Trace Element Accumulating Ability of Different Moss Species Used to Study Atmospheric Deposition of Heavy Metals in Central Russia: Tula Region Case Study

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Abstract Multi-element epithermal neutron activation analysis (ENAA) applied to different moss species collected over the territory of Tula Region (Russia) determined the level of their ability to accumulate heavy metals and metalloids from wet and dry atmospheric depositions. Moss species were revealed with accumulating ability close to that one for moss species recommended for moss biomonitoring purposes (Pleurozium schreberi, etc): Abietinella abietina, Atrichum undulatum, Rhytidiadelphus triquetrus, as well those which are characterized by high accumulation ability of toxic element from the environment: Brachythecium rutabulum, Brachythecium salebrosum, Eurhynchium angustirete, Plagiomnium ellipticum, Orthotrichum speciosum, Oxyrrhynchium hians. These species can be recommended for use in passive moss biomonitoring of atmospheric deposition of trace elements. The species with low accumulating ability of heavy metals and metalloids were also revealed: Climacium dendroides, Plagiomnium undulatum, Sphagnum sp., Using the method of passive moss biomonitoring, air pollution of Tula region (Central Russia) 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.

Keywords biomonitoring, moss species, bioaccumulation of elements, epithermal neutron activation analysis, air pollution, trace elements, heavy metals, rare earth elements

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I. Introduction

• Mosses are higher spore plants that have a number of features to successfully use them for biomonitoring purposes:

- lack cuticles on the leaves preventing the penetration of pollutants; they have no roots and they readily absorb water and elements from wet and dry deposition by rhizoids and leaves;
- the leaves of moss are composed of 1-3 layers of cells;
- effectively accumulate heavy metals and other compounds over a larger time period due to the large surface-to-weight ratio and slow growth.;
- undeveloped vascular bundles allow better adsorption than vascular plants;
- minimal morphological changes during moss lifetime;
- wide distribution and ease of sampling;
- possibility to determine concentrations in the annual growth segments [41].

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. As a passive biomonitor in most cases, mosses 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].

In various studies the characteristics of different moss species to accumulate trace elements from the environment are given: comparative characteristics of *Sphagnum sp*. and *Politrichum commune* [55]; Sphagnum sp. in the Tomsk Region, the Volgograd Region and Siberia [47, 48]; comparison of accumulation ability of four types of forest mosses: *Pleurozium schreberi, Dicranum polysetum, Ptilium crista-castrensis, Hylocomium splendens,* four species of bog mosses: *Aulacomnium palustre, Sphagnum angustifolium, Sphagnum squarrosum, Sphagnum centrale* and two species of epiphytic moss: *Pylaisia polyantha, Orthotrichum obtusifolium*, which finally revealed higher accumulative ability of *Dicranum polysetum and Pylaisia polyantha* in comparison to *Hylocomium splendens* recommended for the classic monitoring purposes. Epiphytic moss *Pylaisia polyantha* was suggested for air pollution monitoring in Russia [50]. It was shown that *Aulacomnium palustre* has a high accumulative ability compared with *Sphagnum* mosses; and two epiphytic mosses*: Pylaisia polyantha, Orthotrichum obtusifolium* and the terrestrial moss *Dicranum polysetum* having the highest accumulating abilities in comparison with *Hylocomium splendens and Pleurozium schreberi* used for monitoring in Europe. However, the necessity to study moss species and extension of their list to be used as biomonitoring in deciduous, small-leaved forests, forest-steppe and steppe regions is still acute.

II. 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 enterprises: 32.8%, chemical 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 forest-steppe regions of Russia, Asia and Europe.

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 23 species of mosses which were collected in the northern, central and southern part of the Tula region, among which some species were recommended for biomonitoring. There are *Pleurozium schreberi* and species that we used for comparison in terms of bioaccumulation of elements from atmospheric deposition:

Bryopsida

Sphagnidae

Sphagnaceae

Sphagnum angustifolium (Russ.) C. Jens. – *S. parvifolium* (Warnst.) Warnst. is found in the central areas of usually open oligo- and mesotrophic bogs formed in karst holes and in suffusion depressions at the sand.

Sphagnum girgensohnii Russ. is a species of typical for eutrophic wooded mires and pine forests with spruce, commonly grows on trees stem.

Shagnum fallax (Klinggr.) Klinggr. – *S. apiculatum* H. Lindb. – *S. recurvum* var. *mucronatum* (Russ.) Warnst are widespread species, occurring both in open and forested mires, on the outskirts of the swamps, small marshy depressions (depressions) [43], [49].

Bryidae

Mniaceae

Plagiomnium ellipticum (Brid.) T. Kop. – *Mnium rugicum* Laur. is a species of typical for moist habitats, grows on forested selvages sphagnum bogs, along the banks of streams, boggy meadows, found in the soil, peat and rotten wood. It is spread in all areas except the south of Central Russian steppe zone.

Plagiomnium undulatum (Hedw.) T. Kop. – *Mnium undulatum* Hedw, the species is confined to the damp and shaded conditions, grows along the banks, the slopes of the ravines in the forests. In the south and south-east of Upland rarer to be found [45], [49], [53].

Dicranaceae

Dicranum polysetum Sw. – *D. undulatum* Web. et Mohr – *D. rugosum* (Funk) Brid., species of ground cover is common in coniferous and mixed coniferous-deciduous forests, grows at the base of tree trunks, found on microelevations among sphagnum quagmire and along the margins of bogs. In the forest it is less common.

Dicranum scoparium Hedw. grows in the soil cover of coniferous and mixed coniferous-deciduous forests, swampy birch, usually confined to the bases of tree trunks. In the forest steppe, it is becoming rare [45], [46], [49], [53].

Polytrichaceae

Polytrichum strictum Brid. – *P. alpestre* Hoppe -
grows along the margins of sphagnum bogs, hummocks on the open marshes and swamp forests.

Atrichum undulatum (Hedw.) P. Beauv. - *Catharinea undulata* Hedw is widely distributed, it is found on nongreensward soil in deciduous forests, on the walls of ravines and ditches along the slopes of beams. It is less common in the southern and steppe regions. Widely distributed to most of Europe, on the Mediterranean coast of Africa and Turkey, in the Far East, Japan and China [45], [46], [49], [53].

