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Moss Biomonitoring in the Evaluation of Air Pollution in the Tver Region, Russia

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Abstract: In the Tver region (Russia), the moss biomonitoring technique was applied to investigate the atmospheric deposition of potentially harmful elements. Using inductively coupled plasma–optical emission spectroscopy and a direct mercury analyzer, a total of 15 elements were identified in 144 moss samples collected in the region. To assess the degree of environmental pollution, ecological indices (pollution load index, enrichment factor, geochemical index, and contamination factor) were computed. The sources of the identified elements were characterized across the territory under investigation using multivariate statistical analysis. The results obtained were compared with the information from other Central Russian regions. GIS technologies were used to create distribution maps for the surveyed territory. Transport and power plants are the primary sources of air pollution in the region, while the influence of industry is suggested to be negligible. Compared to other Russian regions, the area under investigation can be considered relatively clean.

Keywords: Tver region; biomonitoring; potentially toxic elements; ecological indices; pollution

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Citation: Vergel, K.; Zinicovscaia, I.; Yushin, N.; Chaligava, O.; Cepoi, L.; Kravtsova, A. Moss Biomonitoring in the Evaluation of Air Pollution in the Tver Region, Russia. *Atmosphere* **2024**, *15*, 1191. https://doi.org/10.3390/atmos15101191

Academic Editor: Maurice Millet

Received: 31 August 2024
Revised: 28 September 2024
Accepted: 3 October 2024
Published: 4 October 2024

1. Introduction

The wellbeing of the population is associated with industrial and agricultural development. However, the application of existing approaches and technologies will continue to put pressure on the environment, which manifests in air, soil, and water pollution. Among environmental pollutants, chemical elements deserve special attention due to their persistence and bioaccumulation properties [1]. Alongside their negative impact on the environment, the accumulation of potentially toxic elements (PTEs) in the human body results in diseases affecting the cardiovascular, gastrointestinal, hematological, hepatic, renal, neurological, developmental, reproductive, and immune systems [2,3]. One of the main tasks of national authorities in every country is the systematic monitoring of environmental quality, identifying potential sources of pollutant emissions and investigating their toxicological effects [4,5].

PTEs are elements naturally occurring in the environment, but their natural biogeochemical processes are greatly altered by a variety of anthropogenic activities. The main human activities responsible for releasing pollutants into the atmosphere are mining, transportation, industrial processes (particularly those related to metallurgy), and fuel combustion [6–9].

The cost and complexity of large-scale monitoring investigations using instrumental methods led to the development of alternative monitoring techniques [10]. The monitoring technique using moss, developed in the late 1960s [11], has demonstrated high effectiveness in air pollution research. Mosses, due to their lack of root system, thick waxy cuticles, large surface/mass ratio, tolerance to long periods of drought, and slow growth (often for years), are strongly dependent on atmospheric deposition for water and nutrient supply and have the capacity for air pollutants uptake [12,13].

With the establishment of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation), the moss biomonitoring technique gained widespread recognition in the 1990s. Since then, many European nations have joined the initiative [14]. Russia has been taking part in surveys under the ICP Vegetation program since 1995. Biomonitoring studies were carried out mainly in the central regions: Moscow, Tula, Vladimir, Yaroslavl, and Ivanovo, and also in some other regions, such as Udmurtia, North Russia [15–21].

The first moss biomonitoring study in the Tver region was conducted as part of a large survey performed in Central Russia in 2000–2002. However, sampling was carried out only in the eastern part of the region. The enterprises of Konakovo and Kashin were identified as the main sources of air pollution [22]. The next survey, performed in 2004, covered mainly the same area and reaffirmed the air pollution sources: the power plants in Konakovo, Kashin, and Kalyazin [23]. The results of the biomonitoring study performed in 2014 in the eastern part of the region showed that the level of contamination in the vicinity of Konakovo, Kashin, and Kalyazin had decreased and that forest fires were the main local sources of air pollution [24].

Previous studies have shown that the level of elements in the Tver region was lower in comparison with other regions in Central Russia, and it can thus be considered a pristine territory. To confirm the status of this region, the first moss survey covering the whole of the Tver region was conducted in 2021. The main objectives of the study were (1) to determine the content of PTEs in moss samples; (2) to reveal possible pollution sources; (3) to compare the data with the values obtained for other regions in Central Russia and those obtained in previous surveys; and (4) to assess the level of air pollution using ecological indices.

