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Moss Technique Used to Monitor the Atmospheric Deposition of Trace Elements on the Territory of the Ryazan Region, Russia

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Abstract: Instrumental neutron activation analysis in combination with the method of moss biomonitoring for the assessment of atmospheric deposition of heavy metals and other elements was applied for the first time in the Ryazan Region in Russia. Concentrations of 42 macro, micro and trace elements in 63 moss samples (*Hylocomium splendens* and *Pleurozium schreberi*, as well as *Hypnum cupressiforme*, *Sciuro-hypnum* sp., *Plagiothecium* sp. and *Ptilium* sp.), collected on a relatively uniform grid in the study area, were determined. On the basis of analytical results using GIS technologies, maps of the spatial distribution of heavy metals and other toxic elements were constructed for the Ryazan region. The method of multivariate statistical analysis (factor analysis) was used to identify the main sources of pollution—large industrial facilities located in this region. The obtained results were included in the *Atlas of Atmospheric Deposition of Heavy Metals*, which is published by the UN Commission on Long-Range Transboundary Air Pollution (UNECE ICP Vegetation).

Keywords: moss biomonitoring; atmospheric pollution; heavy metals; UNECE ICP Vegetation

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1. Introduction

Metals are present in all spheres of human activity (industry, energy, agriculture, transportation, household and medicine). Heavy metals (hereinafter—HMs) are able to migrate and accumulate in the environment. Over time, this leads to the deterioration of human health [1]. The most important environmental protection tasks are detailed study of the territorial distribution of HMs, identification of the main sources of pollution and the determination of concentrations and forecasting of HM accumulation in environmental objects. Maintaining the balance of HMs in ecosystems is necessary to preserve public health. Chronic exposure to low doses of various heavy metals poses a significant threat to public health [2].

The Ryazan' region has for many years been among the territories of the Central Federal District of the Russian Federation with the highest incidence of malignant neoplasms. The districts of the Ryazan' region with a high level of oncologic diseases, significantly exceeding the average regional indicators, include Mikhailovsky, Pitelinsky, Shilovsky, Ryazhsky, Sarayevsky and Skopinsky [3]. At present, there is no monitoring program for the atmospheric deposition of trace elements in the Ryazan Region.

In Western Europe, since the late 1970s, to study the atmospheric deposition of heavy metals, a single technique proposed by Scandinavian scientists has been used: elemental analysis of widespread species of mosses (biomonitoring mosses) in countries with temperate climates. This standard method of the biomonitoring of atmospheric metal deposition over large areas has been regularly applied over the last 45 years [4–13].

Since the 1990s, the international UN program "Atmospheric Deposition of Heavy Metals in Europe: An Assessment Based on the Analysis of Biomonitoring Mosses" has been in operation [9,11–13]. The purpose of the UN Commission on European Air Program (International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (http://icpvegetation.ceh.ac.uk/) (accessed on 10 October 24), within the framework of the Convention on Long-Range Transboundary Air Pollution (LRTAP) is qualitative and quantitative assessment of the distribution of regional atmospheric deposition of PM in Europe, identification of the location of priority sources of pollution and the possibility of retrospective comparison of results every 5 years.

In Russia, the method of using moss biomonitors, in combination with the use of core physical methods of analysis to solve both specific international and specific local problems, has been used for more than 25 years in the Frank Laboratory of Neutron Physics of the Joint Institute for Nuclear Research (JINR) in Dubna, Moscow Region. Instrumental neutron activation analysis (INAA) in the pulsed fast reactor IBR-2 under epithermal neutron irradiation (ENAA) allows to determine concentrations of more than 40 elements in biomonitoring works in Russia and other JINR member and non-member countries [10].

The present study is a continuation of works in Central Russia on the analysis of moss biomonitors using multi-element epithermal neutron activation analysis and modern GIS (geographical information systems) technologies. For the first time in the Ryazan Region, the method of using moss biomonitors was applied to assess air pollution in this region of Central Russia. In total, 68% of the urban population of the Ryazan Region lives in conditions of high and very high levels of pollutants. The atmospheric pollution monitoring network consists of four stations for regular observations in Ryazan. Additionally, episodic observations are carried out by the FBUZ "Center of Hygiene and Epidemiology" [14].

The aim of the work was to study the atmospheric deposition of trace elements in the Ryazan Region in accordance with the rules of the European program of simultaneous collection of moss biomonitors [9]. The obtained results were included in the European atlas [13].

2. Materials and Methods

Multi-element neutron activation analysis (NAA) of moss biomonitor samples was performed at the pneumatic transport unit of the REGATA radioanalytical complex at the IBR-2 reactor of the Frank Laboratory of Neutron Physics of the Joint Institute for Nuclear Research, Dubna [10].

The activation of moss biomonitor samples by the full spectrum of neutrons (for the determination of elements by their short-lived isotopes) and epithermal neutrons (for determination by long-lived isotopes) made it possible to determine 42 elements: Na, Mg, Al, S, Cl, K, Ca, Sc, Ti, Cr, Fe, Ni, V, Mn, Co, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, W, Au, Th and U.

A detailed description of the methodology of sample preparation and analysis and the processing of gamma-spectrometric information, as well as the quality control of the obtained results, is given in [5,15].

A Descriptive analysis of the data is presented in Table 1, as are the multivariate statistical analysis (principal component method or factor analysis) used to identify and characterize different sources of pollution (factor loadings (varimax normalized) was carried out using Stat-Soft (superscript "HM") and Statistica 12 (StatSoft, Tulsa, OK, USA) (Table 2).

