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Air Pollution Study in the Republic of Moldova Using Moss Biomonitoring Technique

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Abstract Moss biomonitoring using the species *Hypnum cupressiforme* (Hedw.) and *Pleurocarpous* sp was applied to study air pollution in the Republic of Moldova. A total of 41 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Cd, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, W, Pb, Th, and U) were determined by instrumental epithermal neutron activation analysis and atomic absorption spectrometry. Principal component analysis was used to identify and characterize different pollution sources. Geographical distribution maps were prepared to point out the regions most affected by air pollution and relate this to potential sources of contamination. Median values of the elements studied were compared with data from the European moss biomonitoring program. The cities of Chisinau and Balti were determined to experience particular environmental stress.

Keywords Atomic absorption spectrometry · Contamination factor · Heavy metals · Neutron activation analysis

Environmental pollution is one of the largest problems the world faces today. Sources of elements in air can be both natural and anthropogenic, and they may include industrial processes, power plants, transportation, mining, burning of solid waste, fires, and volcanoes. Information on air pollutants can be obtained by conventional methods such as dispersion modeling (source-orientation, a priori known emission sources) or by field measurements of the emission (receptor/effect orientation). Large-scale application of these methods is limited by their cost, sensitivity, necessity for technical installations and a small number of samples that can be collected over a large area of investigation (Wolterbeek 2002; Cucu-Man et al. 2004; Cucu-Man 2006).

The moss biomonitoring technique, introduced in Scandinavian countries in the seventies (Ruhling and Tyler 1971), has proven to be suitable for studying the atmospheric deposition of heavy metals as well as other trace elements (Spiric et al. 2013). Two main factors affect the application of mosses as bioindicators of air pollution: (i) the nature of mosses (i.e., ubiquitous distribution, lack of roots, high surface to volume ratio, and high cation exchange capacity) and (ii) their use; i.e., a simple and inexpensive technique (Makholm and Mladenoff 2005; Barandovski et al. 2015). The moss biomonitoring technique is widely used in European countries (Cucu-Man et al. 2004; Harmens and Norris 2008, 2009; Spiric et al. 2013; Barandovski et al. 2015; Thinova et al. 2014).

The first attempt to apply the moss biomonitoring technique in the Republic of Moldova was made in 2001 but

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only on a limited area, mostly along the Prut River (Cucu-Man 2006). In 2015, Moldova participated for the first time in a moss survey in the framework of the International Cooperative Programme on effects of heavy metal air pollution on natural vegetation and crops in Europe (UNECE ICP Vegetation). Accordingly, the aim of the present study was: (i) to present results from the 2015 moss survey in the Republic of Moldova; (ii) to compare the obtained results with data obtained for other European countries in the latest survey (2010) and (iii) to create a database for future surveys.

Materials and Methods

The Republic of Moldova (RM), a landlocked country with an area of 33,846 km^2 is located in the north-western Balkans (45° to 49° N, 26° to 30° E). It borders with Ukraine in the north, east and south and with Romania in the west, the river Prut River constituting the border line.

The relief of Moldova is represented by hills and plains, with uplands mostly in the central part of the country. The climate is moderately continental, characterized by relatively mild winters with little snow, long warm summers, and low humidity. The mean air temperature varies between 6.3 and 12.3°C and the annual precipitation between 300 and 960 mm, respectively.

The RM has unique land resources characterized by predominant chernozem soil (~75%) with high productivity potential. From a total area of 33,846 km^2, 73.8% is agricultural land, 53.5% representing arable land, and just 13.7% is covered with woody vegetation. The rich soil and a temperate continental climate have made the country one of the most productive agricultural regions in southeast Europe since ancient times, and a major supplier of agricultural products (Salaru 2013).

As the usually preferred carpet-forming moss *Pleurozium schreberi* was found only in some parts of the country, we chose *Pleurocarpous* sp and *Hypnum cupressiforme* for this study, which in May, 2015, were collected at 33 sampling sites evenly distributed over the RM entire territory (Fig. 1). The moss sampling procedure and further preparation of the material for elemental analysis were in accordance with the CLRTAP (2015) manual for mosses sampling.

