



# Moss Biomonitoring of Atmospheric Trace Element Pollution in the Republic of Moldova

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## Abstract

The moss biomonitoring technique was used for the assessment of air pollution in the Republic of Moldova, in the framework of the UNECE ICP Vegetation Programme. The content of 11 chemical elements (Al, V, Cr, Fe, Ni, Zn, As, Sb, Cd, Cu, and Pb) was determined by neutron activation analysis and atomic absorption spectrometry in samples collected in spring 2020. Distribution maps were built to identify the most polluted sites. The highest concentrations of elements in mosses were determined in the north-eastern, central, and western parts of the country. The main element associations were identified using factor analysis. Three factors were determined, of which one of mixed geogenic–anthropogenic origin and two of anthropogenic origin. A comparison of the data obtained in 2020 and 2015 showed a significant decrease in the concentrations of Cr, As, Sb, Cd, Pb, and Cu in 2020. The state of the environment was assessed using Contamination Factor and Pollution Load Index values, which characterized it as unpolluted to moderately polluted. Possible air pollution sources in the Republic of Moldova are resuspension of soil particles, agricultural practices, vehicles, industry, and thermal power plants.

Air pollution is a global environmental problem and presents one of the most serious threats to public health (González-Martín et al. 2021). Among the pollutants affecting human health, the most dangerous are toxic elements, leading to respiratory and cardiovascular diseases, reproductive and nervous system disorders, and cancer (Manisalidis et al. 2020). Air pollution in both urban and rural areas was estimated to cause 4.2 million premature deaths worldwide in 2016 (WHO 2018).

Many countries apply emission reduction policies to reduce the level of air pollution. Despite these actions, in some counties, contamination of the environment is growing, which requires permanent monitoring of the concentrations

of toxic elements and the study of their influence on ecosystems (Stanković et al. 2018).

At present, the technique of moss biomonitoring, introduced by Rühling and Tyler in the 1960s, is widely used to assess air quality (Fernández et al. 2007). The technique presents an approach that allows a time-integrated estimation of toxic element deposition from the atmosphere to terrestrial systems. The absence of roots and a strong reduction in the cuticle in mosses permits the adsorption of nutrients and pollutants over the entire surface and their entrapment to the functional groups on the cell wall (Barkan and Lyanguzova 2018). Consequently, mosses are able to reflect changes in the toxic elements loadings significantly faster than tracheophytes (Stanković et al. 2018). The technique is easier and cheaper than conventional analysis since it eliminates the need for installing large numbers of deposition collectors, and consequently, higher sampling density can be attained. Although the elements' concentrations in mosses provide no direct measurement of deposition, the obtained information can be derived by using regression approaches relating the results from moss surveys to deposition monitoring data (Harmens et al. 2010).

The determination of trace elements in moss surveys was established in 1980 (Harmens et al. 2004). The European moss survey is conducted every 5 years since 1990 and the

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most recent survey was conducted in 2015/2016 with 36 countries participating and mosses sampled at almost 5000 sites across Europe and Asia and the concentration of Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, V, and Zn in naturally growing mosses were reported (Frontasyeva et al. 2020).

In the framework of the International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops (UNECE ICP Vegetation), in 2015, for the first time, the moss biomonitoring technique was applied in air pollution studies in the Republic of Moldova (RM). The main sources of pollution are thermoelectric plants, transport, and industry (Zinicovscaia et al. 2017; Frontasyeva et al. 2020).

In the paper are presented the results of the second moss survey performed in the RM, in 2020. The aim of the study was: (i) to determine current concentrations of elements in RM; (ii) to compare the results of the two moss surveys; (iii) to verify the pollution sources identified in the first national survey performed in 2015; (iv) to assess the state of the environment by calculating the Contamination Factor and Pollution Load Index values.

## Materials and Methods

### Studied Area

The Republic of Moldova is a landlocked country bordered by Romania to the west and Ukraine to the north, east, and south. The surface area of the country is 33,800 km<sup>2</sup> with a population of 3,546,000. The capital is the city of Chisinau. The country is relatively low-lying and hilly with a continental climate. Moldova is a predominantly rural country, 76% of its total area is agricultural land and 9.6% are forest. The country has no coal deposits, oil reserves, or major mineral deposits but natural resources include limestone, sandstone, and gypsum (MARD 2015; MENR 2005).

The main industries in the RM include the production of food and beverages, paper and cardboard, furniture, leather, construction and building materials, equipment and machinery (including heavy machinery), cement and glass, and electricity (MARD 2015).

At present, approximately 4000 stationary sources of air pollution, responsible for V, Ni, As and Sb emissions, are registered in the RM, including three power and heat generation units, 40 regional, 28 interregional, and 1639 local boiler houses, 530 gasoline and gas stations, 24 big fuel storage sites (MENR 2005). The emissions from mobile sources (vehicles) are increasing every year and at present they account for 65% of the total emissions, even rising above 75% in urban areas (MENR 2005).

It should be mentioned that in the RM, the main attention is given to emissions of gases such as SO<sub>2</sub>, CO<sub>2</sub>, NO<sub>2</sub>, CO, hydrocarbons, and volatile organic compounds. Information

regarding heavy metal concentrations is very limited. The concentrations of Cu, Ni, Zn, Pb, Cd, Cr are monitored in the atmospheric precipitation only at the Leova station (MARD 2015). According to a national report (MENR 2005), the concentrations of most heavy metals in precipitation correlate with their concentrations in the soil. Thus, moss biomonitoring can be considered the primary technique for the temporal assessment of the level of air pollution with trace elements in the RM.