The construction of geographical maps of element distributions was performed using the ArcGis software (version 10.4, Esri, Redlands, CA, USA).

Table 1. Element content (mg/kg) in Ryazan moss samples and comparison with other territories (median, min-max value spread). The number of sampling points is given in parentheses, compiled by the authors, 2024.

	Ryazan Region (Present Work) (n = 63)	**Belarus [5] (n = 86)**	**Moscow Region [6] (n = 156)**	**Vladimir Region [7] (n = 73)**	**Norway [8] (n= 229)**
Element	Median (min–max)	Median (min–max)	Median (min–max)	Median (min–max)	Median (min–max)
Na	239 (100–4900)	147 (74–537)	155 (85–508)	128 (75–942)	210 (60–800)
Mg	1730 (831–7960)	–	1790 (166–2970)	1910 (1020–3030)	1350 (470–3280)
Al	1940 (318–17400)	–	853 (108–2990)	650 (190–2300)	460 (100–3050)
Cl	170 (43.9–1180)	188 (55–828)	85 (10–284)	68 (9–434)	–
K	8790 (4250–19,600)	3849 (1529–30,070)	7200 (500–14,300)	4700 (470–14,000)	3560 (1770–6400)
Ca	5400 (6–14,300)	2729 (1416–7375)	4480 (727–9050)	2100 (210–7800)	3030 (1820–7230)
Sc	0.42 (0.08–5)	0.11 (0.03–0.72)	0.17 (0.06–0.52)	0.06 (0.06–0.59)	0.09 (0.02–1.4)
Ti	147 (6–1990)	-	–	—	24 (6–152)
V	3.42 (0.74–28.1)	1.33 (0.40–9.52)	1.9 (0.32–5.3)	1.9 (0.95–6.3)	1.2 (0.3–14)
Cr	4.03 (1.3–56.1)	1.2 (0.18–11.61)	2.63 (1.01–7.5)	2.5 (1.3–7)	0.7 (0.2–17)
Mn	314 (51–735)	403 (43.47–1852)	449 (0.46–1540)	431 (118–931)	400 (40–1660)
Fe	1360 (311–15,700)	394 (166–2243)	690 (254–2270)	500 (250–1600)	310 (78–8125)
Co	0.79 (0.19–7.6)	0.25 (0.11–7.02)	0.38 (0.11–1.07)	0.38 (0.18–0.86)	0.2 (0.06–23)
Ni	4.06 (1.16–22.3)	1.25 (0.55–5.65)	2.87 (0.46–6.3)	2.8 (1.24–5.7)	1.1 (0.4–550)
Zn	50.8 (21.6–194)	31.3 (17.6–65.1)	57 (1.3–145)	48 (32–98)	31(8–409)
As	0.65 (0.33–5.11)	0.15 (0.05–0.49)	0.18 (0.03–0.49)	0.16 (0.01–0.5)	0.13 (0.04–4.72)
Se	0.26 (0.04–0.57)	0.71 (0.09–1.89)	0.17 (0.04–0.36)	-	0.3 (0.009–2)
Br	3.57 (1.73–13.6)	1.30 (0.48–3.50)	2.26 (1.07–4.4)	2.2 (1.1–5)	–
Rb	17.2 (5.55–94.2)	20.9 (5.9–55.2)	13.8 (0.14–39,5_	11 (3.7–50)	12.4 (1.4–81)
Sr	25.8 (8.32–106)	9.2 (3.7–65.9)	15.3 (4.2–30,5)	13 (6.1–66)	136 (3.8–60)
Zr	13.2 (2.34–292)				
Mo	0.089 (0.04–1.05)	0.099 (0.03–0.650)	–	—	–
Sb	0.25 (0.1–13.2)	0.11 (0.04–0.23)	0.23 (0.005–1.13)	0.15 (0.073–0.43)	0.07 (0.007–0.38)
I	1.03 (0.39–4.09)	0.67 (0.19–1.65)	–	-	–
Cs	0.24 (0.09–5)	0.21 (0.06–1.22)	0.14 (0.006–0.47)	0.12 (0.06–0.4)	0.16 (0.02–1.63)
Ba	50.9 (8.14–368)	19.9 (7.2–90.3)	44 (3.1–113)	36 (5.5–93)	25 (5.3–130)
La	1.38 (0.33–19.9)	0.46 (0.20–3.78)	0.54 (0.19–1.76)	0.44 (0.17–2.6)	0.32 (0.07–3.5)
Ce	2.66 (0.79–45.1)	0.93 (0.12–8.71)	1.2 (0.27–3.4)	1.0 (0.49–4.4)	0.61 (0.10–4.78)
Nd	1.89 (0.1–22)	–	–	-	0.23 (0.01–2.24)
Sm	0.17 (0.04–3.33)	–	0.08 (0.03–0.24)	0.056 (0.03–0.39)	0.05 (0.004–0.38)
Eu	0.05(0.01–0.66)	–	–	-	0.040 (1–0.19)
Gd	0.11(0.01–2.95)	–	–	-	0.06 (0.004–0.62)
Tb	0.028 (0.01–0.5)	–	0.013 (0.001–0.04)	0.01 (0.004–0.05)	0.01 (<0.001–0.09)
Tm	0.02 (0.003–0.305)	–	–	–	0.003 (001–0.016)
Yb	0.116 (0.01–1.74)	–	–	–	0003 (<0.001–0.016)
Hf	0.37 (0.06–7.32)	–	0.13 (0.02–0.61)	0.09 (0.017–0.6)	–
Ta	0.038 (0.0067–0.62)	–	–	–	–
W	0.2(0.08–1.53)	0.45 (0.07–1.46)	0.18 (0.04–1.13)	0.1 (0.02–0.53)	–
Au	0.0005 (0.00007–0.0522)	–	–	–	–
Th	0.36 (0.12–6.79)	0.11 (0.03–1.0)	0.14 (0.04–0.44)	0.11 (0.03–0.7)	0.03 (0.007–1.5)
U	0.12 (0.03–1.45)	0.05 (0.01–0.41)	0.052 (0.003–0.16)	0.04 (0.01–0.17)	0.006 (0.002–0.08)

Principle component analysis (factor analysis) was applied to identify potential pollution sources of natural and anthropogenic origin.