2. Materials and Methods

2.1. Study Area

The Tver region is the biggest region in Central Russia, with an area of 84.2 thousand km^2 and a population of 1.4 million people. The studied region is located in the west of the central part of the East European Plain. The Tver region borders with the Yaroslavl region in the east; the Vologda and Novgorod regions in the north; the Moscow and Smolensk regions in the south; and the Pskov region in the west. The climate of the region is moderately continental, with average temperatures of −10 °C in January and +19 °C in July. The average annual precipitation is 560–720 mm [25].

The basis of the region's economy is industry and agriculture. The main industries in the Tver region are machine building (Tver Carriage Factory, Torzhok, Russia, Tver Machine Tool plant), metal processing, energy complex (Konakovo Power Plants, Konakovo, Russia), food production, and chemical (Redkino Catalyst Company, Moscow, Russia, Tver paint and varnish plant) enterprises. Due to its large area, the region has a sizeable transport network. The territory of the Tver region is crossed by two highways: from south to north (Moscow–Saint Petersburg) and from south to west (Moscow–Riga). There are also many agricultural companies located in the region. The Tver region has a developed mining base, with brown coal, cement raw materials, building stones, peat, sapropel, and other materials being extracted [26].

2.2. Sampling

During the summer of 2021, 144 samples of *Pleurosium shreberi* were collected over the entire territory of the Tver region (Figure 1). Moss samples were collected according to the Monitoring Manual of the European Survey ICP Vegetation [27]. Moss samples were collected on the ground or surface of decaying stumps at least 3 m away from the nearest projected tree canopy. Samples were collected at a distance of least 300 m away from villages and industries and at least 100 m from smaller roads. The main criteria regarding the sampling were about 0.5 kg of fresh moss collected at each sampling point, consisting of five to ten sub-samples of the same moss species. A separate set of polyethylene gloves was used for the collection of each sample. The collected samples were stored in air-permeable bags.

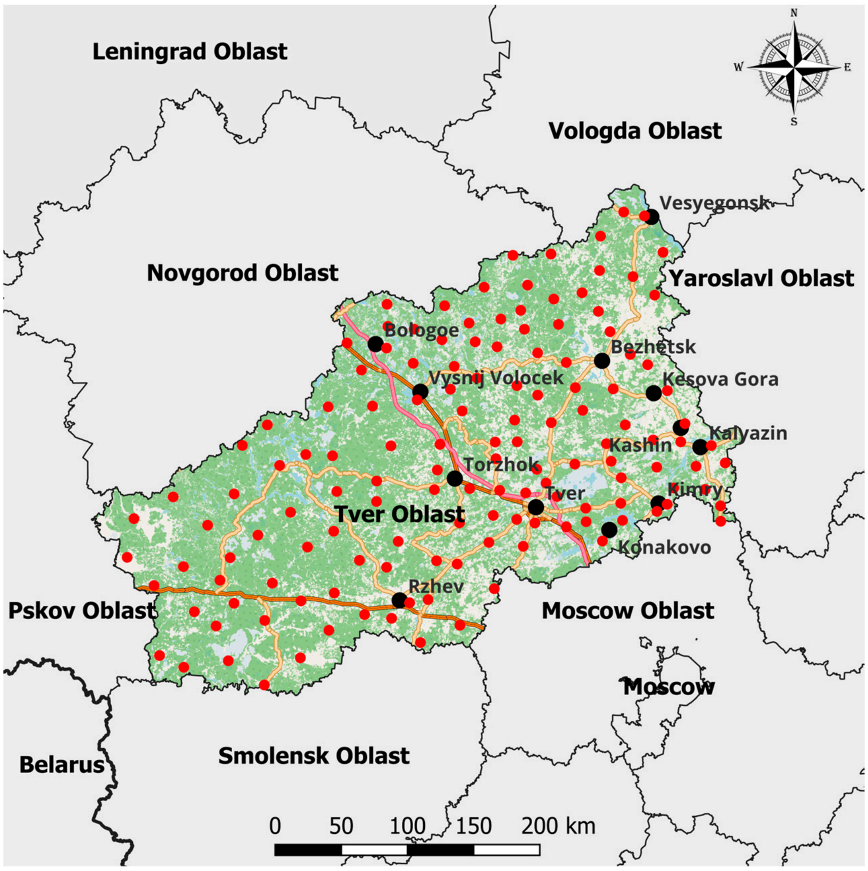

Figure 1. Moss sampling map in the Tver region (red dots—sampling sites, black dots—towns and settlements).

2.3. Sample Preparation and Analysis

All the reagents used for chemical analysis were of a high purity level (Merck, Darmstadt, Germany).