### Sampling and Sample Preparation

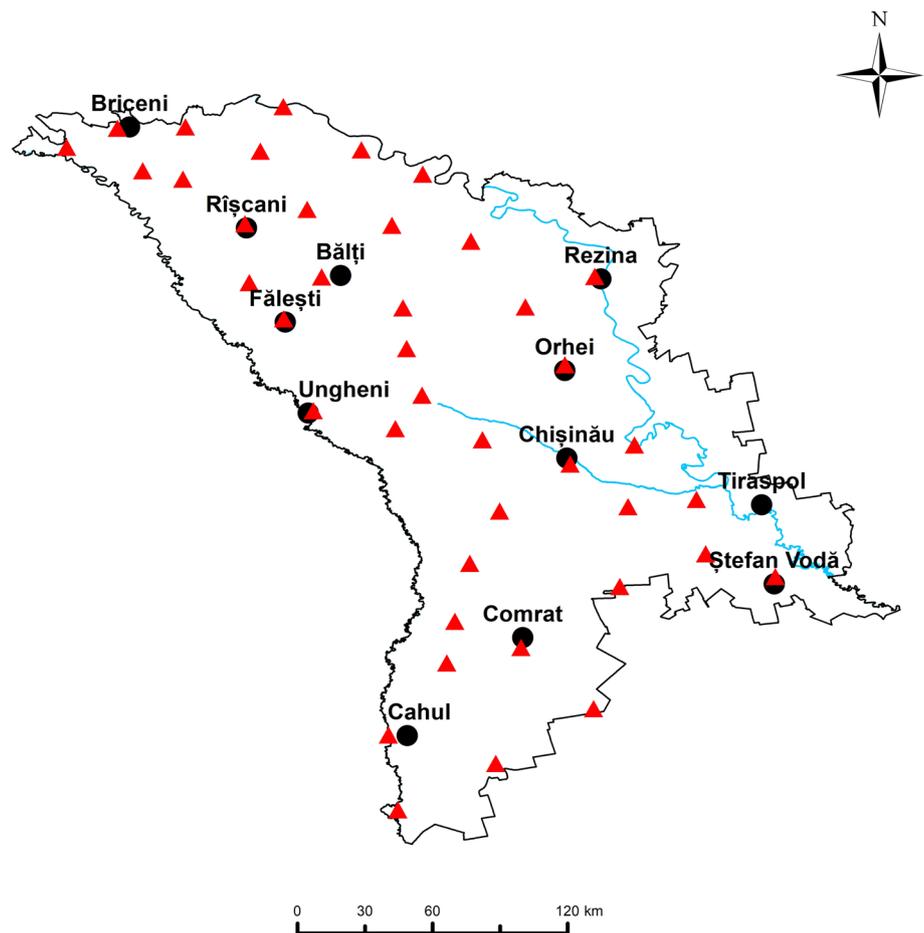
Moss samples (*Hypnum cupressiforme*) were collected across the country in April 2020 (Fig. 1) at the same 33 locations as in 2015 (Zinicovscaia et al. 2017), and 8 new sampling sites were added to cover the SOUTH part of the country. The samples were collected following the monitoring manual of the International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops (Frontasyeva and Harmens 2015). According to the manual, each country should aim to collect at least 1.5 moss samples/1000 km<sup>2</sup>. If this is not feasible, a sampling density of at least two moss sample sites per grid (50 km × 50 km) is recommended. In our case, moss samples were collected in a grid with a spacing of approximately 30 km × 30 km. 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 was collected at each sampling point, consisting of five to ten subsamples of the same moss species. A separate set of polyethylene gloves was used for the collection of each sample. Collected samples were stored in air-permeable bags (Zinicovscaia et al. 2021).

In the laboratory, the collected moss samples were cleaned of foreign material and the green and green–brown shoots from the top of the moss were separated and dried at 105 °C to constant weight. Samples for neutron activation analysis (NAA) were dried, pelletized, and packed in polyethylene foil bags and in aluminum cups for the determination of elements with short-lived and long-lived isotopes, respectively. The sample preparation procedure for atomic-absorption analysis (AAS) is described in detail in our previous work (Zinicovscaia et al. 2017). To determine Cd, Cu and Pb content, the samples were treated with 2 mL concentrated nitric acid and 1 mL hydrogen peroxide and then digested in a microwave digestion system (Mars; CEM, USA). Next, the digests were quantitatively transferred to 50 mL calibrated flasks and made up to the volume with double-distilled water.

### Analysis

The content, in mg/kg dry weight, of Al, V, Cr, Fe, Ni, Zn, As, Rb, Hg, and Sb in the samples was determined by NAA

**Fig. 1** Location of sampling points



at the IBR-2 reactor (JINR, Dubna, Russia). The content of Al and V was determined by sample irradiation for 3 min at a thermal neutron flux of  $1.6 \times 10^{12}$  n/cm<sup>2</sup>/s and direct measurement after irradiation for 15 min. The content of Cr, Fe, Ni, Zn, As, Rb, Hg, and Sb was determined by sample irradiation for 4 days at a neutron flux of  $3.31 \times 10^{11}$  n/cm<sup>2</sup>/s. After irradiation and cooling period the samples were re-packed and measured twice using HPGe detectors after 4 and 20 days of decay, respectively. Genie2000 software was used for spectra processing in order to determine the activity of elements and calculation of element content was done using the “Concentration” software (Pavlov et al. 2016). The content of Cd, Cu, and Pb in samples was measured using an iCE 3400 AAS Atomic Absorption Spectrometer with electrothermal (graphite furnace) atomization (Thermo Fisher Scientific, Waltham, MA, USA).

A set of standard reference materials, namely NIST SRM 1547 (Peach leaves), NIST SRM 2710 (San Joaquin Soil), NIST SRM 2709a (San Joaquin soil), NIST SRM 1632c (Trace Elements in Coal (Bituminous)), and IC-INCT-OBTL-5 (Oriental Basma tobacco leaves) was used to ensure quality control of NAA results. The quality of the AAS results was ensured by the standards NIST SRM 1575a

(Trace Elements in Pine Needles) and IC-INCT-OBTL-5 (Oriental Basma tobacco leaves). A good accordance between the calculated and certified values was achieved (Table S1). The content of the determined elements is given in Table S2.

### Statistical Analysis and Mapping

Median Absolute Deviation, Standard deviation, first and third quartiles, coefficient of variation were calculated using Excel (Microsoft, Redmond, Washington, USA). Principal component analysis (PCA) and visualization of the results were performed using the R language (Krakovská et al. 2020). To reveal differences between the concentrations of the elements in 2015 and the present moss survey the Wilcoxon signed-rank test (Wilcoxon 1945) was used.