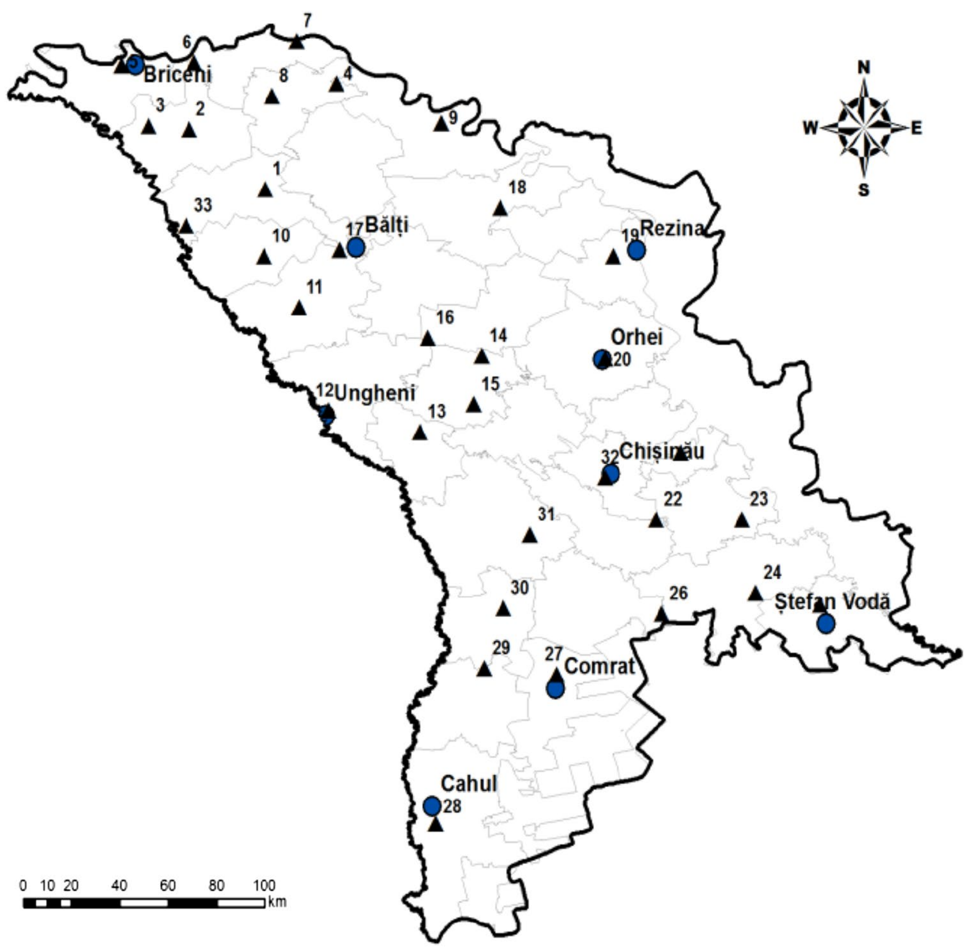

Fig. 1 Locations of sampling points

Once collected, samples were cleaned of soil particles and other contaminants. The upper 3–4 cm of green and green–brown shoots from the top of the moss, which represents the last 3 years of growth, was separated and dried at 40°C to constant weight. For neutron activation analysis (NAA) moss samples of about 0.3 g were packed in polyethylene foil bags for short-term irradiation and in aluminum cups for long-term irradiation (Culicov et al. 2016). For AAS analysis, approximately 0.3 g of moss was placed in a Teflon vessel and treated with 5 mL of concentrated nitric acid (HNO_3) and 1 mL of hydrogen peroxide (H_2O_2). The moss material was introduced in a microwave digestion system (Mars; CEM, Matthews, NC, USA) for complete digestion. Digestion was performed in two steps: (1) ramp: temperature 160°C, time 15 min, power 400 W, and pressure 20 bar; (2) hold: temperature 160°C, hold time 10 min, power 400 W, and pressure 20 bar. Digests were quantitatively transferred to 100-mL calibrated flasks and made up to the volume with bi-distilled water. All of the reagents used for this study were of analytical grade: nitric acid; trace pure (Merck, Darmstadt, DE); hydrogen peroxide, p.a. (Merck); and bi-distilled water.