For analysis, the samples were cleaned of impurities and dried in an oven at 105 °C. Next, the samples were digested in the MARS 6 microwave system. For this, 0.5 g of moss was placed in a Teflon vessel containing a mixture of 5 mL HNO_3 and 2 mL H_2O_2. The content of 14 elements—Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb S, Sr, V, and Zn—in the collected samples was determined using an inductively coupled plasma–optical emission spectrometer PlasmaQuant PQ 9000 Elite (Analytik Jena, Jena, Germany). Using a direct mercury analyzer DMA-80 evo (Milestone, Italy), the amount of mercury was determined. The technique does not require preliminary samples preparation. The quality control of the measurement was ensured by the use of a certified reference material OBTL-5 (tobacco leaves). The relative uncertainty was in the range of 5–15%. More details about samples preparation and analysis are provided in [28].

2.4. Data Evaluation

Microsoft Excel 2021 software was used to perform basic statistics (minimum, maximum, average, median, standard deviation, 25th (Q_1) and 75th (Q_3) percentiles, and coefficient of variance (CV)) [20]. For multivariate analysis (factor analysis), Statistica

8.0 was used. Distribution maps of factor scores were created using the GIS-programme ArcGIS software version 10.6 (Esri, Redlands, CA, USA).

2.5. Pollution Indices

The contamination factor (CF) is counted to calculate the level of air contamination [29] and is presented as the ratio of the concentration of an element in the sample to its background value [30]:

$$CF = \frac{C_{el}}{C_{bkg}}, \tag{1}$$

where C_{el} is the content of a selected element and C_{bkg} is the background concentration for the same element. As background data, the mean values of three samples collected in pristine zones (National parks and reserves) were used.

The level of contamination was rated according to a scale developed by Fernandez and Carballeira: CF < 1—no contamination; 1–2—suspected; 2–3.5—slight; 3.5–8—moderate; 8–27—severe; and >27—extreme [30].

The pollution load index (PLI) is defined as the square root of the product of the CFs for a given sample [31]:

$$PLI = \sqrt[n]{\prod_{i=1}^{n} CF_i}, \tag{2}$$

where n is the total number of elements.

PLI < 1 denotes unpolluted; 1 < PLI < 2—unpolluted to moderately polluted; 2 < PLI < 3—moderately polluted; 3 < PLI < 4—moderately to highly polluted; 4 < PLI < 5—highly polluted; and PLI > 5—very highly polluted environment [31].

The enrichment factor (EF) was calculated as the ratio of element content in the moss samples to the concentration of a reference element (RE). The REs used in studies are mainly Al, Fe, Mn, and Rb. In many studies, including the present one, Al was used as a conservative element to calculate EF c [32].

$$EF = \left(\frac{\text{Element}}{\text{RE}}\right)\text{sample}/\left(\frac{\text{Element}}{\text{RE}}\right)\text{Background} \tag{3}$$

Values of $0.5 \le EF \le 1.5$ suggest that an element may come entirely from natural sources, while higher values indicate anthropogenic influence.

The geoaccumulation index (Igeo) was used to calculate the pollution of the environment:

$$Igeo = \log_{10}\left(\frac{C_n}{1.5Bkg}\right), \tag{4}$$

where C_n is the mean content of the selected element and Bkg is the geochemical background; 1.5 is the coefficient of natural variations in the content of the given element in environment [33]. Six classes were identified for I_{geo} values: I_{geo} values range from practically uncontaminated at 0 to 1; unpolluted to moderately polluted at $0 < I_{geo} < 1$; moderately contaminated at $1 < I_{geo} < 2$; moderately to heavily contaminated at $2 < I_{geo} < 3$; heavily contaminated at $3 < I_{geo} < 4$; heavily contaminated to extremely contaminated at $4 < I_{geo} < 5$; and extremely contaminated at $I_{geo} > 5$ [34].

3. Results and Discussion

3.1. Basic Statistics and Comparison with Literature Data

The content of 15 elements was determined using ICP-OS analysis and a direct mercury analyzer. The results of the descriptive statistics are shown in Table 1.

Table 1. Descriptive statistics for elements determined in mosses collected in the Tver region (in mg/kg).