To discover associations of chemical elements and decrease the number of variables for the obtained data, factor analysis (FA) was applied. FA is a multivariate statistical method, which is applied in environmental studies to simplify large data sets with the purpose to identify pollution sources and their relative elemental composition and to determine the contribution of each source to the total

pollution level (Kuik and Wolterbeek 1995). To compare the results of the two surveys and to identify the number of major components principal component analysis (PCA) was used. PCA allows the transformation of the original set of intercorrelated variables into a set of uncorrelated variables that are linear combinations of the original variables. The principal components are statistically independent and, as rule, the first few components explain almost all the variability of the whole data set (Schaug et al. 1990; Chaligava et al. 2021). In PCA, the main goal is to reduce the number of the observed variables to a smaller set of independent variables while maximizing the total variance. FA can to a certain degree be considered an extension of PCA but unlike it, FA can be applied with the aim to explain the relationship between the observed variables by assuming the existence of a common latent factor. While PCA is dependent on the scale of the variables, the FA approach is not and thus provides the possibility to eliminate this shortcoming (Krakovská et al. 2020).

To generate maps presenting the geographical distributions of concentrations of elements and factor scores the radial basis functions method in the ArcGIS software (Esri, Redlands, California, USA) was used.

### Determination of the Origin of Elements

To determine geogenic origin of elements, in the present study Rb was used as a tracer. Rubidium is an element mainly emitted in the atmosphere from eroded rocks (K-feldspars, micas, and clay) and soils, while its industrial application is very limited. A relatively high coefficient of correlation (0.75–0.99) may indicate a geogenic origin of an element, while  $R < 0.75$  may point at the anthropogenic origin of elements.

### Pollution Indices

Several indices were calculated to estimate the degree of air pollution. The contamination factor (CF) is defined as the ratio between the content of an element in the sample and its background value (Fernández and Carballeira 2001):

$$CF = \frac{C_m}{C_b} \quad (1)$$

where  $C_m$  is the content of a selected element and  $C_b$  is the background concentration for the same element. According to (Carballeira et al. 2002), the background concentrations of heavy metals were considered to be those obtained by measuring the levels of different elements in areas assumed to be unaffected by human activity. In the present study, as background were considered values determined for moss samples collected in the area of the Capriana national reserve.

Contamination degrees can be categorized as follows:  $CF < 1$ —no contamination;  $1-2$ —suspected;  $2-3.5$ —slight;  $3.5-8$ —moderate;  $8-27$ —severe; and  $> 27$ —extreme (Fernández and Carballeira 2001).

The PLI represents the  $n$ th order geometric mean of the entire set of CF values (Wu et al. 2018):

$$PLI = \sqrt[n]{\prod_{i=1}^n C_{F,i}} \quad (2)$$

where  $n$  is the total number of elements.

The PLI data are classified in several groups:  $PLI < 1$ —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 (Wu et al. 2018).

## Results and Discussion

### Spatial Distribution of the Elements

The order of the mean concentrations of the elements in moss samples was  $Al > Fe > Zn > Cu > V > = Cr > Ni > Pb > As > Sb > Cd$  and their distribution is presented in Fig. 2.

According to the distribution maps, the highest content of Al was determined near Balti (11,700 mg/kg), followed by Comrat (10,600 mg/kg), Briceni (9520 mg/kg), and Chisinau (9180 mg/kg). Content of Fe was also higher in mosses collected near towns, in particular near Edinet (7810 mg/kg), Balti (6930 mg/kg), and Chisinau (6150 mg/kg). Important sources of Al and Fe in Moldova can be considered the resuspension of road dust and rock weathering. However, since high content of Al was determined in samples collected near cities, additional likely sources of Al emissions could be coal combustion, motor vehicle exhaust, waste incineration, and exhaust gases of the metallurgical industry (Barabasz et al. 2002). In the case of Fe, another important source attributing to the determined high content can be considered fuel combustion in urban and rural areas, where mainly coal and wood are used for heating (Wang et al. 2015).

The highest content of Zn was determined near Cahul (86 mg/kg), followed by Rezina (78 mg/kg), Vadul lui Voda (77 mg/kg), and Chisinau (73 mg/g). Zinc is known to be released from vehicular activities such as tire wear (Aksu 2015). As in 2015, the main source of Zn emissions in Moldova can be considered transport (Zinicovscaia et al. 2017). The content of Cu in mosses collected near two cities, Chisinau (22 mg/kg) and Balti (12.9 mg/kg), greatly exceed the values obtained for the rest of the sampling sites. Moldova is an agricultural country and the determined high Cu mass