Anomodontaceae

Anomodon longifolius (Brid.) Hartm. is a species of typical for steppe oak forests formed on rocky substrates in situ limestone and chalk, is less common in alder, grows at elevations near the trunks and the bottom of the tree trunks (oak stump, ash, linden) [45], [46], [49], [53].

Thuidiaceae

Abietinella abietina (Hedw.) Fleisch. - *Thuidium abietinum* (Hedw.) B.S.G. is a steppe species dedicated to the calcareous soils on the outputs of limestone and chalk, is less common on sandy soil, and grows on the slopes of the beams, at least in the steppe oak woods on stem rises. Distributed throughout the Holarctic from the Arctic to southern Europe and the Middle East [45],[46],[49], [53].

.***Bracytheciaceae***

Brachythecium rutabulum (Hedw.) B.S.G. is a type of wide ecological amplitude growing in waterlogged habitats in humid forests, rotten wood, on the slopes of ravines, in man-made environments. It is widespread in Europe and in the Caucasus in the deciduous forest zone.

Brachythecium salebrosum (Web. et Mohr) B.S.G. is a widespread species, which grows on the bare soil, rotten wood, on the base of tree stems of different breeds on rocky substrates, resistant to human impacts.

The Holarctic spread from the Arctic to North Africa, the Middle East, South China.

Cirriphyllum piliferum (Hedw.) Grout - *Eurhynchium piliferum* (Hedw.) B.S.G. - species grows on the exposed soil, stem of trees and litter (fallen leaves) in the coniferous and broad-leaved and broad-leaved forests, at least on the turf-covered limestone and sandstone. It is rare in the forest and steppe.

Eurhynchium angustirete (Broth.) T.J. Kop. - species is common in coniferous and broad-leaved and broad-leaved forests (oaks), grows on bare soil and litter. In the forest becomes rare, grows clumps at the base of tree trunks. It is widely spread in Europe to the mountain areas of the Mediterranean and the Caucasus. In the European part of Russia it is found in the forest and steppe zones.

Oxyrrhynchium hians (Hedw.) Loeske - *Eurhynchium hians* (Hedw.) Sande Lac. - is a species of wide ecological amplitude grows on bare soils of different types (chernozems, gray forest), on limestone, chalks, sandstones, man-made rocky substrates and boggy meadows. It is common in the zone of coniferous and deciduous forests of Europe [45], [46], [49], [53].

Climaceaceae

Climacium dendroides (Hedw.) Web. et Mohr is a species often found in the wet forests, along the edges of marshes and swampy depressions, usually confined to the bumps and stem enhancements. In the forest it is becoming rare.

Hylocomiaceae

Hylocomium splendens (Hedw.) B.S.G. – *Hypnum proliferum* Lindb. – is a species which grows in the soil cover of coniferous and mixed forests occur on limestone and chalky substrates.

Pleurozium schreberi (Brid.) Mitt. – *Hypnum schreberi* Brid. – typical species of ground cover spruce and pine forests of the taiga zone, in deciduous forests found on rotting wood, and on the bumps sphagnum bogs. In the forest it is becoming rare.

Rhytidiadelphus subpinnatus (Lindb.) T.J. Kop. - *R. calvencens* (Lindb.) Warnst. – the species often found on the marshy meadows and river valleys, rarely observed in the litter of coniferous-deciduous forests [45], [46], [49], [53]. .

Orthotrichaceae

Orthotrichum speciosum Nees is a species often found on the trunks of aspen, ash, birch, oak and willow, epiphyte. It is widespread, found throughout the Holarctic.

Aulacomniaceae

Aulacomnium palustre (Hedw.) Schwaegr. Is a species of wetland habitats, grows on peat, decaying wood, on hummocks among Sphagnum mosses, on the outskirts of the marshes, at the base of the trunks of birch trees.

Amblystegiaceae

*Drepanocladus polygamous (*Bruch et al.) Hedenas - *Campylium polyganum* (Bruch et al.) C.E.O. Jensen - is a species of wet habitats, mires, can occur on the basis of the diameter fallen in trunks. It is widespread in the forest zone, the northern steppe regions pretty rare. [45], [46], [49], [53].

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.

Each moss was cleaned from extraneous materials (leaves, bark residues, soil, fallen pine needles and other debris), and stored in paper bag. Green and greenish-brown moss segments of 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 a 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. For determination of elements with short lived isotopes (Cl, V, I, Mg, Al, and Mn) the moss 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 processing and determination 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

An analysis of the elemental composition of mosses collected in Tula region showed that species differ in their ability to accumulate the elements from the environment (Table. 1).

Table 1 contains data on average elemental content of moss species collected in different phytocenoses area differing in the degree of contamination (n = 3 ... 14, depending on the type and frequency of a sampling point).

Different species of the same genus differ in the degree of accumulation of elements. The last row of the table presents data on the content of the amount of trace elements (heavy metals and metalloid) from V to U in the moss samples.

If recommended by the UNECE ICP Vegetation Programme moss species *Pleurozium schreberi* taken as the standard, then the ability to accumulate heavy metals, non-metals and rare earth elements close to it is inherent to such species as *Abietinella abietina, Atrichum undulatum, Rhytidiadelphus triquetrus. A number of species: Brachythecium rutabulum, Brachythecium salebrosum, Eurhynchium angustirete, Oxyrrhynchium hians* has 1.8-3.5 times higher ability to accumulate trace elements from the environment than *Pleurozium schreberi.*

Two species presented in Table 1: *Orthotrichum speciosum* and *Plagiomnium ellipticum* 6 - 8 times exceed the accumulating ability of the recommended for biomonitoring species (Fe, As and the group of rare earth elements). Thus, for *Orthotrichum speciosum* this ability may be linked to his life-form (epiphytic species, which is able to absorb the flows down precipitation, atmospheric deposition, and interact with the organisms that live on the bark).

For *Plagiomnium ellipticum* findings may be related to man-made contamination of the sampling points: the impact of wet and dry deposition from the metallurgical enterprises of Tula (air transfer) and Shchekino district: factory of concrete products, large enterprises located in Shchekinsky region - JSC "Shchekinoazot "(producer of nitrogen fertilizers and petrochemicals) and JSC" Khimvolokno "(nylon thread and cord), concrete production and coal mining (West mine), oil refining and oil and Shchekinskaya CHP on the one hand and enterprises of Novomoskovsk (air transfer): OAO "Knauf Gips Novomoskovsk", OOO «P & G - Novomoskovsk". And location of the moss when sampling: reduction of relief - side of the stream.