Elements	Min	Max	Mean	Median	SD	Q1	Q3	CV, %
Al	178	898	428	414	118	354	476	27
Ba	4.3	93	31	30	15	22	40	48
Cd	0.09	0.98	0.23	0.21	0.10	0.17	0.26	43
Co	0.10	0.56	0.27	0.26	0.09	0.20	0.32	34
Cr	0.45	2.4	0.87	0.83	0.25	0.71	0.96	29
Cu	2.6	11	4.9	4.7	1.3	3.9	5.5	27
Fe	180	705	329	308	88	275	364	27
Mn	46	1137	438	417	224	296	592	51
Ni	0.57	5.8	1.8	1.6	0.93	1.2	2.2	51
Pb	1.5	7.6	2.8	2.7	0.76	2.3	3.0	28
S	744	1721	1033	1022	138	947	1113	13
Sr	5.7	74	16	15	6.6	12	18	42
V	0.49	2.5	1.1	1.0	0.31	0.89	1.2	28
Zn	23	88	41	38	12	34	45	29
Hg	21	68	37	37	9	30	42	24

Min—minimum; Max—maximum; SD—standard deviation; Q1, Q3—quartile 1 and 3; CV—coefficient of variance.

The CV values of all identified elements ranged from 13% to 51%, which correspond to slight or moderate levels of variation. A low level of CV showed a uniform level of contamination, while high values reflected the instability of elements content in the samples [20]. High CV values of 43%, 51%, 51%, and 42% were obtained for Cd, Mn, Ni, and Sr, respectively. This variation may be related to the influence of local anthropogenic activities and relatively high spatial variability [35].

The results of the current study were compared to those of earlier moss surveys conducted in the Tver region in 2000, 2004, and 2014, as well as in the Moscow, Vladimir, and Yaroslavl regions in 2018 and 2019 (Table 2).

The median values of elements in the Tver region were lower than in other regions of Central Russia, except Mn and Zn, whose content was slightly lower in the Yaroslavl region. Low PTEs content in the Tver region can be explained by low transport activity and the absence of large industrial enterprises.

In 2021, the Mn content in the region increased significantly (by 43%) in comparison with the previous surveys. This can be explained by a large number of sample sites, an increased number of vehicles and wildfires [36]. The content of Pb in 2021 decreases by 54% compared with the first survey. In 2003, the use of Pb additives in gasoline was banned in the Russian Federation, which led to a decrease in its concentrations in the air [37]. The higher content of elements in moss samples collected in 2014 can be explained by huge forest fires during that period, which provoked PTEs emissions [36,38]. The data obtained from moss samples collected in 2004 and during the present survey at the same sites were compared using the Mann–Whitney test. The test showed that the content of Cd, Co, Cr, and V did not change significantly between 2004 and 2021, whereas the content of some elements changed significantly in these two surveys; an increase was reported for Al, Ba, Fe, Ni, Sr, and Zn, and a decrease was reported for Mn. It should be mentioned that V concentrations decreased by 44% since the first survey in 2000. This can be explained by the fuel that is used at power plants; nowadays, natural gas is used as the main fuel; while in 2000, fuel oil residue was mainly applied.

Table 2. A comparison of the content of the elements obtained in the present study and literature data (mg/kg).

Nr. Samples	**Tver Region 144 (Present Study)**		**Tver Region 37 [22]**		**Tver Region 74 [23]**		**Tver Region 45 [24]**		**Moscow Region 156 [20]**		**Vladimir Region 73 [19]**		**Yaroslavl Region 53 [19]**	
Elem.	**MD**	**Range**	**MD**	**Range**	**MD**	**Range**	**MD**	**Range**	**MD**	**Range**	**MD**	**Range**	**MD**	**Range**
Al	414	178–898	589	123–3090	368	79–2558	-	-	900	110–3000	650	190–2300	500	330–1700
Ba	30	4.3–93	23	6.0–78	20	2.2–82	35	14–112	44	3.1–113	36	5.5–93	30	2.34–218
Cd	0.21	0.09–0.98	0.22	0.03–0.63	0.24	0.03–1.1	-	-	0.24	0.08–0.54	0.29	0.14–0.67	0.15	0.082–0.43
Co	0.26	0.10–0.56	0.39	0.08–3.51	0.23	0.05–1.27	0.39	0.15–1.2	0.38	0.11–1.07	0.38	0.18–0.86	0.29	0.13–0.87
Cr	0.83	0.45–2.4	0.79	0.20–6.3	0.96	0.21–6.0	2.7	0.82–19	2.63	1.01–7.5	2.5	1.3–7	1.8	0.39–5.8
Cu	4.7	2.6–11	5.0		-	-	-	-	7.61	3.03–43	6.1	4.3–9.3	5.8	3.7–10
Fe	308	180–705	347	68–2055	237	26–1113	674	322–2500	700	250–2300	500	250–1600	400	230–1100
Hg	37	21–68	-	-	-	-	-	-	-	-	-	-	-	-
Mn	417	46–1137	239	45–1897	808	114–3540	364	50–954	449	0.46–1540	431	118–931	382	48–964
Ni	1.6	0.57–5.8	1.26	0.25–4.9	0.64	0.43–5.3	1.6	0.52–3.3	2.87	0.46–6.3	2.8	1.24–5.7	1.83	0.8–6.5
Pb	2.7	1.5–7.6	5.9	2.06–9.9	-	-	-	-	4.82	1.33–14	4.2	1.9–8.8	2.8	0.003–0.07
S	1022	744–1721	-	-	-	-	-	-	-	-	-	-	-	-
Sr	15	5.7–74	12	5.1–44	7.1	1.6–29	13	4.67–29	-	-	-	-	-	-
V	1	0.49–2.5	1.8	0.34–6.0	1.1	0.08–14	2.3	1.0–7.3	1.9	0.32–5.3	1.9	0.95–6.3	1.7	0.8–8
Zn	38	23–88	30	19–72	26	11–122	44	21–131	57	1.3–145	48	32–98	34	23–169

