system of the population of the studied area.

Of the studied species of mosses for biomonitoring cannot be used: *Plagiomnium undulatum* and *Cirriphyllum piliferum*.

For passive biomonitoring of atmospheric deposition of trace elements can be recommended such species as: Abietinella abietina, Aulacomnium palustre, Brachythecium rutabulum, Brachythecium salebrosum, Climacium dendroides, Dicranum polysetum, Dicranum scoparium, Eurhynchium angustirete, Rhytidiadelphus subpinnatus, Orthotrichum speciosum, Oxyrrhynchium hians.

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