The three studied species: *Climacium dendroides, Plagiomnium undulatum, and Sphagnum angustifolium* absorb and accumulate 1.8-2.9 times less of trace elements than the standard species used in biomonitoring. This may be due to their habitat: marsh biogeocoenoses and wet habitats on the outskirts of the marshes. It may also be due to the influence of trees shielding elements distributed air transport, the possibility of washing water, the structure features: the lack of rhizoids in *Sphagnum angustifolium*, 1 layer of cells in the sheet *Plagiomnium undulatum and Sphagnum sp* .

To assess the status of environmental pollution and comparison of species, were used indicators developed for geochemical and environmental research geohygienic existing sources of pollution [52]:

$$Кс = Кel./Кb., \text{ where}$$

Кel. is the element content in the sample;

Кb is the element content in the background samples.

The concentration ratio and total indicator of pollution (of Zc) were calculated for the species studied with respect to background concentrations (minimum values in the region).

$$Zc = \sum Кс/(n-1)$$

Based on the data presented in Table 2 can be ranked according to their types of activity as the biomonitors using Kc and Zc. Studied species are ranked by the degree of accumulating ability: *Oxyrrhynchium hians* > *Eurhynchium angustirete* = *Orthotrichum speciosum* > *Brachythecium rutabulum* > *Atrichum undulatum* = *Brachythecium salebrosum* > *Abietinella abietina* > *Pleurozium schreberi* = *Rhytidiadelphus triquetrus* = *Cirriphyllum piliferum* = *Climacium dendroides* > *Plagiomnium undulatum* > *Sphagnum angustifolium.*

Table 1

Comparison of accumulation ability of mosses growing in natural habitat (Tula Region, Russia) (average: n=3-14), mg/kg .

Species	*Abietinella abietina*	*Atrichum undulatum*	*Brachythecium rutabulum*	*Brachythecium salebrosum*	*Cirriphyllum piliferum*	*Climacium dendroides*	*Eurhynchium angustirete*	*Oxyrrhynchium hians*	*Orthotrichum speciosum*	*Plagiomnium undulatum*	*Plagiomnium ellipticum*	*Rhytidiadelphus triquetrus*	*Rhytidiadelphus subpinnatus*	*Sphagnum angustifolium*	*Pleurozium schreberi*
Na	150	483	445	428	244	520	615	598	528	275	0	164	269	72	283
Mg	3380	3130	3554	3314	2610	2555	4573	7283	3153	2807	9000	2110	2070	1470	2501
Al	3145	5010	5546	4115	1545	1475	8020	11697	4877	1406	**15300**	1469	1150	434	2316
Cl	131	258	652	501	324	1336	385	456	230	1128	1920	176	583	433	304
K	7010	14592	13971	13101	14550	10070	11916	14033	7617	15283	15900	12735	15400	7070	12471
Ca	10835	5705	9211	8116	6610	8095	7034	11690	8607	9183	8610	4770	4980	2000	5741
Sc	0.47	1.02	1.04	0.88	0.43	0.17	1.48	1.93	0.92	0.24	**4.38**	0.25	0.29	0.08	0.43
Ti	150	463	387	323	110	76.4	724	766	321	114	**1210**	134	105	73.3	173
V	6.03	6.47	9.42	8.78	2.46	2.92	11.4	15.7	39.7	2.09	**25.8**	8.24	1.6	0.71	3.53
Cr	5.82	7.87	10.26	10.4	4.95	1.88	12.0	25.3	16.4	2.35	**27.7**	4.39	3.0	0.65	3.76
Mn	76	203	158	227	124	79.2	334	254	203	119	**521**	251	206	238	224
Fe	2040	2626	3629	3680	1242	771	3868	5497	10547	710	**13200**	1901	814	293	1353
Ni	2.62	3.71	4.46	4.09	1.93	1.69	5.83	6.75	5.59	1.87	**12.7**	2.63	3.6	0.64	2.69
Co	0.68	1.05	1.16	1.08	0.52	0.32	1.71	2.35	1.19	0.36	**5.34**	0.48	0.40	0.16	0.61
Zn	32	46.4	61.5	65.0	55.1	43.8	52.8	50.5	75.3	41.9	43	34.0	61	21.0	41.4
As	0.70	0.66	0.87	0.81	0.51	0.30	1.06	1.62	0.88	0.29	4.92	0.18	0.24	0.13	0.36
Se	0.18	0.13	0.18	0.21	0.17	0.12	0.15	0.27	0.40	0.13	0.23	0.20	0.12	0.12	0.14
Br	1.95	2.80	4.40	4.38	3.20	7.05	2.50	4.48	5.23	5.92	6.0	4.06	2.6	1.58	2.50
Rb	6.58	11.9	11.8	12.7	7.41	10.6	14.9	16.7	10.2	8.80	**39.0**	15.3	10.1	12.3	8.53
Sr	26.2	29.2	35.9	33.8	29.1	25.6	41.4	61.8	38.3	28.1	60	20.4	16	8.30	23.4
Zr	6.56	45.2	32.1	28.5	13.2	4.42	68.2	51.6	20.5	7.86	**92.8**	5.91	11.7	2.05	13.9
Mo	0.19	0.18	0.38	0.24	0.13	0.12	0.26	0.37	0.58	0.15	0.31	0.17	0.14	0.08	0.16
Cd	0.18	0.81	0.37	0.47	0.37	0.54	0.59	0.35	0.50	0.41	0.99	0.20	0.23	0.14	0.26
Sb	0.25	0.12	0.16	0.20	0.07	0.10	0.15	0.16	0.86	0.06	0.30	0.12	0.06	0.02	0.08
I	1.00	0.76	1.21	1.50	0.75	1.01	1.22	6.73	2.63	0.71	2.13	0.66	0.34	0.57	1.02
Ba	25.5	73.4	57.7	63.3	47.3	16.3	97.3	77.07	65.6	24.5	171	31.4	28	9.00	45.2
Cs	0.27	0.33	0.38	0.33	0.18	0.11	0.53	0.70	0.44	0.10	**1.56**	0.18	0.12	0.27	0.19
La	1.34	3.76	3.17	3.12	1.39	0.59	5.59	6.26	3.33	0.88	**12.5**	0.78	1.01	0.25	1.50
Ce	2.75	7.77	6.52	6.26	2.89	1.22	11.7	13.02	7.33	1.76	**27.5**	1.51	2.2	0.42	3.07
Nd	1.88	3.89	3.58	3.19	2.01	0.81	5.61	5.03	4.45	1.18	**10.9**	1.71	0.77	0.67	1.66
Sm	0.25	0.56	0.55	0.50	0.27	0.11	0.86	1.09	0.41	0.14	**2.13**	0.16	0.37	0.02	0.26
Eu	0.07	0.16	0.13	0.14	0.07	0.05	0.25	0.28	0.21	0.06	**0.56**	0.09	0.08	0.04	0.08
Gd	0.17	0.42	0.36	0.52	0.11	0.04	1.22	1.17	0.67	0.06	**1.88**	0.03	0.10	0.02	0.07
Tb	0.03	0.10	0.09	0.08	0.04	0.02	0.16	0.15	0.08	0.02	**0.31**	0.02	0.03	0.01	0.04
Tm	0.04	0.06	0.09	0.06	0.04	0.01	0.11	0.07	0.13	0.02	**0.17**	0.08	0.07	0.01	0.03
Yb	0.12	0.44	0.37	0.35	0.21	0.08	0.61	0.64	0.33	0.10	**1.08**	0.09	0.14	0.07	0.17
Hf	0.21	1.34	0.92	0.84	0.37	0.13	1.97	1.43	0.65	0.23	**2.79**	0.15	0.35	0.05	0.41