MD—median.

3.2. Factor Analysis

To reveal possible sources of pollution, factor analysis with varimax normalized rotation was used. Factor analysis is a multivariate statistical method, which is applied in environmental studies to simplify large datasets with the purpose of identifying pollution sources and their relative elemental composition and to determine the contribution of each source to the total pollution level. Three factors were identified, accounting for 60% of the variability of the selected elements. The matrix of factors is given in Table 3, and the special distribution of factors is presented in Figures 2–4.

Factor 1 (Al, Co, Cr, Cu, Fe, Pb, S, and V) covers 33% of the total variance and can be identified as a geogenic/anthropogenic association. The highest concentrations of elements included in factor 1 were determined in the vicinity of Konakovo and along the M10 and M11 highways from Moscow to Saint Petersburg (Figure 2).

Table 3. Matrix of factor loadings.

	Factor 1	Factor 2	Factor 3
Al	0.85	−0.07	0.24
Ba	0.11	0.23	0.82
Cd	0.15	0.55	0.27
Co	0.62	0.26	0.30
Cr	0.78	0.07	0.15
Cu	0.59	0.20	−0.18
Fe	0.92	−0.03	0.17
Mn	−0.12	0.55	−0.07
Ni	0.18	0.63	0.08
Pb	0.73	0.19	0.20
S	0.63	0.44	0.11
Sr	0.14	−0.06	0.81
V	0.88	0.12	0.14
Zn	0.20	0.78	−0.08
Hg	0.45	−0.10	0.47
Expl.Var	4.96	2.03	1.95
Prp.Totl	0.33	0.14	0.13

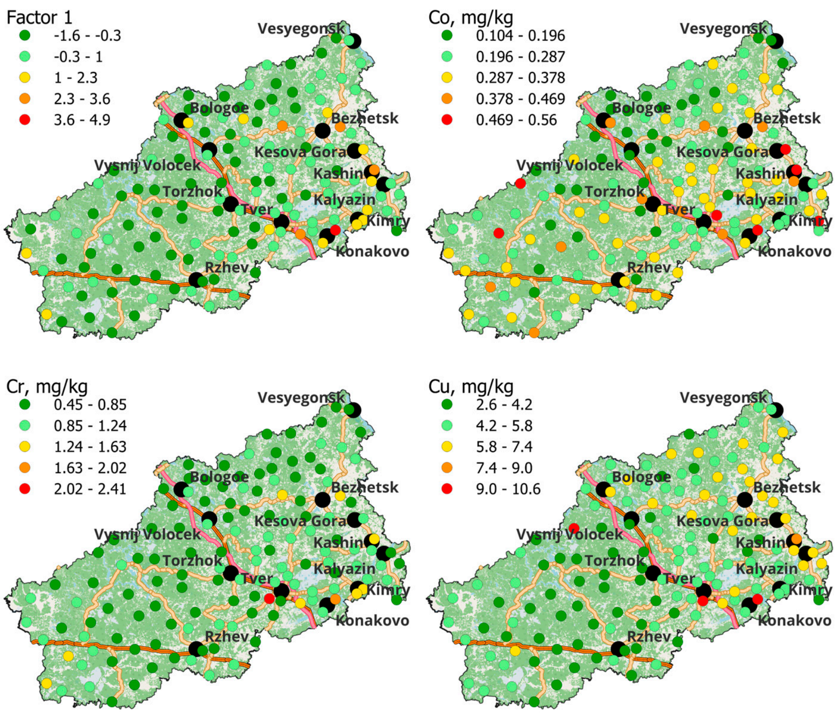

Figure 2. Spatial distribution of Factor 1 and distribution maps of selected elements.