Table 2. Results of factor analysis and factor loadings.

Element	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Na	0.81	0.40	−0.02	0.23	0.03
Mg	0.52	0.80	0.18	0.09	0.02
Al	0.44	0.87	0.10	0.10	0.04
Sc	0.50	0.83	0.13	0.15	0.03
Ca	0.34	0.23	0.77	−0.1	0.09
Ti	0.35	0.87	0.17	0.08	0.02
Cr	0.81	0.49	0.10	0.24	0.06
V	0.45	0.85	0.19	0.11	0.05
Ni	0.52	0.76	0.23	0.11	0.15
Fe	0.77	0.50	0.19	0.25	0.04
Co	0.77	0.50	0.18	0.22	0.06
Zn	0.23	0.09	0.27	−0.1	0.87
Se	−0.21	−0.07	0.79	0.12	0.15
As	0.74	0.48	0.24	0.27	0.04
Br	0.55	0.22	0.61	0.03	0.04
Sr	0.87	0.29	0.14	−0.02	0.04
Rb	0.37	0.12	−0.02	0.88	−0.01
Zr	0.74	0.57	−0.01	0.19	0.06
Mo	0.75	0.17	0.21	0.11	0.04
Sb	−0.03	0.03	0.03	0.05	0.96
I	0.19	0.50	0.75	0.00	0.07
Ba	0.77	0.45	0.09	0.07	0.02
Cs	0.20	0.15	0.05	0.91	−0.05
W	0.75	0.30	0.09	0.33	0.11
Th	0.81	0.52	−0.02	0.21	0.06
U	0.80	0.52	−0.03	0.20	0.09
Expl. Var.	9.39	6.96	2.62	2.26	1.79
Prp. Totl	0.36	0.27	0.10	0.09	0.07

Factor 1 (Na, Cr, Fe, Co, As, Sr, Zr, Mo, Ba, W, Th, U)—elements characteristic of the Earth's crust probably got into the moss samples with soil particles. However, the association of As and U with this factor indicates a possible anthropogenic source, probably suspended coal ash particles. Just like Fe and Cr can also have an anthropogenic origin. Factor 2 (Mg, Al, Sc, Ti, Cr, V, Fe, Ni)—elements associated with industrial sources of air pollution. Factor 3 (Ca, Se, Br, I)—combines elements/halogens of marine origin, probably brought to the region of Central Russia as a result of air mass transport. Factor 4—rare and scattered elements Rb and Cs found in the mosses of the Ryazan Region, presumably of plant origin. Factor 5—Zn and Sb are most likely to be associated with the production of non-ferrous metals and processing plants in Ryazan.

2.1. Study Area

The area of the Ryazan Region is 39.6 thousand km^2, which is similar to European countries such as Switzerland (41.3 thousand km^2), the Netherlands (41.5 thousand km^2) and Denmark (43.1 thousand km^2). According to Rosstat (http://www.gks.ru/), as of 1 January 2018, the population of the Ryazan Region was 1.121 million people. This is a densely populated, well-developed in industrial and agricultural terms, part of Central Russia [16].

The Ryazan Region is located within the boundaries of the sub-taiga, broad-leaved forest and forest steppe zones and has valuable biological resources, including specially protected natural areas with a total area of more than 103 thousand hectares [17,18].

Ryazan is an old industrial region that was industrialized after the Second World War. It has a favorable intra-Russian economic and geographical position, being 150 km from the Moscow agglomeration.

The main types of industrial and economic activities of the Ryazan Region are oil refining; woodworking; machine building; metalworking; the production of construction, roofing and finishing materials; electric power; food and light industry; and non-ferrous metallurgy. According to official statistics, about 50% of the total production is the production of petroleum products, coke and electrical and electronic equipment [18]. Within the city boundaries of Ryazan, there are more than 300 air-polluting enterprises, about 100 of which are large-scale.

In the Ryazan region, there are explored deposits of brown coal; phosphorites; glass and molding sands; refractories and refractory clays; mineral paints; fusible clays and loams for various purposes; cement raw materials; building stones and sands; carbonate rocks for the production of building lime and use in agriculture; peat; sapropel; therapeutic mud; fresh and mineral groundwater. The main consumers of coal are Ryazanskaya GRES and local CHPPs. Moscow Region coal is humus brown coal formed from peat under reducing conditions. The peculiarity of Mosbass coals is increased ash content.

2.2. Sampling

Samples were collected from July 11 to 14 August 2017. The sampling sites were distributed throughout the territory (including the city of Ryazan and 25 districts of the Ryazan Region). The sampling network included 63 sites (63 moss samples). The sample collection sites were selected taking into account the long-term studies of scientists at Ryazan State Medical University and Ryazan State University [3,17]. The sampling map scheme is presented in Figures 1 and 2.