Neutron activation analysis was carried out at the pulsed fast reactor IBR-2 of the Frank Laboratory of Neutron Physics, JINR, Dubna, Russia (Frontasyeva 2011, Dmitriev and Pavlov 2013). A total of 42 elements (Na, Mg, Al Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Cd, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, W, Pb, Th and U) were analyzed using both short and long time activation. More details concerning irradiation time and gamma spectra processing can be found in Culicov et al. (2016).

The amount of Cd, Cu and Pb in the moss samples was determined by means of a iCE 3300 AAS Atomic Absorption Spectrometer with electrothermal (graphite furnace) atomization (Thermo Fisher Scientific, Waltham, MA, USA). The calibration solutions were prepared from a 1 g/L stock solution (AAS standard solution; Merck, DE).

National Institute of Standard and Technology (NIST, Gaithersburg, MD, USA) certified reference materials: SRM 1633b (constituent elements in coal fly ash), SRM 2709 (San Joaquin soil) and SRM 2711 (Montana soil), and Institute for Reference Materials and Measurements (IRMM, Geel BE) standard reference material BCR-667 (estuarine sediment) were used to calibrate the NAA determinations.

In the case of AAS analyses, quality control was performed by using the NIST certified reference materials SRM 1570a (spinach leaves) and SRM 1575a (pine needles). In both cases, the experimentally measured contents were in good agreement with the recommended values. The difference between certified and measured content of elements of the certified material varied between 1% and 10%.

To evidence any association of chemical elements as well as to decrease the number of variables for the obtained data, factor analysis (FA) was used. All statistical analyses were performed using Stat-Soft(superscript "TM") Statistica 9 (StatSoft, Tulsa, OK. USA). Maps showing the geographical distribution of the factor scores were built using ArcGis software (Esri, Redlands, CA, USA).

Results and Discussion

Final results regarding the content of all 41 elements, i.e. range, median and mean are reproduced in Tables 1 and 2. For a better understanding, the content of the same elements in the reference plant (Markert 1992), and those reported by Cucu-Man (2006) for the Republic of Moldova, by Harmens et al. (2013) for Romania, and by Steinnes et al. (2011) for Norway are included for comparison. The Norway site may be regarded as a location with only minor air pollution.

The median values of V, Cr, Fe, Ni, As, Br, La, Ce, Th, U obtained in the RM were higher than in Norway, but very similar to those reported for the province of Moldavia (Romania) and for Romania as a whole. The contents of the other elements were comparable or lower than those for Romania. With respect to Norway, RM had higher median values for almost all elements, excepting Mg, Mn, and Rb, but the maximum content of Mg, Mn, Fe, Ni, Co, Zn, Cu, Rb, Cd, and Ba was significantly lower than in Norway. With respect to Romania, the maximum values of all elements were lower, most probably due a reduced industrial activity.

It is worth mentioning that the moss content of the six elements closely related to industrial activity, i.e. Ni, Zn, Cu, As, Cd, and Pb, remained almost unchanged in RM with respect to the last study (Cucu-Man 2006) (see Table 2). Only V and Cr showed increased concentrations from 4.3 to 5.5 and 3.1 to 7.2 mg/kg, respectively. But, in 2006 Cucu-Man used ICP-MS, while our data were obtained by NAA. It is well known that NAA determines the total content of elements in the samples, whereas ICP-MS (Cucu-Man 2006) data refer to the fraction soluble in nitric acid. Since the industrial sector in Moldova did not show considerable development over the past 11 years, it is highly probable that the apparent increase in Cr and V may be explained by moss contamination with mineral particles.