Ta	0.03	0.11	0.10	0.08	0.04	0.02	0.16	0.16	0.09	0.02	**0.36**	0.02	0.03	0.01	0.04
W	0.13	0.17	0.26	0.35	0.08	0.06	0.32	0.24	1.42	0.06	0.57	0.14	0.07	0.03	0.12
Au	0.004	0.002	0.01	0.004	0.002	0.01	0.003	0.002	0.001	0.006	0.001	0.005	0.001	0.000	0.004
Th	0.43	1.17	1.04	0.89	0.44	0.17	1.71	1.75	1.14	0.28	**3.83**	0.31	0.40	0.09	0.48
U	0.17	0.24	0.30	0.25	0.12	0.06	0.38	0.49	0.35	0.07	**0.92**	0.08	0.05	0.03	0.12
La/Yb	**11**	**9**	**8**	**9**	**7**	**8**	**9**	**10**	**10**	**9**	**12**	**9**	**7**	**4**	**9**
Th/U	**2.6**	**4.8**	**3.4**	**3.5**	**3.8**	**2.6**	**4.5**	**3.6**	**3.3**	**3.9**	**4.2**	**3.7**	**8.2**	**3.0**	**3.9**
bioaccumulation activity (trace elements)	**2240**	**3080**	**4036**	**4159**	**1541**	**970**	**4544**	**6105**	**11054**	**959**	**14280**	**2284**	**1166**	**590**	**1733**

Table 2

~~Таблица 2.~~ Concentration coefficients and the total index of pollution using moss as biomonitors (Russia, Tula Region)

Species	***Abietinella abietina***	***Atrichum undulatum***	***Brachythecium rutabulum***	***Brachythecium salebrosum***	***Cirriphyllum piliferum***	***Climacium dendroides***	***Eurhynchium angustirete***	***Oxyrrhynchium hians***	***Orthotrichum speciosum***	***Plagiomnium undulatum***	***Rhytidiadelphus triquetrus***	***Sphagnum angustifolium***	***Pleurozium schreberi***
Na	2.1	6.7	6.2	5.9	3.4	7.2	8.5	8.3	7.3	3.8	2.3	1.0	3.9
Mg	2.6	2.4	2.7	2.5	2.0	1.9	3.5	5.5	2.4	2.1	1.6	1.1	1.9
Al	7.2	**11.5**	**12.8**	9.5	3.6	3.4	**18.5**	**27.0**	11.2	3.2	3.4	1.0	5.3
Cl	1.9	3.8	9.6	7.3	4.8	**19.6**	5.6	6.7	3.4	**16.5**	2.6	6.3	4.5
K	1.3	2.8	2.6	2.5	2.7	1.9	2.2	2.6	1.4	2.9	2.4	1.3	2.4
Ca	5.4	2.9	4.6	4.1	3.3	4.0	3.5	5.8	4.3	4.6	2.4	1.0	2.9
Sc	6.0	**12.9**	**13.1**	**11.2**	5.5	2.1	**18.7**	**24.5**	11.7	3.0	3.1	1.0	5.4
Ti	3.2	9.9	8.3	6.9	2.3	1.6	**15.4**	**16.3**	6.8	2.4	2.8	1.6	3.7
V	8.5	9.1	**13.3**	**12.4**	3.5	4.1	**16.1**	**22.2**	56.0	2.9	**11.6**	1.0	5.0
Cr	9.0	**12.1**	**15.8**	**16.0**	7.6	2.9	**18.4**	**39.0**	25.2	3.6	6.8	1.0	5.8
Mn	1.2	3.3	2.5	3.6	2.0	1.3	5.4	4.1	3.3	1.9	4.0	3.8	3.6
Fe	7.0	9.0	**12.4**	**12.6**	4.2	2.6	**13.2**	**18.8**	36.0	2.4	6.5	1.0	4.6
Ni	4.1	5.8	7.0	6.4	3.0	2.7	9.1	**10.6**	8.8	2.9	4.1	1.0	4.2
Co	4.2	6.5	7.1	6.7	3.2	2.0	**10.6**	**14.5**	7.3	2.3	2.9	1.0	3.8
Zn	1.7	2.5	3.3	3.5	2.9	2.3	2.8	2.7	4.0	2.2	1.8	1.1	2.2
As	5.5	5.1	6.8	6.3	4.0	2.3	8.3	**12.5**	6.9	2.3	1.4	1.0	2.8
Se	5.5	3.9	5.6	6.5	5.3	3.8	4.7	8.3	12.3	4.0	6.2	3.7	4.2
Br	1.4	2.0	3.2	3.2	2.3	5.1	1.8	3.2	3.8	4.3	2.9	1.1	1.8
Rb	2.1	3.7	3.7	4.0	2.3	3.3	4.7	5.2	3.2	2.8	4.8	3.9	2.7
Sr	3.2	3.5	4.3	4.1	3.5	3.1	5.0	7.4	4.6	3.4	2.5	1.0	2.8
Zr	3.2	**22.0**	**15.7**	**13.9**	6.5	2.2	**33.3**	**25.2**	**10.0**	3.8	2.9	1.0	6.8
Mo	2.5	2.4	5.1	3.1	1.7	1.6	3.5	4.9	7.7	2.0	2.3	1.1	2.1
Cd	1.3	5.9	2.7	3.4	2.7	3.9	4.3	2.5	3.7	3.0	1.5	1.0	1.9
Sb	**10.7**	5.0	6.7	8.7	2.8	4.1	6.6	6.6	**36.5**	2.7	4.9	1.0	3.5
I	5.6	4.2	6.8	8.4	4.2	5.6	6.8	**37.6**	**14.7**	3.9	3.7	3.2	5.7
Ba	2.8	8.2	6.4	7.0	5.3	1.8	**10.8**	8.6	7.3	2.7	3.5	1.0	5.0
Cs	5.7	6.8	7.8	6.9	3.8	2.2	**10.9**	**14.4**	9.1	2.1	3.7	5.5	3.9