Figure 1. Map of the study area: Ryazan Region, Central Federal District of the Russian Federation, 2017.

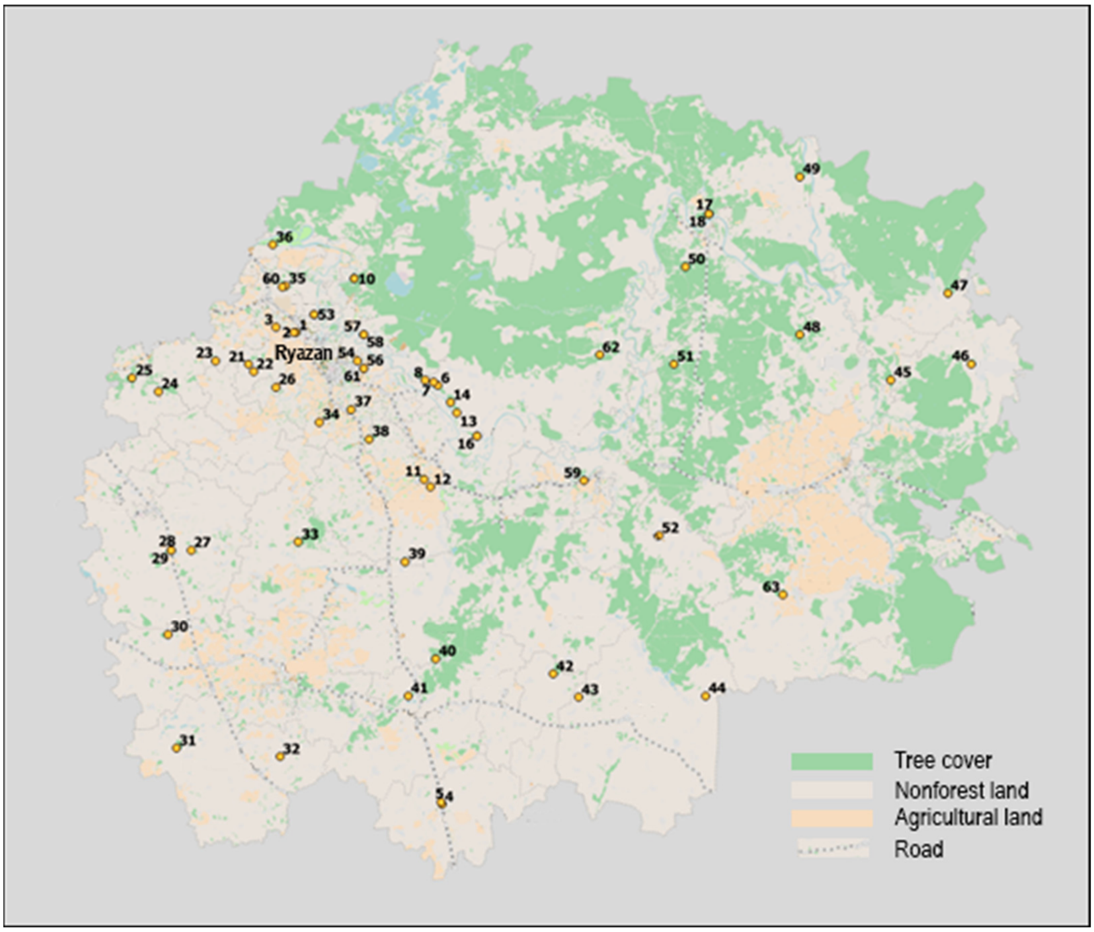

Figure 2. Map of sampling sites with numbers in the Ryazan Region, 2017.

The predominant moss species in the samples is *Pleurozium schreberi* (22 samples); in addition to this species, the following were also investigated: *Hypnum cupressiforme* (16 samples), *Sciuro-hypnum* sp. (17 samples), *Hylocomium splendens* (4 samples), *Plagiothecium* sp. (3 samples) and *Ptilium* sp. (1 sample).

These mosses can be used in subsequent studies, as they are widely distributed in the Ryazan Region and meet the conditions of the standard methodology. Green and green-brown moss segments, corresponding to a three-year period of element accumulation, were used for analysis.

Sampling sites were selected at least 300 m from main roads, 100 m from local roads and 200 m from villages. Each sample consisted of five to ten subsamples collected from a $50 \times 50\ m^2$ area. Disposable polyethylene gloves were provided to collect each sample.

2.3. Data Analyses

Analysis of the data values of Table 1 shows that the Ryazan Region, in comparison with the Vladimir and Moscow regions, as well as the Republic of Belarus and Norway, is characterized by the highest median values for Al (4.2 times higher compared to Norway), K (2.5 times higher compared to Norway), Ca (2.5 times higher compared to the Vladimir Region), Sc (7 times higher compared to the Vladimir region), Ti (data on Ti are not available for all studied regions), V (2.85 times higher in comparison with Norway), Cr (5.76 times higher in comparison with Norway), Fe (4.4 times higher in comparison with Norway and 3.45 times higher in comparison with the Republic of Belarus), Co (3.95 times higher compared to Norway), Ni (3.69 times higher compared to Norway), As (5 times higher compared to Norway), Sb (3.57 times higher compared to Norway), U (200 times higher compared to Norway).

Table 1 shows the medians and ranges of the obtained values of elements together with the data of similar studies conducted earlier in the Moscow and Vladimir regions, which border the territory of the Ryazan Region.

For comparison, in Table 1, the corresponding data for the Republic of Belarus [5], Moscow [6] and Vladimir regions [7], as well as relatively environmentally pristine Norway [8], are presented.