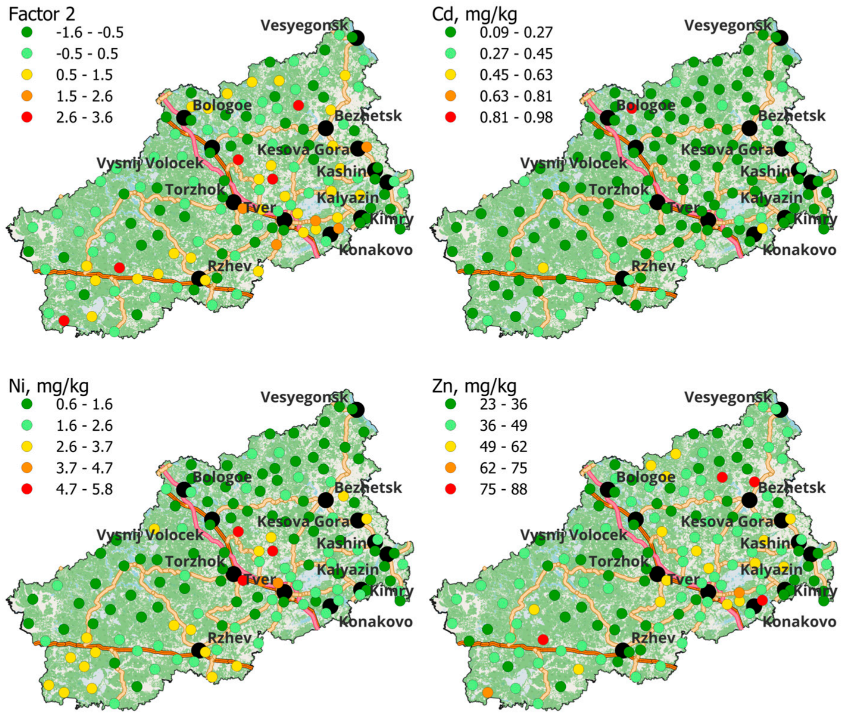

Figure 3. Spatial distribution of Factor 2 and distribution maps of selected elements.

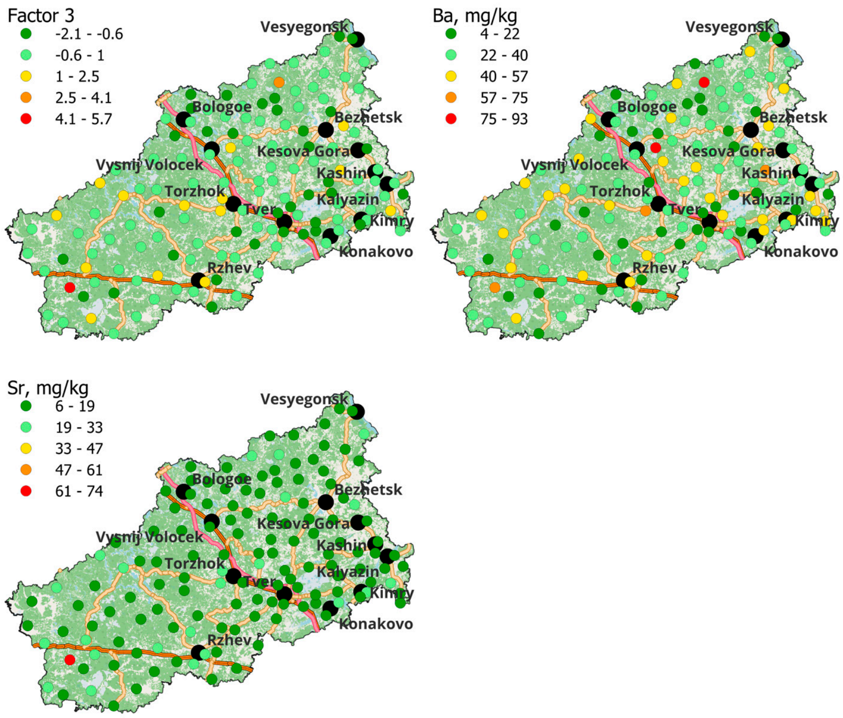

Figure 4. Spatial distribution of Factor 3 and distribution maps of selected elements.

The set of these elements can be associated with resuspended road dust and vehicles emissions [39]. The high content of the elements in the vicinity of towns confirms the contribution of vehicles to metals emission, while relatively high levels of elements, for example, Co, in the entire territory of the region indicate their geogenic origins. The regional power plant located in Konakovo, where oil is used as fuel, can result in the release of pollutants (Cr, Co, Cr, etc.) into the atmosphere [40]. Oil is one of the sources of V and S emissions [41].