La	5.3	**15.0**	**12.6**	**12.4**	5.6	2.4	**22.3**	**24.9**	**13.3**	3.5	3.1	1.0	6.0
Ce	6.5	**18.3**	**15.4**	**14.8**	6.8	2.9	**27.7**	**30.7**	**17.3**	4.2	3.6	1.0	7.2
Nd	5.4	**11.2**	**10.3**	9.1	5.7	2.3	**16.1**	**14.4**	**12.8**	3.4	4.9	1.9	4.8
Sm	**11.8**	**26.5**	**26.0**	**23.8**	**12.7**	5.4	**41.2**	**52.0**	**19.7**	6.5	7.5	1.0	**12.2**
Eu	2.0	4.4	3.8	3.9	1.9	1.4	7.0	7.9	5.8	1.8	2.6	1.1	2.3
Gd	**17.7**	**43.5**	**37.7**	**53.9**	**11.0**	4.2	**127**	**122**	**69.3**	6.1	3.5	2.3	6.8
Tb	5.4	**16.7**	**14.3**	**12.9**	5.9	2.6	**25.9**	**25.5**	**12.5**	3.8	2.8	1.0	6.6
Tm	7.9	**12.7**	**20.4**	**13.7**	7.7	2.7	**23.7**	**16.0**	**27.6**	4.0	**17.0**	1.3	7.5
Yb	2.5	8.8	7.6	7.2	4.3	1.5	**12.3**	**12.9**	6.7	2.0	1.8	1.4	3.4
Hf	4.4	**28.3**	**19.4**	17.9	7.8	2.8	**41.6**	**30.1**	**13.8**	4.8	3.2	1.0	8.6
Ta	3.8	**11.9**	**10.6**	9.4	4.2	1.7	**17.8**	**18.0**	9.8	2.6	2.2	1.0	4.9
W	8.4	**11.1**	**16.8**	22.7	5.3	4.1	**20.6**	**15.9**	**92.9**	4.1	9.1	2.0	7.8
Au	**20.2**	**12.2**	**56.6**	22.0	**12.3**	**54.2**	**17.4**	**10.2**	6.6	**27.5**	**24.3**	1.5	**19.5**
Th	4.7	**12.9**	**11.5**	9.8	4.8	1.9	**18.9**	**19.3**	**12.5**	3.1	3.5	1.0	5.3
U	5.4	7.9	9.9	8.2	3.8	2.1	**12.5**	**15.9**	**11.3**	2.4	2.8	1.0	4.0
∑ Kc (trace elements V…U)	**226**	**415**	**469**	**428**	**198**	**191**	**684**	**760**	**641**	**174**	**190**	**68**	**209**
Zc	**6**	**11**	**12**	**11**	**5**	**5**	**18**	**20**	**18**	**4**	**5**	**2**	**5**

Table 3

Significant correlations between the elements in mosses - biomonitors

Element	Chemical assiciations	Correlation coefficient	Origin of pollution
Mg	Al, Sc, Ti, Cr, Mn, Fe, Ni, Co, As, Rb, Sr, Zr, Cd, I, Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, Th, U	0.61…0.98	Technogenic soil (emission)
Al	Sc, Ti, V, Cr, Mn, Fe, Ni, Co, As, Rb, Sr, Zr, Cd, I, Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, Th, U	0.66…0.95	Technogenic soil (emission)
Cl	Se, Br, Rb, Ni, Cd, Cs, La, Ce, Sm, Eu, Ta, Th	0.51…0.70	Biological, atmospheric deposition
Sc, Ti	V, Cr, Mn, Fe, Ni, Co, As, Rb, Sr, Zr, Cd, I, Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, Th, U	0.57…0.99	Technogenic soil (emission)
V	Cr, Fe, Ni, Co, As, Sr, Mo, Sb, Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, W, Th, U	0.51…0.95	Atmospheric deposition (technogenic pollution)
Cr	Mn, Fe, Ni, Co, As, Rb, Sr, Zr, Mo, Cd Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, Th, U	0.57…0.94	Atmospheric deposition (technogenic pollution)
Mn	Fe, Ni, Co, As, Rb, Zr, Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, Th, U	0.68…0.86	Atmospheric deposition (technogenic pollution)
Fe	Ni, Co, As, Se, Rb, Sr, Zr, Mo, Cd, Sb, Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, W, Th, U		Soil emission, air pollution
Ni, Co	Co (Ni), As, Rb, Sr, Zr, Cd, Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, Th, U	0.69…0.98	Soil emission, air pollution
Zn	Se, Mo, W	0.53…0.65	Aerosol particles of atmospheric deposition (technogenic pollution)
As	Rb, Sr, Zn, Cd, Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, Th, U	0.70…0.95	Atmospheric deposition (technogenic pollution)
Cd	Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, Th, U	0.57…0.80	Atmospheric deposition (technogenic pollution)
Sb	W	0.97	Atmospheric deposition (technogenic pollution)