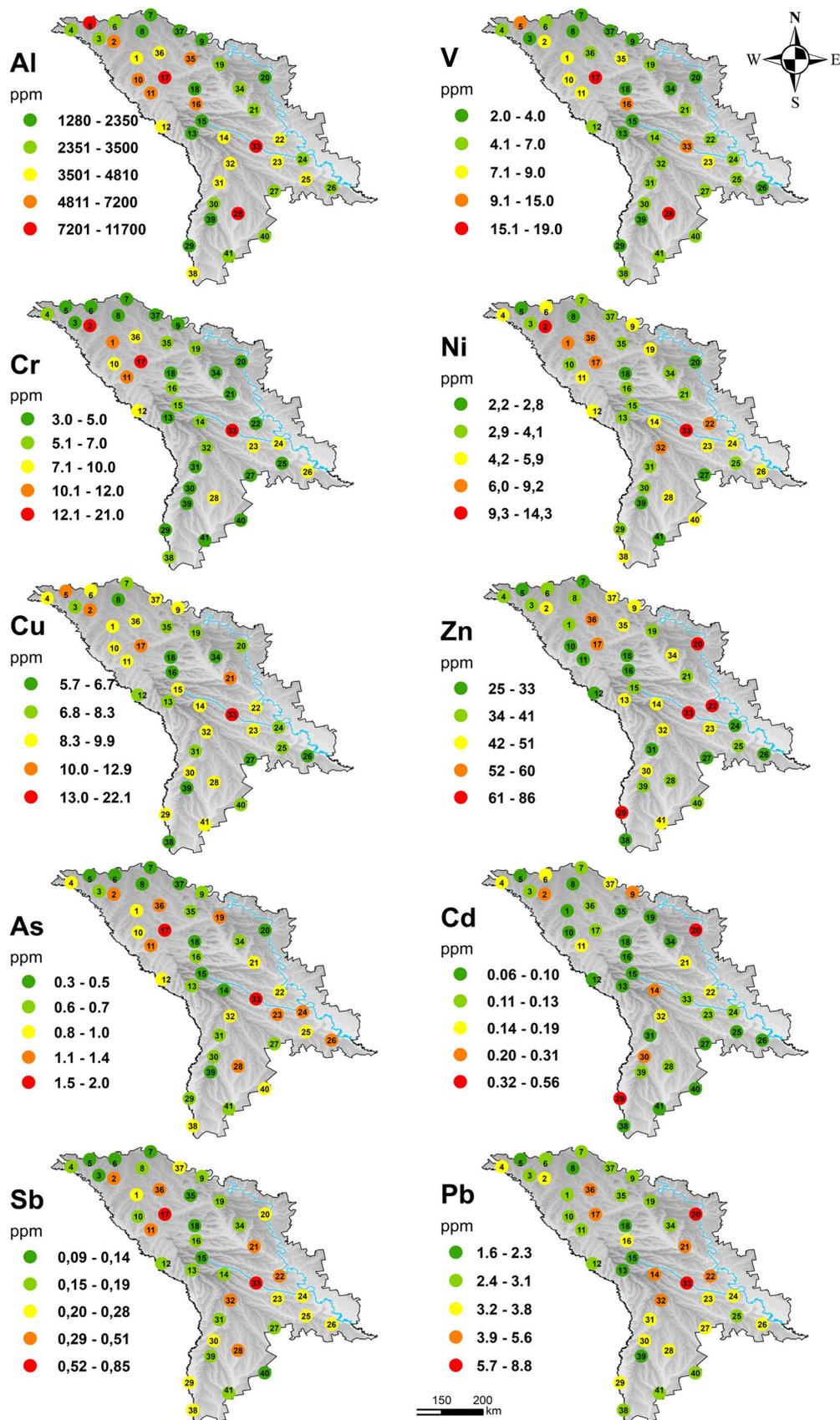


Fig. 2 GIS maps of the distribution of elements in the Republic of Moldova

fractions, especially in the north and central parts of the country, can be explained by the application of copper-containing pesticides. Copper pesticides play an important role in plant protection and are used to control fungal and bacterial diseases, such as grapes downy mildew, downy mildew of hops, apple scab, firelight, and potato late blight (Kuehne et al. 2017). The highest content of V was determined in Comrat (18.8 mg/kg) and Balti (18.5 mg/g) while in rural areas its content changed in the range 2.4–9.3 mg/kg. Vanadium accumulation in moss samples can be explained by its application as a heterogeneous catalyst used in the after-treatment of vehicle exhaust gasses (Visschedijk et al. 2013). The maximum values for Cr, Ni, As, Sb, and Pb were also determined for areas near Chisinau and Balti. Fuel combustion and transport are important sources of Cu, V, Ni, Pb, and Sb emissions (Visschedijk et al. 2013; Aksu 2015). Other important sources of Cr, Ni, Cd, and Fe emissions in the country are metal processing and non-ferrous metal production, production of paints and plastic, as well as industrial and domestic waste incineration. According to the Pb content, the central part of the country appeared more polluted than the rest (Chisinau area), Rezina, Balti, and Drochia (Fig. 2). The highest mass fractions of Cd were found near Cahul (0.56 mg/kg) and Rezina (0.42 mg/kg). According to the obtained data, the highest mass fractions of the described elements were found near urban areas, mainly near Chisinau and Balti.

Besides the anthropogenic sources, in the RM, all aforementioned elements can be emitted by natural sources, including wind-blown dust derived from the weathering of rocks and soils, forest fires, and vegetation.

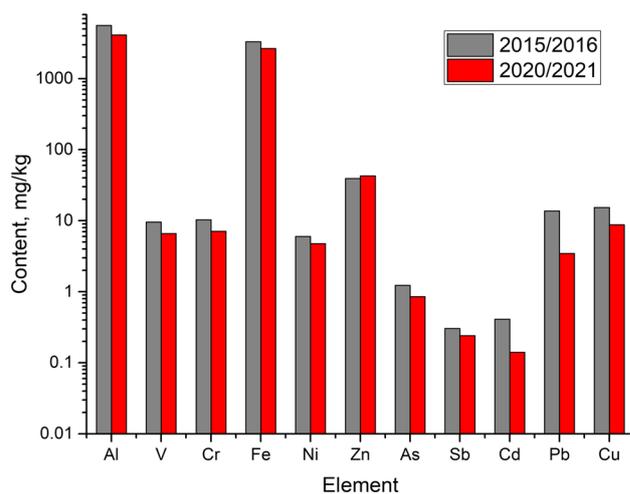
According to the national authorities in Moldova, the air pollution index values are the highest in Chisinau, Balti, and Tiraspol (however, samples in Transnistria were not collected), with an absolute maximum in Balti (MARD 2015). The data obtained in the present study confirm this fact since the content of almost all elements determined in the moss samples from the Balti area was either the highest or among the highest in the country. In Balti are registered 40 industrial companies (with more than 250 employees) and 62.3% of them are enterprises for food and beverage production. The main sources causing air pollution in Balti can be considered transport, the Combined Heat Power Plant “North”, the machinery companies “Moldagrotehnica” and “Draex-lmaier automotivei”, a wood processing company, concrete and construction materials production by “Raut”, leather processing and the textile industry, and facilities used for storage of petroleum products. In other cities, the transport and thermal power plants mainly contribute to the emissions of toxic elements in the atmosphere (MARD 2015).

## Comparison of the Results of the Two Moss Surveys

The values obtained for 11 elements in 2020 were compared with data from the previous sampling campaign (May 2015) (Fig. 3). According to the Wilcoxon test, significant differences ( $p < 0.05$ ) between the median values were revealed for more than half of the elements, namely Cr, As, Sb, Cd, Pb, and Cu. At the same time, it should be mentioned that the mean values for all elements were lower in 2020, except Zn, the content of which slightly increased in 2020. The most significant decrease was observed for Pb and Cd. The median concentrations of these metals were reduced by 75% and 66%, respectively. The concentrations of Cu declined by 43% and of V and Cr by 31% for both elements. The content of Al, Fe, Ni, As, and Sb decreased by less than 30%, while the content of Zn increased by 8.9%.