The second factor (Cd, Mn, Ni, and Zn) accounts for 14% of the total variability. Cd, Ni, and Zn can be attributed to traffic emissions [42], while Mn can be emitted from cement manufacture, ore processing, and similar industrial activities [42,43]. Mn is also used as an additive in gasoline [44]. According to some researches, Ni can be released due to coal combustion [45,46], while Cd can be emitted into the atmosphere as the result of coal, peat, or sapropel combustion and mining [47–49]. Increased contents of Ni in the southern and southeastern parts of the Tver region can be explained by the use of coal for heating. The Tver region has the richest peat reserves in Central Russia, and the biggest coal mine in the region is located in the Nelidovo and Bologoe districts, where high contents of the elements included in the factor are observed. From Figure 3, it can be seen that the highest content of the mentioned elements was found along the highways and in the vicinity of the towns in the Tver region. Thus, transport and energy complex enterprises can be considered the main sources of these contaminants.

The third factor (Ba and Sr) accounts for 13% of the total variance. The source of Ba is non-exhaust traffic emissions [50]. This element is part of vehicles' tires and brakes, and due to the abrasion of brakes, Ba particles are released into the atmosphere [51]. As shown in Figure 4, the highest content of Ba was determined in samples around Rzhev, Vysnij Volocek, and Torzhok and in the northern part of the region. Sr is released into the atmosphere due to rock weathering, the migration of dust particles with the wind, etc. [52,53]. The content of Sr throughout the region was relatively low; its increased content was determined only in samples collected near the M9 highway. Thus, transport, along with road dust, can be considered the main source of these elements.

3.3. Environmental Asessment

For a better interpretation of the results, several ecological indicators were calculated (Table 4). Based on CF and PLI coefficients, the Tver region can be characterized as unpolluted (no contamination or suspected contamination). For Ba, Cd, Mn, S, Pb, Zn, and Hg, the coefficients were less than 2 at all sampling sites, which corresponds to no or suspected contamination (Figure 5). However, at some sampling sites, the CF values corresponded to minor contamination. Thus, in the vicinity of Konakovo, high CF values were obtained for Co (2.36), Cr (3.1), Cu (3.08), Fe (2.15), Pb (2.62), and V (2.16). Konakovskaya GRES can be considered the main source of pollution via emissions of the above elements. In the area between Kashin, Bezheck, and Kesova Gora, high CF values were obtained for Al (1.5–2.77), Co (1.09–2.3), Cu (1.74–2.17), and Fe (1.1–2.05). These elements reflect air contamination by vehicle emissions and local power plants. Also, in the area from Tver to the north (Spirovo), high CFs were obtained for Ni (2.1–3.15).

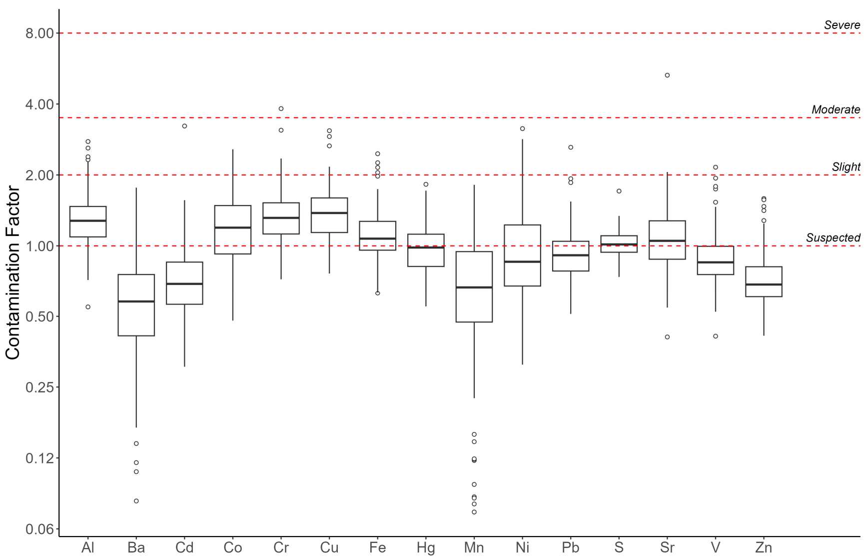

Figure 5. Boxplot diagram of CF for moss samples collected in the Tver region.