Earlier studies have shown that epiphytic mosses (*Pylaisia polyantha, Orthotrichum obtusifolium*) have similar accumulating ability as epiphytic mosses and can exceed them, which was the basis for recommendations for their use in biomonitoring atmospheric deposition [51]. Our research confirms this fact by the example of epiphytic moss

Orthotrichum speciosum. Thus, the list of mosses - biomonitors, which can be used for the analysis of atmospheric precipitation can be significantly expanded such soil and epiphytic moss species as *Oxyrrhynchium hians, Eurhynchium angustirete, Orthotrichum speciosum, Brachythecium rutabulum, Atrichum undulatum, Brachythecium salebrosum, Abietinella abietina, Rhytidiadelphus triquetrus.*

Statistical analysis of the results of studies of accumulation of heavy metals, metalloids and rare earth elements in mosses - biomonitors showed the presence of correlative links in the accumulation of elements by moss cells (Table 3.).

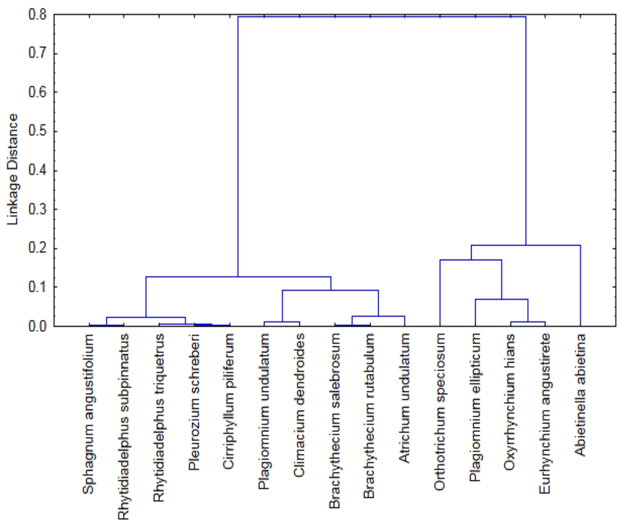

Fig. 1. Hierarchic cluster analysis of mosses

Conducted cluster analysis subdivided studied mosses in the closest group in their ability to accumulate the elements of the environment:

o *Pleurozium schreberi, Rhytidiadelphus subpinnatus, Rhytidiadelphus triquetrus, Cirriphyllum piliferum, Sphagnum sp.;*

o *Climacium dendroides, Plagiomnium undulatum;*

o *Brachythecium rutabulum, Brachythecium salebrosum, Atrichum undulatum;*

o *Oxyrrhynchium hians, Eurhynchium angustirete.*

o

We performed a comparative analysis of the content of elements in mosses of marsh phytocenoses. Mosses collected in two sampling points: swamp (I) village Ozerniy - a neighborhood of the city of Tula, Leninsky district (columns 2-4) and wetland coniferous-deciduous forest near the village Varushitsy of Suvorovskiy district (columns 5-10). These areas are characterized by intensive industrial load, but different forms of human impact: the neighborhood of the village Ozerniy exposed to the air transport of the steel mills and the defense industry enterprises of Tula, and the territory of Suvorov district - Cherepetskaya GRES plant and concrete products and constructions.

For each species a mixed sample (500 g wet weight) was composed in each sampling point. The data obtained for the *Sphagnum* moss in the village. Ozerniy clearly reveal the picture of air pollution: Kc > = 10 for V, Mn, Fe accumulated by the mosses from atmospheric deposition which are the main elements - pollutants from Kosogorsky Iron Works.

Table 4.

Concentration coefficients and the total index of pollution comparison of marsh mosses

	Plagiomnium ellipticum	*Sphagnum angustifolium*	*Sphagnum girgensohnii*	*Sphagnum girgensohnii*	*Sphagnum fallax*	*Dicranum polysetum*	*Brachythecium salebrosum*	*Polytrichum strictum*	*Pleurozium schreberi*
Na	3.0	7.9	7.1	2.9	3.2	3.6	3.8	1.2	2.1
Mg	1.5	2.8	1.2	0.8	1.0	1.1	1.5	0.9	0.9
Al	0.8	4.4	3.2	1.8	2.4	5.7	6.4	3.3	3.4
Cl	4.3	**15**	**18**	9.8	**12**	1.3	5.5	1.8	1.7
K	4.7	2.2	2.3	1.6	1.5	1.2	1.7	1.7	1.3
Ca	1.9	4.2	3.0	1.6	1.7	1.9	6.0	1.1	1.5
Sc	2.2	3.4	3.6	2.0	2.5	6.5	6.4	1.4	3.7
Ti	3.8	6.0	3.6	4.1	3.1	4.6	7.1	2.0	3.3
V	2.2	**10**	8.8	1.3	1.9	5.4	**20**	2.2	3.1
Cr	6.6	9.8	6.3	5.2	3.7	4.6	**11**	3.6	3.6
Mn	8.3	**14.9**	9.2	5.6	4.6	9.9	**11.8**	3.6	8.7
Fe	5.7	**13.2**	**10.6**	2.0	2.7	5.8	**16.5**	1.5	3.8
Ni	6.6	6.4	8.6	3.4	4.5	3.6	7.2	1.1	5.2
Co	2.1	3.2	3.4	2.1	2.4	5.1	4.9	2.3	3.3
Zn	3.0	4.1	2.1	1.8	1.9	2.1	2.9	2.2	1.7
Se	5.9	4.9	**12.2**	3.3	4.9	8.4	5.8	3.4	5.1
As	2.5	3.9	4.7	1.2	1.9	2.7	3.8	1.0	1.9
Br	2.0	3.2	5.0	2.3	2.6	1.9	4.0	1.4	1.6
Rb	9.9	5.5	5.4	7.4	7.7	**10**	4.4	6.6	5.1
Sr	**20**	**27**	**22**	**17**	**17**	**13**	**21**	**16**	**22**
Zr	5.8	5.8	4.2	4.5	3.7	**18**	**10**	2.1	4.2
Nb	3.2	2.1	3.1	2.6	2.0	4.1	2.4	1.1	2.1
Cd	2.5	2.4	2.6	1.0	2.1	2.1	3.6	1.1	1.5
Sb	6.2	7.7	7.4	2.3	3.1	9.7	**15**	2.4	5.7
I	5.2	5.9	8.7	4.1	5.8	4.1	**13**	6.9	7.7
Ba	3.1	5.4	3.7	1.8	2.7	5.3	**10**	1.7	3.5
Cs	**19**	6.0	5.1	4.1	5.1	**11.5**	4.6	**10.2**	6.4
La	2.7	4.2	4.4	3.0	3.8	8.5	7.8	1.8	5.1
Ce	3.7	2.4	2.5	3.8	4.4	8.0	8.5	1.8	5.9
Nd	3.6	3.1	3.5	3.1	3.0	6.8	5.7	3.3	3.7
Sm	4.8	6.9	6.9	4.4	6.4	**18**	**18**	3.7	7.9
Eu	2.0	2.0	1.3	2.5	1.2	2.2	2.0	1.1	1.8
Tb	2.7	4.4	2.9	1.9	2.9	7.6	8.6	1.7	3.8
Tm	2.7	4.4	6.6	3.6	2.3	5.5	6.0	2.2	4.0