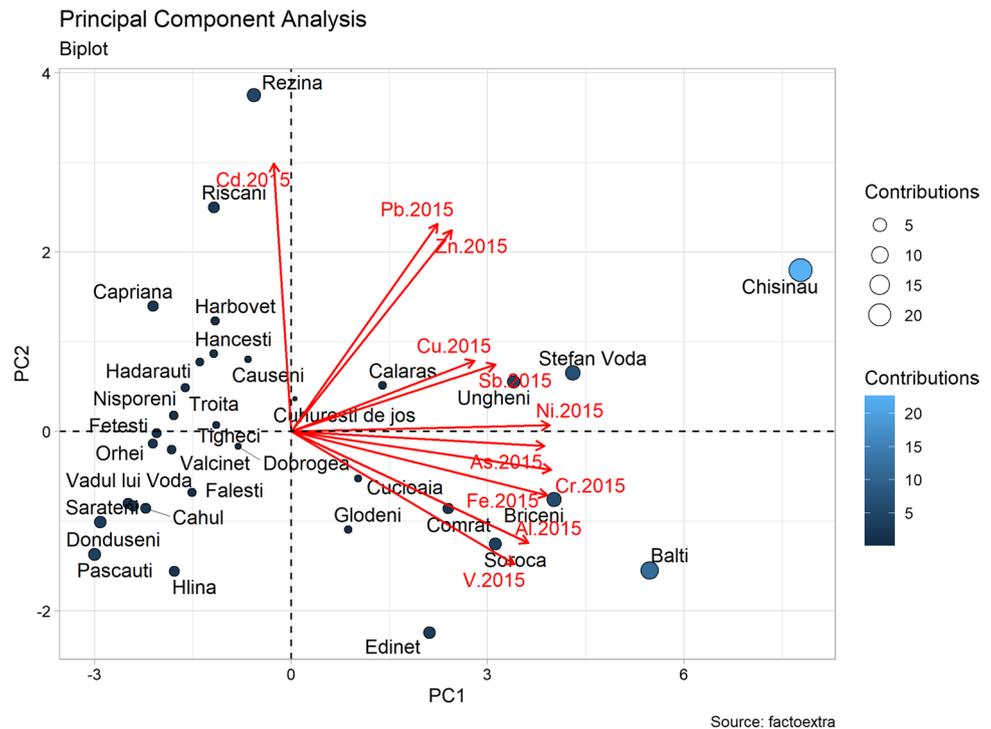
On the PCA biplots presented in Figs. 4 and 5, the component weights for the two main components are shown, which allows comparing the distances between the variables. The sampling points Balti, Rezina, and Chisinau, located the farthest from the axis origin, are considered extremes. The highest content of almost all elements was determined in samples namely from these regions, both in the 2015 and 2020 moss surveys. In the diagram, sites located close to each other can be considered similar, whereas those far from each other are distinctly different. Thus, the main part of the sampling sites, for example, Pascauti, Sarateni, Fetesti, Hlina, Hadarauti, Valcinet, Donduseni, Troita, Nisporeni, etc., which formed one cluster, are rural areas where the main sources of air pollution are resuspended soil particles, vehicles, as well as coal and wood burning.

All variables projected close to the origin are considered of little importance. The short distances between the variables indicate a strong correlation (Krakovská et al. 2020).

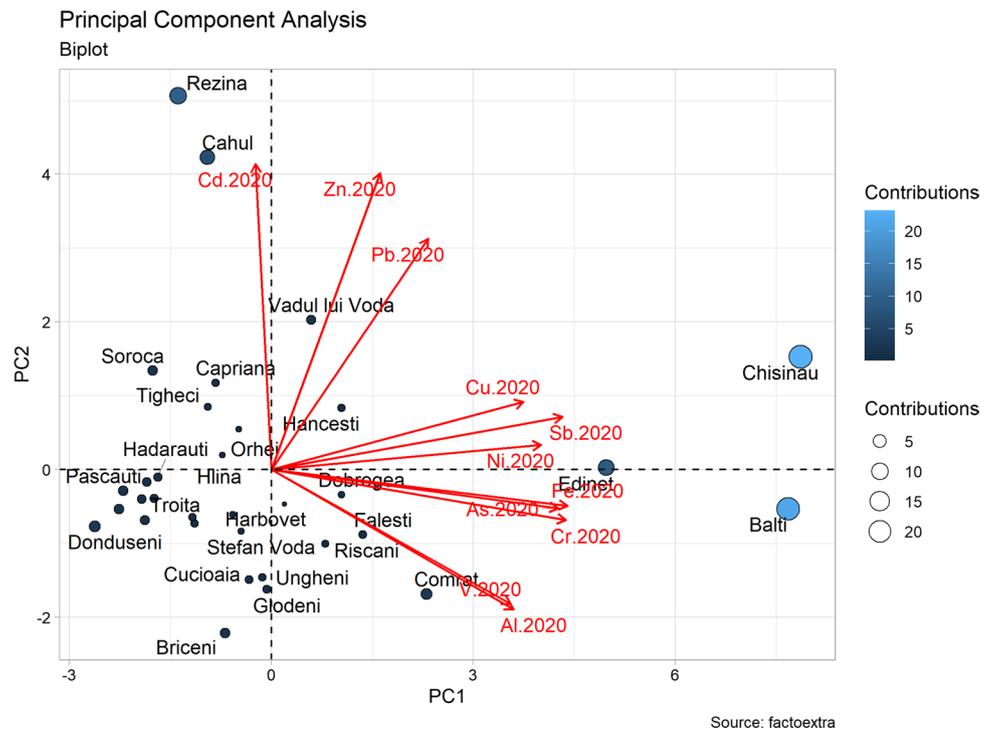


**Fig. 3** Comparison of the results from the present study with values from the 2015/2016 moss survey

**Fig. 4** Scatterplot of the component scores of individual sampling sites (the colour scale distinguishes the quality of the data representation in the graph) and plot of the component weights of individual elements for the 2015 survey



**Fig. 5** Scatterplot of the component scores of individual sampling sites (the colour scale distinguishes the quality of the data representation in the graph) and plot of the component weights of individual elements for the 2020 survey



Thus, the elements Cd, Zn, and Pb from both surveys (Figs. 4, 5) had strong correlations with each other, indicating that transport was their main emission source. In 2015, (Fig. 4) strong correlation was observed for Cu and Sb and the main sources of these elements' emissions are located in

Ungheni, Stefan Voda, and Chisinau. The elements Ni, Cr, Fe, Al, V, and As (Fig. 4) had strong correlations with each other. Briceni, Comrat, Soroca, and Balti mainly contributed to these elements' emissions. In 2020 (Fig. 5) as well as in 2015, strong correlations were observed for Cd, Zn, and Pb.