The source of Ni in this area can be considered to be transport, i.e., tires, oil burning, abrasion of parts [43]. PLI for the whole territory of the Tver region shows that the area is unpolluted (Figure 6). The highest value (1.65) observed in the vicinity of Konakovskaya GRES (Konakovo) indicates the influence of the thermal power plant on air quality. According to EF, the origin of the determined elements is mainly geogenic. Only in several zones were high EFs obtained for Ni: to the north of Rzhev, between Torzhok and Tver, along the M10 highway, and to the north of Lihoslavl′. The I_{geo} values suggest the unpolluted status of the investigated territory.

Previous surveys, performed in 2000, 2004, and 2014, revealed only one source of pollution in the region: a power plant located in Konakovo [22–24]. The results of the present study have confirmed that power plants contribute to air pollution and have also shown that transport is another important source of PTEs emission.

Table 4. Mean values of contamination factors, the geoaccumulation index, enrichment factors, and the pollution load index for moss samples collected in the Tver region.

	CF	Igeo	EF
Al	1.32	−0.23	RE
Ba	0.60	−1.51	0.46
Cd	0.75	−1.10	0.59
Co	1.24	−0.35	0.96
Cr	1.38	−0.17	1.06
Cu	1.42	−0.12	1.13
Fe	1.15	−0.43	0.88
Mn	0.70	−1.35	0.57
Ni	1.00	−0.74	0.80
Pb	0.95	−0.71	0.74
S	1.03	−0.56	0.82
Sr	1.13	−0.49	0.88
V	0.92	−0.76	0.70
Zn	0.73	−1.08	0.59
Hg	0.98	−0.65	0.77
PLI		0.95	

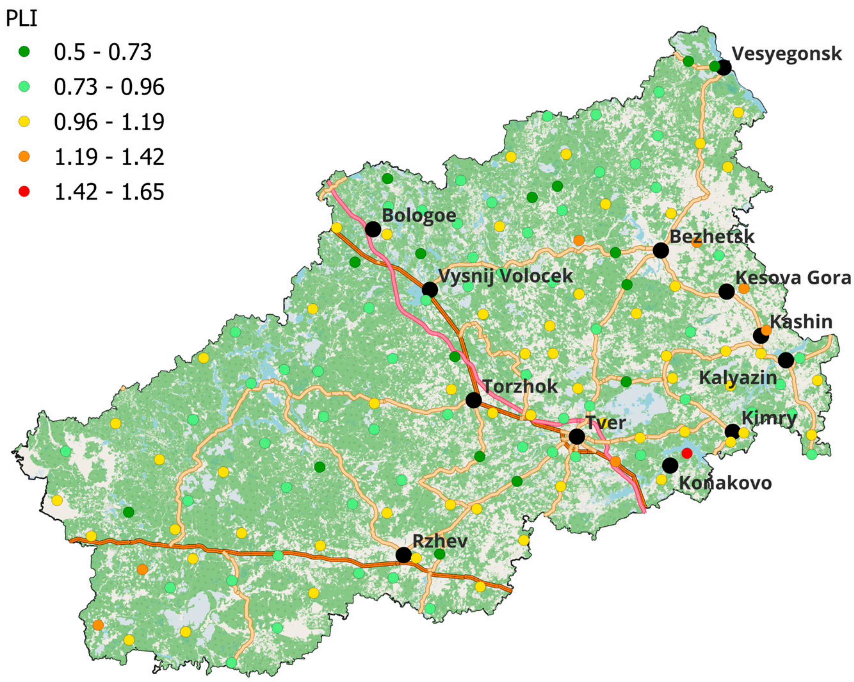

Figure 6. Distribution map of PLI for moss samples collected in the Tver region.

4. Conclusions

The fourth moss survey was carried out in the largest region of Central Russia in 2021. According to the moss biomonitoring survey, the Tver region is less polluted than the Yaroslavl, Moscow, and Vladimir regions. The investigation found that transport and energy power plants are the main contributors to air pollution and did not reveal any strong influence of industrial activity. When comparing the data obtained from the current survey to those from earlier studies, the levels of Cd, Co, Cr, and V did not differ significantly, while the content of Al, Ba, Fe, Ni, Sr, and Zn increased and the content of Mn and V decreased. The Tver region in Central Russia can be considered as a background territory because of its generally unpolluted environmental status.

Author Contributions: Conceptualization: K.V., I.Z., L.C. and N.Y.; moss samples collection: K.V. and N.Y.; samples analysis: N.Y. and A.K.; statistical analysis: O.C.; validation: I.Z., L.C. and A.K.; visualization: N.Y. and O.C.; manuscript draft preparation: K.V. and I.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Experimental data will be made available on request.

Conflicts of Interest: The authors declare no conflicts of interests.

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