Yb	2.0	0.5	2.8	0.8	1.3	4.2	3.7	1.1	2.2
Hf	2.5	4.6	4.4	2.7	3.6	**18**	**12**	2.3	5.4
Ta	2.1	3.0	3.3	2.4	3.1	8.3	5.2	1.7	4.7
W	5.2	**10.2**	9.8	3.3	4.2	6.9	**15.2**	1.6	5.3
Th	2.0	3.0	3.0	1.8	2.7	7.4	5.9	1.5	3.3
U	1.9	3.4	3.1	2.5	3.1	6.9	6.0	1.5	4.1
∑ Kc	**158**	**197**	**190**	**111**	**124**	**239**	**282**	**99**	**156**
Zc	**5**	**6**	**6**	**3**	**4**	**7**	**9**	**3**	**5**

Sphagnum mosses from village Varushitsy accumulate less than or comparable to the first point amount of heavy metals and rare earth elements. For all analyzed species without exception high levels of Sr content (Kc = 13 ... 27) was observed, that reflects the regional characteristics of the underlying rocks and may be due to close bedding of limestone rich in strontium.

Comparison of the data for the Sphagnum moss bogs region with data for *Sphagnum* moss of Central Forest State Biospheric Reserve [54] shows a high degree of air pollution with Sr (its concentration is 23 times higher) (likely deposition in the form of oxides and compounds of metals), V (25 times higher: the impact of "Vanadium" emissions), Cr (5 times higher) of Fe (10 times higher: the air transfer from the metallurgical and mining enterprises), Sr (31 times higher, especially in the bedrock of the region); Nb, Zr (19 - 45 times higher); rare earth elements: Nd (55 times higher), Dy (150 times higher), other rare earth elements from 2 to 3.5 times higher (dirt reflect the influence metallurgical, chemical and defense industries).

Comparison of the activity of Sphagnum mosses used as biomonitor did not reveal significant differences between species: *Sphagnum angustifolium*, *Sphagnum girgensohnii*, *Sphagnum fallax*, growing in swamp. The element content depends only on the state of the environment of the sampling site. Thus, in the *Sphagnum* moss swamp near the village of Ozerniy Fe content is 3.5-5 times higher, Mn is 2 times higher, V is 4-5 times higher, and As is two times higher than in Sphagnum from Suvorovsky district (Varushitsy).

According to the content of some elements in *Shagnum fallax* exceeds those in *Sphagnum girgensohnii* (it contains 30-45% more of V, Fe, Ni, Sb, Ba, Cs, La, Ce, Sm, Tb, Yb, Hf, W, Th, and U), that could be due to its growth in the open marsh area, without affecting the projection of tree crown. In general, all three tested species of *Sphagnum* can be used for active biomonitoring (moss bags method). It should be noted that among a *Sphagnum* as well as among green mosses, most suitable for biomonitoring purposes the moss Brachythecium salebrosum should be recognized, which usually grows in fallen trunks and can accumulate V, Cr, Mn, Fe, Sr, Zr, I, Ba, Sm, Hf, W. *Dicranum polysetum* also has a great potential for the biomonitoring purposes. Kc of this species is 1.5 times higher than the recommended species have.

Accumulating ability of Sphagnum fallax in a marsh areas is close to the recommended moss species. *Polytrichum strictum* having low accumulation ability is not suitable for biomonitoing of atmospheric deposition: its Kc 1.5 times lower than that of Pleurozium schreberi. Hierarchical cluster analysis (dendrogram in Fig. 2.) subdivided the species into the closest clusters by habitat:

1 is *Dicranum polysetum and Pleurozium schreberi* – forest areas in wetland habitat;

2 is *Shagnum fallax and Sphagnum girgensohnii* – swamps of Suvorovsky district;

3 is *Sphagnum girgensohnii and Sphagnum angustifolium* – swamp, village Ozerniy;

4 is *Dicranum polysetum, Pleurozium schreberi, Shagnum fallax and Sphagnum girgensohnii* – similar character of elements accumulation.

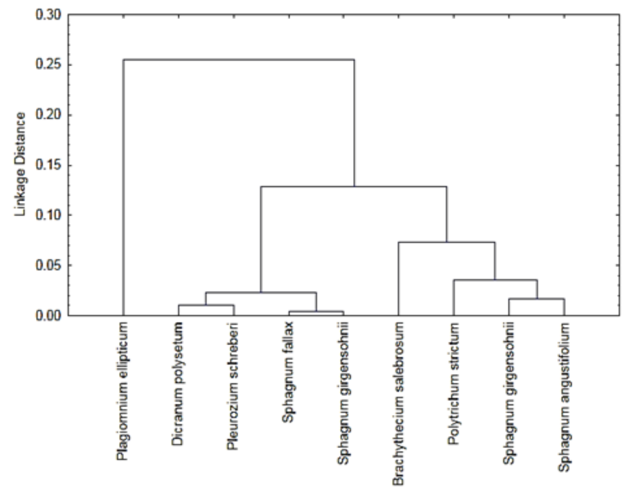

Fig. 2. Hierarchic cluster analysis of wetland mosses

Table 5 presents the data of ENAA of 41 elements of moss-biomonitors for Tula region in retrospective. The data reflects the improvement of the ecological situation in the region with regard to the content in air the next heavy metals: Mn, Zn, and V. This is may be due to a production decrease at one of metallurgical enterprises "Vanadium-Tula" which is located in Tula city. 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 which were 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. 6, 7).