Chisinau could be considered an important source of Cu, Ni, and Sb emissions. A strong correlation of V and Al was observed in samples collected near Comrat and of As, Fe, Cr in samples collected near Edinet and Balti. In general, elements determined in both surveys correlated well, therefore it can be concluded that they had a common source of emission. As main sources of emissions can be mentioned resuspended soil particles, thermal power plants, transport, and industrial activities (Table 1).

### Factor Analysis

Factor analysis was used to identify and characterize all element associations based on the determined mass fractions. The matrix of the dominant rotated factors obtained using FA is shown in Table 2 and the distribution maps of the factor scores are presented in Fig. 6.

Three factors were identified, which included 86% of the variability of the treated dataset. The first factor (F1) was dominated by Cr, Fe, Ni, As, Cu, and Sb, explaining 43% of the total variance. These elements can originate from natural sources, as well as industrial and agricultural activities. Their highest concentrations were determined in moss samples collected in the north-east (Riscani, Edinet, Balti, and Drochia) and the center-west (Chisinau, Causani, Stefan-Voda) parts of the country. The plots of the F1 elements *versus* the Rb content are presented in Fig. 7. Relatively high coefficients of correlation (0.75–0.9) were obtained for Cr, Fe, Ni, and As, which indicated their geogenic origin. The content of these elements in mosses is remarkably influenced by mineral particles released into the atmosphere due to the weathering of rocks and soils (Barandovski et al. 2015). The sparse plant coverage and dry climate in the RM result in extensive soil erosion and suspension of soil material on moss. However, high concentrations of these elements were determined

**Table 2** Matrix of rotated factor loadings

Element	Factor 1	Factor 2	Factor 3	Communality (%)
Al	0.35	−0.05	0.91	99
V	0.34	−0.03	0.91	99
Cr	0.92	0.05	0.33	96
Fe	0.95	0.08	0.27	99
Ni	0.92	0.20	0.12	88
Zn	0.12	0.89	0.04	64
As	0.82	0.12	0.39	86
Sb	0.69	0.39	0.44	83
Cd	−0.07	0.81	−0.29	60
Pb	0.27	0.77	0.22	60
Cu	0.49	0.45	0.49	66
Expl.Var, %	43	22	21	

in urban areas, too, therefore, the resuspension of road dust particles could be considered one of the important sources of air pollution. The main sources that contribute to road dust are tire, brake, and clutch wear, road surface wear, and other vehicle and road component degradation (Adamiec et al. 2016; Zhou et al. 2017).

The correlation coefficients obtained for the ratios Sb/Rb and Cu/Rb were less than 0.7, thus, Sb and Cu may originate from both natural and anthropogenic sources. In Moldova, one of the important contributors of Cu, Sb, and As emissions can be considered agricultural practices since these elements are components of different pesticides (Wagner et al. 2003).

The second factor (F2) contained high loadings for the elements Zn, Cd, and Pb, accounting for 22% of the total variance. The elements of F2 are characteristic mainly of traffic (Zhou et al. 2017). The correlation coefficients for Zn/

**Table 1** Descriptive statistical analysis of the results (in mg/kg)

Element	Range	Median ± MAD	Mean ± SD	Q1	Q3	CV (%)	Percentile 90
Al	1280–11,700	3430 ± 1200	4114 ± 2477	2515	4780	60.2	8784
V	2.4–18.8	5.4 ± 1.7	6.58 ± 4	3.90	8.20	60.8	13.7
Cr	3.2–21.3	5.4 ± 1.6	7.07 ± 4.17	4.40	8.95	59.0	11.7
Fe	951–7810	2190 ± 610	2646 ± 1487	1740	3125	56.2	4524
Ni	2.2–14.3	4.1 ± 0.9	4.74 ± 2.41	3.27	5.40	50.9	7.74
Zn	25–86	39 ± 7	42.7 ± 14.4	32.3	47.0	33.7	70.4
As	0.31–2.03	0.73 ± 0.21	0.85 ± 0.38	0.56	1.06	45.4	1.35
Sb	0.09–0.85	0.18 ± 0.04	0.24 ± 0.16	0.15	0.26	67.1	0.41
Cd	0.06–0.56	0.11 ± 0.03	0.14 ± 0.1	0.078	0.16	72.3	0.25
Pb	1.56–8.82	3.14 ± 0.42	3.45 ± 1.38	2.76	3.74	39.9	5.12
Cu	5.7–22.2	8.62 ± 1.19	8.78 ± 2.74	7.12	9.42	31.2	11.7

MAD median absolute deviation, SD standard deviation, Q1 and Q3 first and third quartiles, CV coefficient of variation

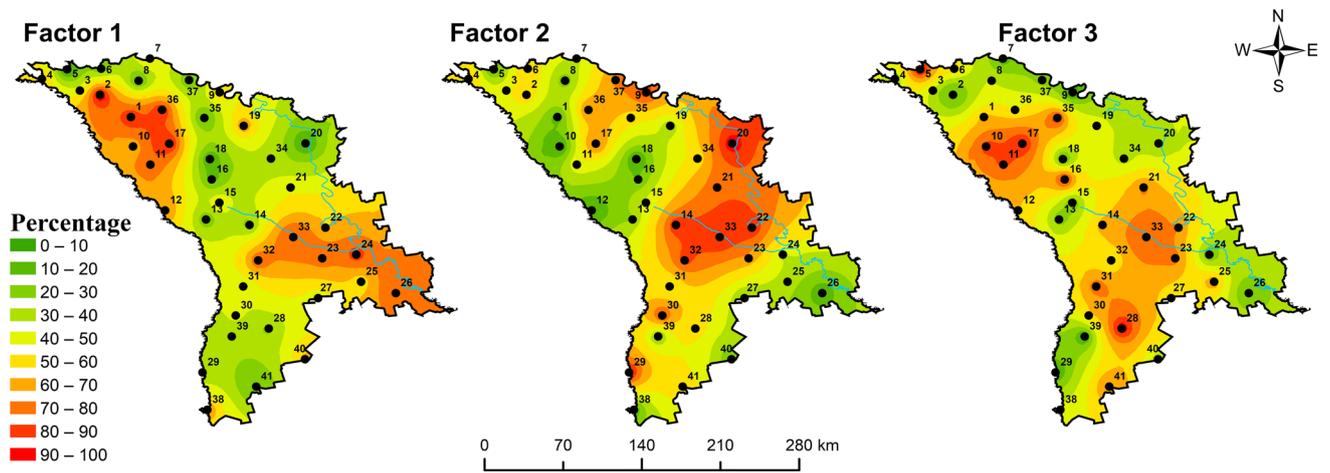


Fig. 6 Spatial distribution of the factor scores (Factors 1–3)