Mapping the investigated area on the basis of data obtained with the use of GIS technologies clearly shows the areas of the deposition of HMs and other trace elements. Four zones of the Ryazan Region experience environmental stress characterized by elevated concentrations of pollutant elements of anthropogenic origin—Ti, Ni, V, Mn, Cr, Zn, As, and others:

1. The Ryazan agglomeration, including Ryazan District;
2. The western part of the territory of the Ryazan Region between two large thermal power plants;
3. The southern part of the Ryazan Region (Miloslavsky and Alexandro-Nevsky districts);
4. The eastern part of the Ryazan Region (Sasovsky District).

Levels of atmospheric deposition concentrations of most heavy metals and other pollutant elements in the northern and central parts of the Ryazan Region are similar to the European average.

The most polluted parts of the Ryazan region, with the contribution of various sources of pollution, are the administrative center of Ryazan and Ryazan District. Local sources of pollution, including elements such as Mn, Fe, Cr, Cr, Ni, Zn, etc., belong to enterprises of the I category of danger:

- An oil refinery, located on an area of more than 900 hectares, processing about 17 million tons of oil per year and generating 85% of the emissions from all enterprises in Ryazan, the composition of which includes an increased content of Mn, Fe, Cr and Ni;
- The largest enterprise of sheet glass and specialized glass products including Cg, Al, Pb, Fe, Mn, Ni, Ca and Cu as part of its atmospheric air emissions;
- An enterprise specializing in processing lead and copper secondary raw materials—spent acid batteries and lead, copper, brass and bronze scrap of all types—which generates more than 2 t of Pb per year and more than 1 t of Ca as part of its emissions into the atmospheric air;
- Enterprises of the 2nd category of hazard: production of non-ferrous metals—Cg, Mn, Fe, Al; production of radio-electronic products—Cg, Mn, Fe, Ni, silicon, tin, fluorine, etc.; as well as the production of electronic products—Cg, Mn, Fe, Ni.

The mosses acting as biomonitors sampled in the zones of influence of these enterprises (sampling sites 54 (the village of Plakhino) and 56 (the settlement Vishnevka) contain: As up to 2.7 mg/kg (34 times more than background concentrations); V up to 30.6 mg/kg (9 times more than background concentrations); Cg up to 65.3 mg/kg (460 times more than background), Fe up to 10.0 mg/kg (15 times more than background); Ni up to 27.6 mg/kg (7 times more than background).

The toxic semi-metal Sb was found as a scattered element in Ryazan city samples in high concentrations (up to 13.2 mg/kg, 44 times higher than the average regional background) (Figure 3). Sb compounds are components of lead alloys used in the production of paints and enamels, as well as technical and electro-vacuum glasses.

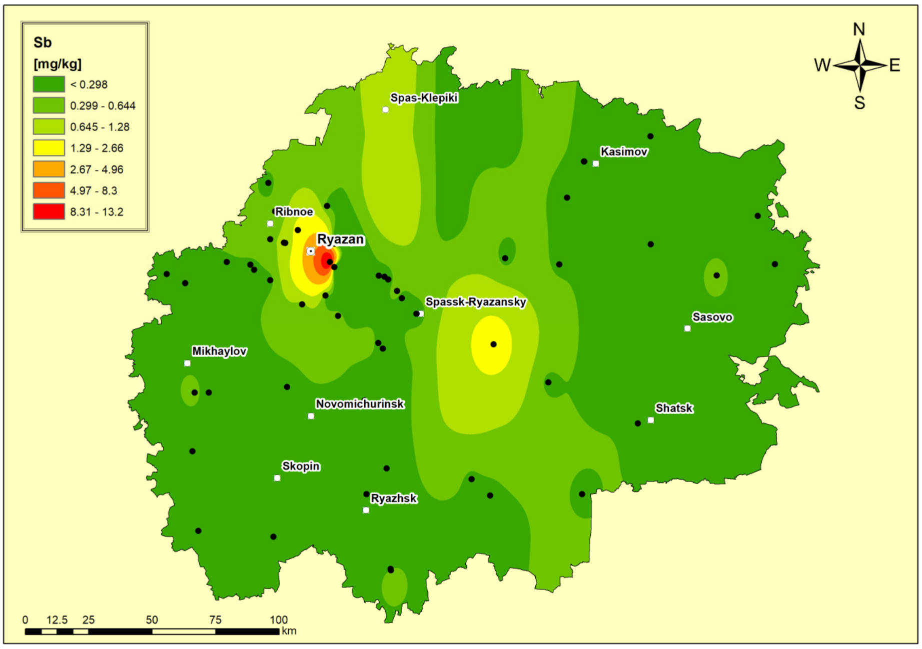

Figure 3. Distribution of atmospheric deposition of antimony (Sb) in the Ryazan Region, 2017. White dots are cities, black dots are sampling sites.

Enterprises of the "big" power industry are the largest polluters of atmospheric air. The western part of the territory of the Ryazan Region is located between two large thermal power plants: Ryazanskaya GRES in Novomichurinsk and Novomoskovskaya GRES in the Tula region (Figure 4). As a result of fuel combustion and the accumulation of ash and slag waste, Zn, Cr, Fe, Ni and V are released into the atmosphere.