Table 5

Comparative elemental content in moss from moss surveys in 2000 and 2015

(n>90)	2000 [4, 6]		2015		
	mean	mediana	range	mean	Md ± σ
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	10000	5300-23200	13034	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**	**46±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
Co	**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	**26.5**	**25**	**8-110**	**33**	**29±4**
Cd	**0.32**	**0.3**	**0.14-1.77**	**0.5**	**0.38±0.06**
I	1.5	1.5	0.18-16.2	1.4	0.99±0.16
La	2.6	2	0.25-12.5	3.1	1.7±0.4
Ce	4.6	3.8	0.42-27.5	6.4	3.6±0.8
Nd	-	-	0.35-10.9	3.3	2.1±0.4
Zr	-	-	2-119	31	15±4
Se	-	-	0.03-0.51	0.18	0.16±0.02
Mo	0.43	0.36	0.08-0.91	0.24	0.18±0.03
Sb	0.15	0.13	0.02-1.51	0.17	0.13±0.02
Cs	0.25	0.21	0.05-1.56	0.34	0.20±0.04
Sm	**0.39**	**0.29**	**0.02-2.13**	**0.50**	**0.33**±0.06
Eu	-	-	0.04-0.56	0.144	0.09±0.02
Gd	-	-	0.01-4.08	0.46	0.19±0.05
Tb	0.052	0.042	0.006-0.314	0.081	0.04±0.01
Tm	-	-	0.005-0.355	0.065	**0.046±0.008**
Yb	**0.15**	**0.11**	**0.05-1.34**	**0.34**	**0.20±0.04**
Hf	0.82	0.64	0.05-3.71	0.91	0.46±0.11
Ta	0.078	0.058	0.009-0.363	0.087	0.05±0.01
W	0.16	0.13	0.02-3.11	0.26	0.14±0.03
Th	0.65	0.49	0.09-3.83	0.95	0.53±0.11
U	0.2	0.15	0.03-0.92	0.24	0.16±0.03

Table 6

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

	Tula region	Moscow region [40]	Tver region [5]	Ivanovo [2, 3]	Kostroma	Udmurtia
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
Co	**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
Mo	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
Ta	**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

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. 6).

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].

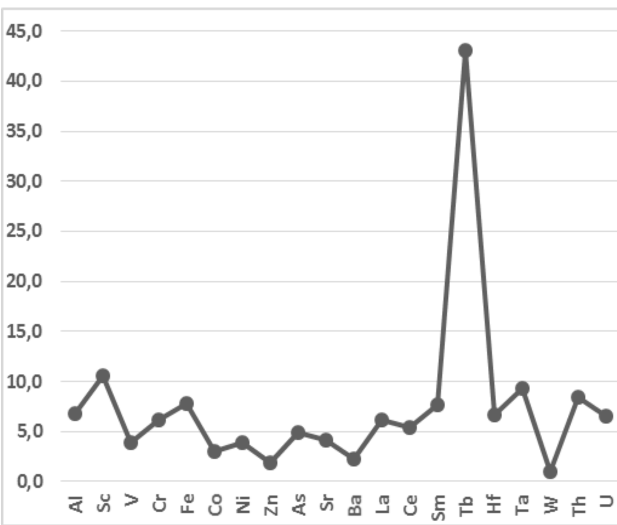

Fig.3 Coefficients of accumulation of elements in mosses of Tula region compare with background values

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. 3).

Comparison of the data with the values for the European countries represented in the atlas of atmospheric deposition (Tab. 7) 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.

Table 7

Comparison of atmospheric pollution of Tula region with different countries [14, 18], (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
Switzerland	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

Results of the factor analysis revealed four factors (Tab. 8):

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 from different phytocenosis of Tula region to accumulate trace elements from atmospheric deposition revealed that part of analyzed moss species is characterized by a low accumulative capacity.

Among them: *Plagiomnium undulatum*: 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.

The species of sphagnum mosses show the differences between sites of taking samples but characterized by low accumulation activity comparing with other mosses. Itdepends on morphology, growing conditions and physiological features. By this way, sphagnum mosses is not good examples for passive biomonitoring, better to use for comparative characteristics of mire ecosystems in different vegetation zones with different degree of anthropogenic press. All sphagnum species are good for active biomonitoring (moss bags), *Sphagnum fallax* is better for this goal.

Such species as *Plagiomnium ellipticum* can be used for biomonitoring. It is good accumulator of trace elements from the atmospheric deposition in contaminated sampling points, exceeds the extent of accumulation of all the studied species. But we do not recommend to collect it for passive biomonitoring in wetland biocenosis.

From the studied moss species have good accumulative capability and close to the recommended for biomonitoring of atmospheric deposition of trace elements species are such moss species as: *Atrichum undulatum*, *Abietinella abietina*, *Brachythecium rutabulum*, *Brachythecium salebrosum*, *Eurhynchium angustirete*, *Plagiomnium ellipticum*, *Orthotrichum speciosum*, *Oxyrrhynchium hians*. These species can be recommended for use for passive biomonitoring in a moderately-continental zone of Russia, Europe and Asia.

IV 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, 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 passive biomonitoring cannot be used: *Plagiomnium undulatum and Sphagnum sp./*

For biomonitoring of atmospheric deposition of trace elements can be recommended such species as: *Oxyrrhynchium hians, Eurhynchium angustirete, Orthotrichum speciosum, Brachythecium rutabulum, Atrichum undulatum, Brachythecium salebrosum, Abietinella abietina, Rhytidiadelphus triquetrus.*

Species *Rhytidiadelphus triquetrus, Cirriphyllum piliferum* are similar to *Pleurozium scheberi* by ability of element accumulation.

In general, *Oxyrrhynchium hians, Eurhynchium angustirete* and *Orthotrichum speciosum* are characterized by highest accumulation ability comparing with other species.

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