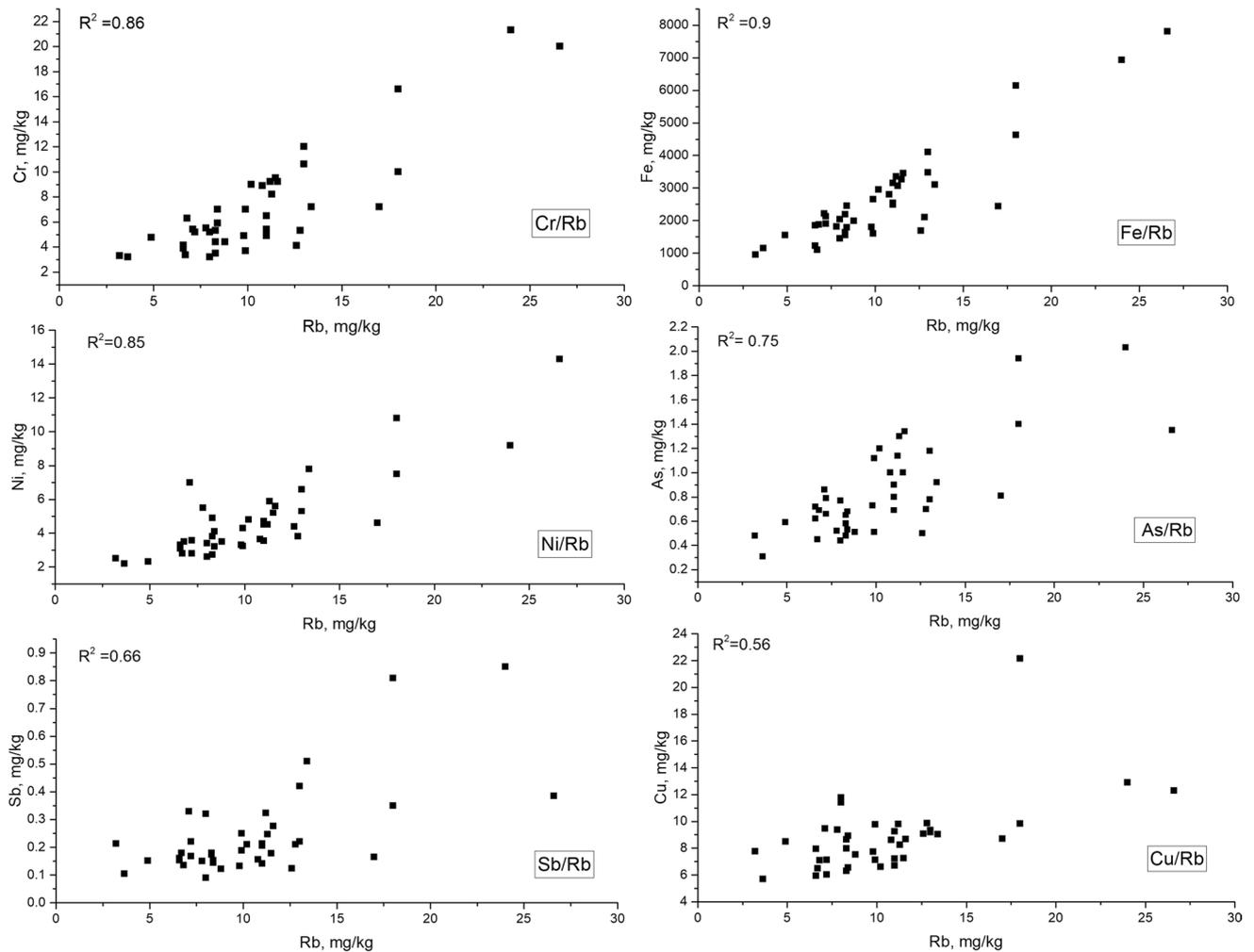


Fig. 7 The ratio of the content of each element in factor 1 versus Rb content in moss samples