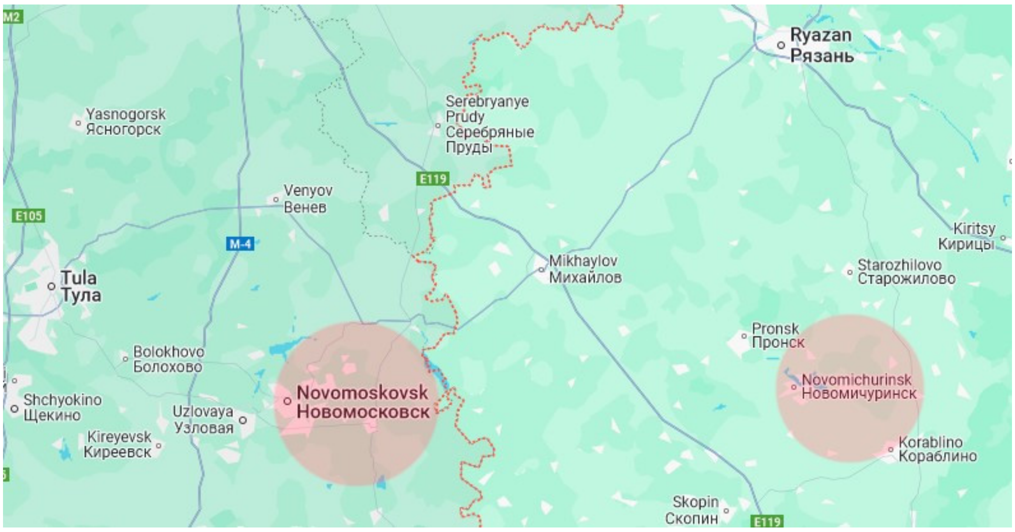

Figure 4. Location map of Ryazan and Novomoskovsk GRES.

In the areas heavily contaminated with anthropogenic elements—Pronsky (under the influence of Ryazanskaya GRES), Mikhailovsky (as a result of the aerosol migration of elements from enterprises of Novomoskovskiy District in the Tula Region—Novomoskovskaya GRES, large chemical industry enterprises and Korablinsky (under the influence of Pronsky) concentrations of V reach 30.6 mg/kg (9 times higher than background concentrations of V in the Ryazan Region) (Figure 5), Ni—27.6 mg/kg (7 times higher than background concentrations of Ni in the Ryazan region) (Figure 6).

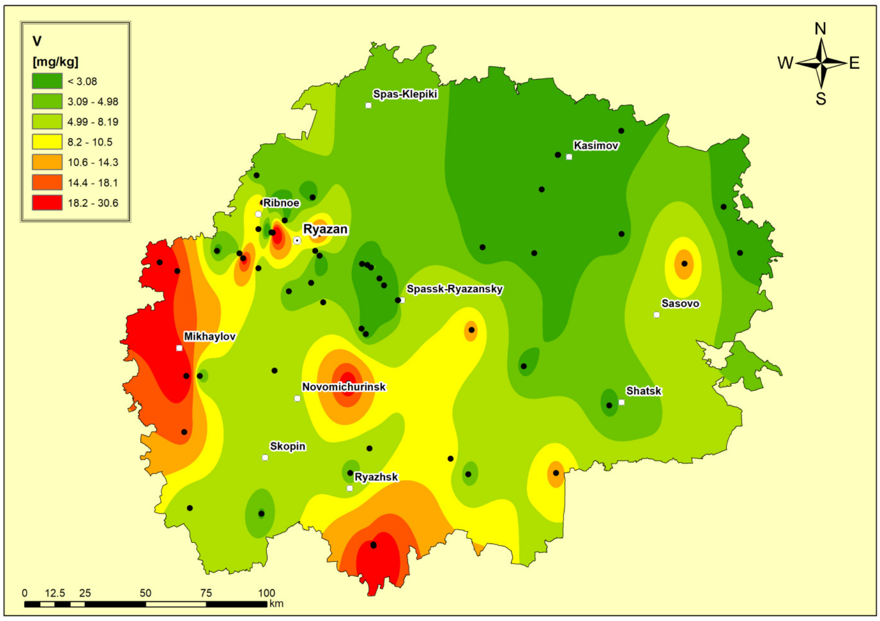

Figure 5. Distribution of the atmospheric deposition V on the territory of the Ryazan' region, 2017. White dots are cities, black dots are sampling sites.

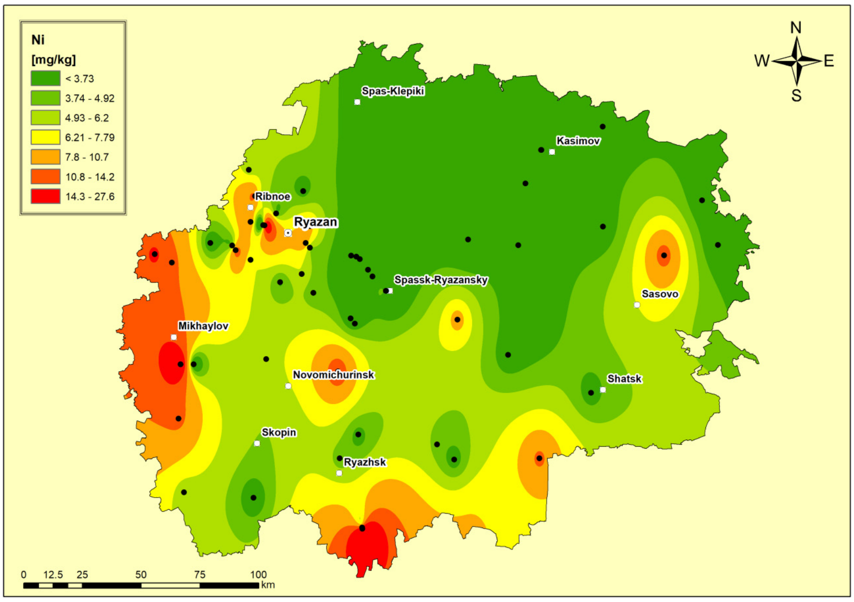

Figure 6. Distribution of the atmospheric deposition of Ni on the territory of the Ryazan Region, 2017. White dots are cities, black dots are sampling sites.

On the borders of the Skopinsky and Miloslavsky districts of the Ryazan Region, there is a potential source of pollution by HMs—a spoil heap known as a "coal mountain". Coal can contain increased concentrations of a number of valuable metals—Zr, W, Ti, V, etc. [19]. Ti is a generally toxic metal that is found in the smog of industrial cities. In the Ryazan Region, in concentrations four times higher than background indicators for the region, Ti was found in the mosses of Ryazan, the village of Nikitino in Korablinsky District and in the village of Goldino in Mikhailovsky District, probably due to the influence of thermal power enterprises.

In the radius of influence of cement plants in the Mikhailovsky and Ryazansky districts, there are increased concentrations of Zn (three times more than background concentrations), Mg (three times more than background concentrations) and Ca (four times more than background concentrations).

In the east of the Ryazan Region, Kadomsky District, which does not have a developed industry, is located in a zone of high technogenic pollution; however, at sampling site 45, possibly under the influence of enterprises in Sasovsky District—such as machine tool manufacturers and foundry enterprises and the chemical production of butyl acetate, ethyl acetate, solvents—high concentrations of HMs are found: As up to 3.7 mg/kg (47 times higher than background concentrations in the Ryazan Region) (Figure 7); Cr up to 65.3 mg/kg (460 times higher than background concentrations) (Figure 8); Fe up to 10.0 mg/kg (15 times higher than background concentrations) (Figure 9).

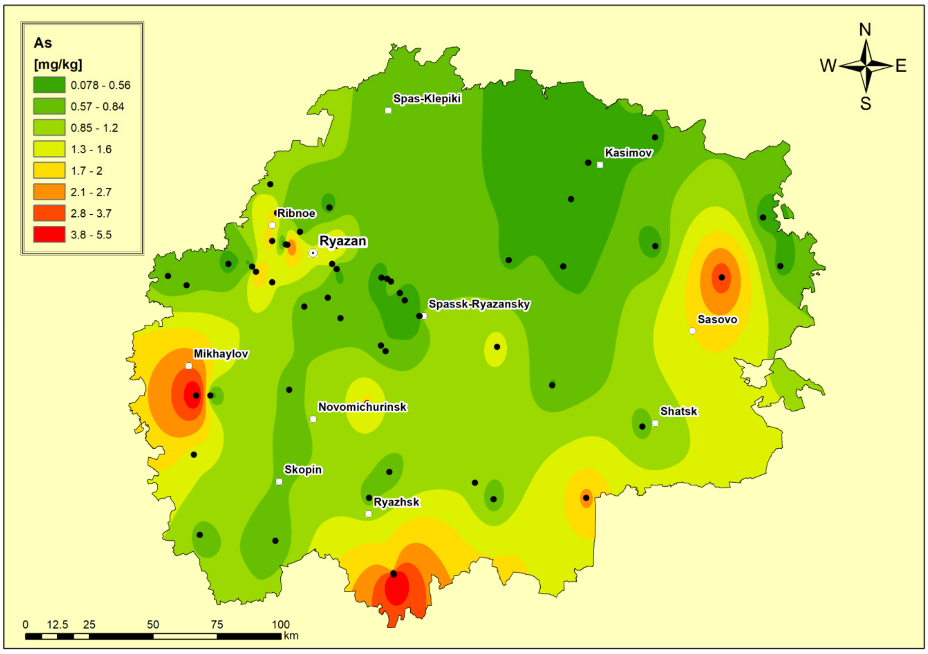

Figure 7. Distribution of the atmospheric deposition of As on the territory of the Ryazan Region, 2017. White dots are cities, black dots are sampling sites.

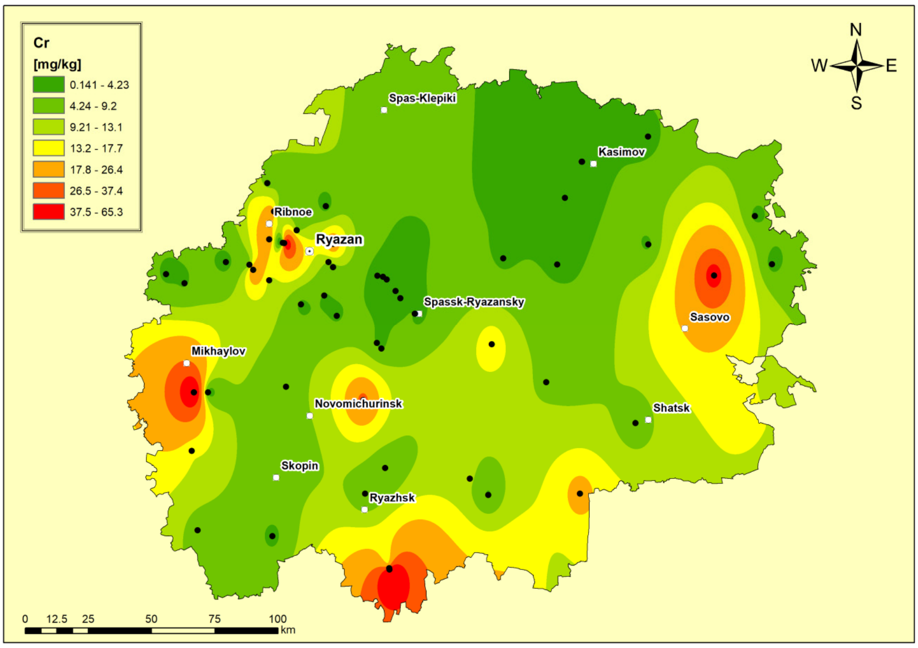

Figure 8. Distribution of the atmospheric deposition of Cr in the Ryazan Region, 2017. White dots are cities, black dots are sampling sites.