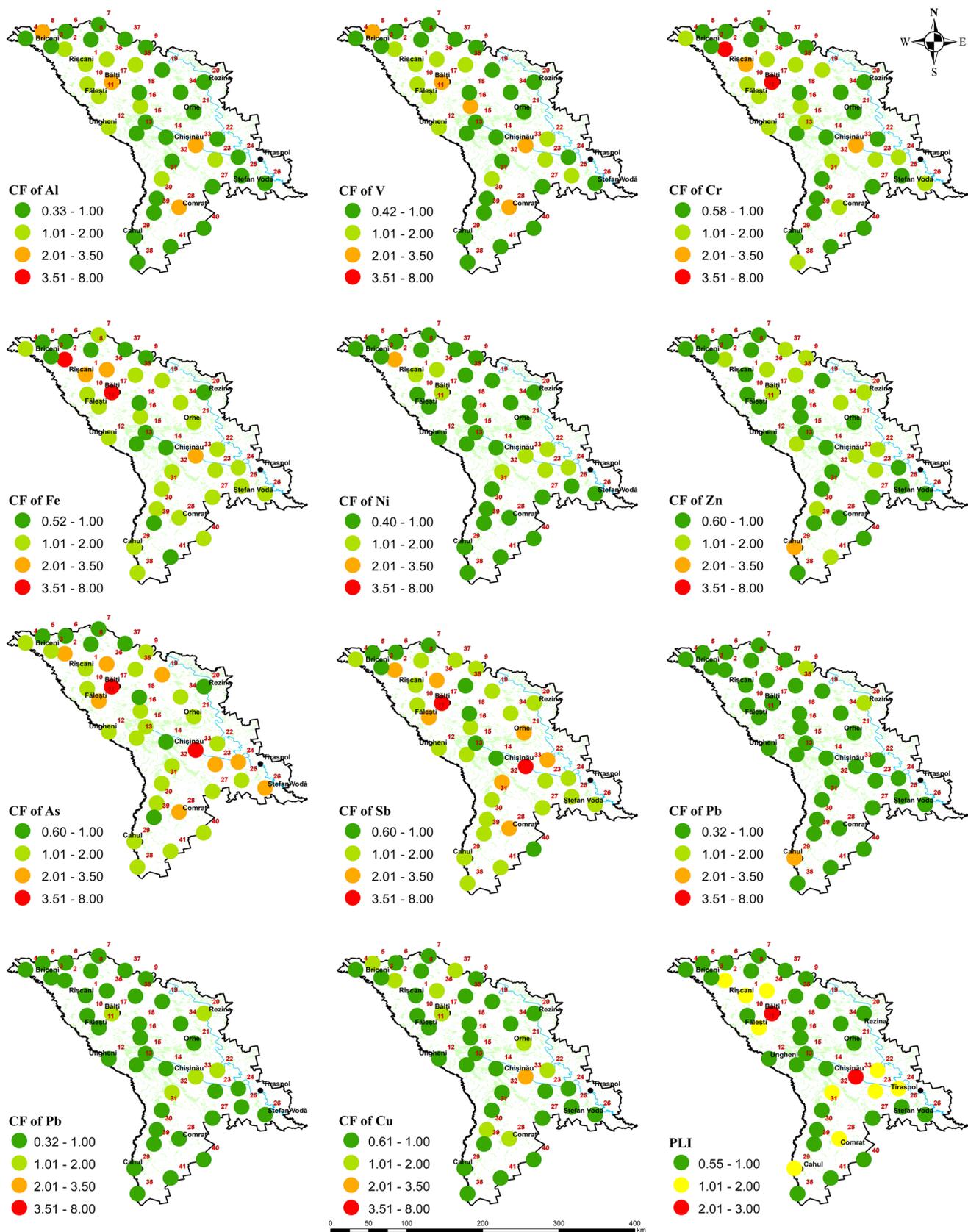


Fig. 8 Distribution of the contamination factor and pollution load index values

Rb, Cd/Rb, and Pb/Rb pointed at their anthropogenic origin (Fig. S1). The highest concentrations were determined in the central part of the country (Chisinau, Hincesti, Rezina, Vadul lui Voda).

The third factor (F3) associated Al and V, accounting for 21% of the total variance. High concentrations of Al and V were characteristic of Chisinau, Balti, Comrat, and Briceni. The elevated levels of V in Chisinau and Comrat can be associated with the activities of the oil refinery “Vitoil Trading”. These elements can be also emitted by the two electrical and heat generation stations in Chisinau and the electrical and heat generation station “Nord” in Balti. In the case of the environmental distribution of Al, natural processes far exceed any contributions by anthropogenic releases (Atsdr 2002). However, the weak correlation between the Al/Rb and V/Rb ratios (Fig. S2) indicated the anthropogenic origin of these elements in the moss samples. Since, in Moldova, besides oil, coal is used for heating, the major anthropogenic source of Al in the country can be considered coal combustion in urban and rural areas, as well as waste incineration. No sources of high Al and V content were identified in Briceni, thus, long-range transport could be the source of pollution in this area (Motyka et al. 2020).

Copper was the only element characterized by high factor loadings in all three factors, which indicated multiple sources of atmospheric emissions: natural, industrial, and agricultural.

## Pollution Indices

CF and PLI were used to assess pollution levels in the RM (Fig. 8). The mean CF values indicated that the elements determined across the whole country were associated with the first and second categories of the contamination scale. In Chisinau, the CF levels of Cd, Zn, Pb, and Ni ranged from 1 to 2, which indicated an uncontaminated status or suspected level of contamination. Aluminium, Cu, Fe, and V were associated with the third category of the contamination scale, whereas As and Sb—with the fourth category of the contamination scale, implying slight and moderate pollution, respectively. In Balti, the CF values for Cd, Cu, Ni, Pb, and Zn pointed at suspected contamination. Aluminium and V were associated with slight contamination, while As, Cr, Fe, and Sb—with moderate contamination.

According to the PLI values, the entire country could be characterized as unpolluted to moderately polluted, while Chisinau and Balti, where the highest values of CF were obtained for As and Sb, are associated with moderate pollution.

## Conclusion

For the second time, the atmospheric depositions of trace elements were studied in the Republic of Moldova using the moss biomonitoring technique. By applying NAA and AAS techniques, the content of 11 elements was determined in the moss samples collected in 2020. The highest concentrations of almost all elements were depicted near Chisinau and Balti. Comparison of the obtained data with the results of the 2015 moss survey showed a significant decrease in Cr, As, Sb, Cd, Pb, and Cu content. Three main factors were revealed in the 2020 dataset, one of which was identified as a geogenic-anthropogenic (F1) and the rest were related to anthropogenic activities (F2 and F3). The high coefficients of correlation between Me/Rb ratios obtained for Cr, Fe, Ni, and As (0.75–0.9) indicated their geogenic origin. According to the Me/Rb ratio, Cu (0.56) and Sb (0.66) may have originated from both natural and anthropogenic sources, whereas values of Me/Rb ratios lower than 0.25 pointed at the anthropogenic origin of Zn, Cd, Pb, Al, V. According to the calculated PLI values, 55% the territory of the Republic of Moldova can be characterized as unpolluted, 40% as slightly to moderately polluted and 5% as moderately polluted. The obtained data complemented the first moss survey results and can be used for the establishment of a database for further monitoring of the atmospheric deposition of elements over the RM using the moss technique.

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**Data Availability** All data, models, and code generated or used during the study appear in the submitted article.

## Declarations

**Conflict of interest** All authors declare that they have no conflict of interest.

**Consent to Publish** Not applicable.

**Ethical Approval and Consent to Participate** Not applicable.

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