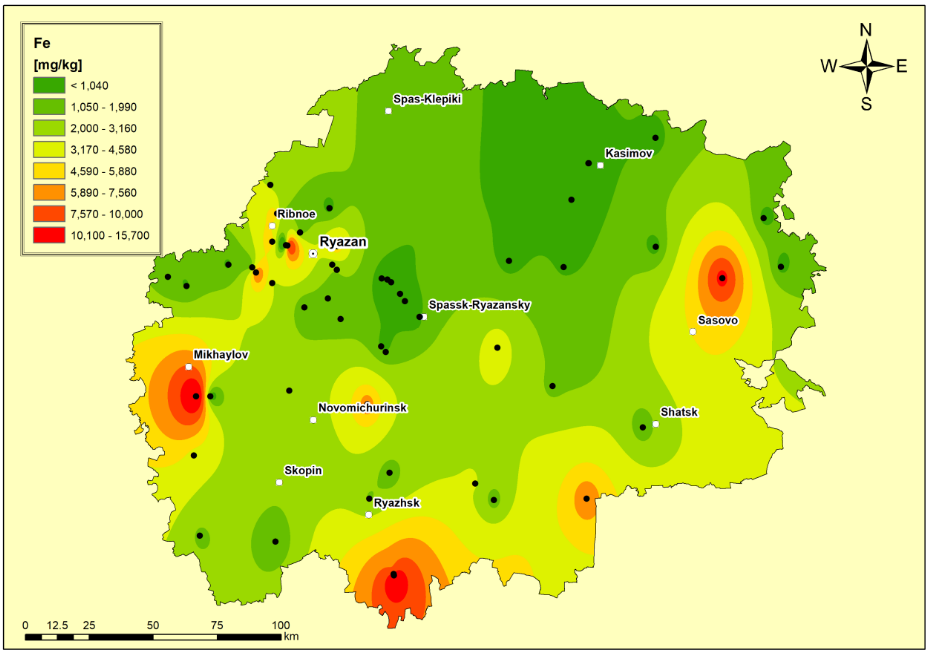

Figure 9. Distribution of the atmospheric deposition of Fe on the territory of the Ryazan Region, 2017. White dots are cities, black dots are sampling sites.

The agricultural south of the Ryazan Region showed high concentrations of HMs.

One of the main means of controlling pests in cultivated plants are derivatives of As used as insecticides. The sampling points were in the Alexandro-Nevsky District (sites 4, 5) and village. Chernava in Miloslavsky District (site 31) is presumably influenced by the southeastern railroad of the Ryazan Region, enterprises of neighboring regions and agriculture.

Within 30–40 km from the sampling points, there are welding, machining, assembly and foundry industries in the Tambov region, a starch factory and production of pipeline valves and pumping equipment in the Lipetsk region and also possible sources of V, Fe and Mn.

High Cl concentrations (580 mg/kg) were detected in Shilovsky District of the central part of the Ryazan Region, where there are no industrial enterprises, and are most likely related to agro-industrial activities. High Cl concentrations were also found in the city of Ryazan, probably resulting from the activity of an oil refinery.

Factor analysis indicates the anthropogenic origin of Cl and Bg halogens. Oil industry reagents may be an anthropogenic source of these elements.

According to the *Information and Technical Guide to Best Available Techniques* (ITS 30-2017 Petroleum Refining):

- Organochlorine reagents are used to modify the structure of hydrocarbons in the oil refining process;
- Organobromine biocides are used to prevent biological contamination, equipment corrosion and scale formation on heat exchange surfaces and in pipelines.

High concentrations of rare-earth elements (La, Ce, Sm, Eu, Tb, Yb) at site 45 of Sasovsky District are probably related to deposits of low-quality iron ore of no industrial importance.

According to the observations of local residents, water in bogs and streams in these places has a "rusty" color. An increased concentration of rare-earth elements was found at site 39 under the influence of the ash and slag wastes of Ryazanskaya GRES and at sampling sites 54, and 56 in the zone of influence of the industrial enterprises of Ryazan.

3. Conclusions

Ryazan Region has for decades been a region with high levels of air pollution. In 2017, the Ryazan Region for the first time became a participant in the UNECE ICP Vegetation. The moss biomonitors collected across the territory of the Ryazan Region were analyzed using epithermal neutron activation analysis, which made it possible to reveal the anthropogenic origin of elements recognized as environmental pollutants (V, As, Sb, Cr, Fe, Ni, Zn, Al, etc.) present in the atmospheric air of the Ryazan Region.

With the help of modern GIS technologies, local areas with concentrations strongly exceeding the average values are shown. The maps and charts trace the areas of deposition of trace elements and the area of heavy metal pollution.

Data on concentrations of trace elements included in the European atlas can be used for objective, scientifically based assessment of the possible health risk to the population living in polluted areas of the Ryazan Region, for spatial and temporal monitoring of atmospheric air, for the development of measures for environmental protection and for the preservation of air quality.

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