A further comparison with other European countries (Harmens et al. 2013) shows higher values for As, V and Sb in the RM, while the Al, Cu, and Pb content were close to the values for Romania.

Principal component analysis (factor analysis) was used to identify and characterize different pollution sources and to point out the most polluted areas. The results of factor

Table 1 Range, median, mean, and standard deviation (in mg/kg, excepting Al, Ca, K and Fe whose content is expressed in % dw) of 41 elements as determined by NAA (38 elements) and AAS (Cu, Cd and Pb)

Elem.	Range	Md	Mean ± SD	RP	Elem.	Range	Md	Mean ± SD	RP
Na	151–2110	308	454 ± 370	150	Zr	5–126	0.24	0.3 ± 23	0.1
Mg	182–905	328	340 ± 203	2000	Cd	0.2–0.95	0.39	0.4 ± 0.2	0.05
Al	0.16–1.72	0.31	0.56 ± 0.44	0.008	Sb	0.1–1.1	0.2	0.3 ± 0.2	0.1
Cl	46–373	104	129 ± 87	2000	Cs	0.15–1.4	0.3	0.5 ± 0.4	0.2
K	0.26–0.97	0.71	0.66 ± 0.19	1.9	Ba	25–137	61	68 ± 31	40
Ca	0.53–1.72	0.89	0.96 ± 0.27	1.0	La	0.9–11.7	2.1	3.4 ± 2.6	0.2
Sc	0.3–3.3	0.6	1.1 ± 0.8	0.02	Ce	1.9–27	4.4	6.8 ± 5.5	0.2
Ti	103–1300	232	410 ± 332	0.05	Nd	0.5–10.7	1.9	3.0 ± 2.6	0.2
V	2.9–29	5.5	9.6 ± 8.1	0.5	Sm	0.1–1.6	0.3	0.5 ± 0.4	0.04
Cr	2–33	7.2	10.3 ± 7.4	1.5	Eu	0.02–0.4	0.07	0.1 ± 0.1	0.008
Mn	42–401	120	132 ± 76	200	Gd	0.04–1.5	0.2	0.4 ± 0.4	0.04
Fe	0.10–0.92	0.21	0.33 ± 0.24	0.015	Tb	0.02–0.3	0.05	0.08 ± 0.07	0.008
Co	0.4–4.7	0.8	1.4 ± 1	0.2	Tm	0.01–0.1	0.03	0.03 ± 0.04	0.004
Ni	2.3–17	4.7	5.9 ± 3.9	1.5	Yb	0.06–0.9	0.2	0.3 ± 0.2	0.02
Cu	5.9–28	14.7	15.3 ± 5	10	Hf	0.17–3.3	0.47	0.7 ± 0.7	0.05
Zn	20–79	37	39 ± 13	50	Ta	0.03–0.3	0.06	0.09 ± 0.08	0.001
As	0.4–4.06	0.8	1.2 ± 0.8	0.1	W	0.1–1.1	0.2	0.4 ± 0.2	0.2
Se	0.2–0.4	0.3	0.3 ± 0.06	0.02	Pb	5.4–27	12	14 ± 5.1	1.0
Br	1.6–9	4.7	4.7 ± 1.6	4.0	Th	0.27–3.8	0.65	1.0 ± 0.9	0.005
Rb	4.3–31	9.8	12.5 ± 7.6	50	U	0.1–1.25	0.23	0.3 ± 0.2	0.001
Sr	21–125	41	48 ± 23	50					

For comparison, the contents of the same elements in reference plant, RP (Markert 1992), are presented

analysis are given in Table 3. Three factors were identified, explaining a total of 81% of the variability in the data set. Factor 1 (F1) was the strongest factor representing 53% of the total variability. Factor 2 (F2) and Factor 3 (F3) included 10% and 16% of total variance, respectively.

Factor 1 is interpreted to represent a combined geogenic/anthropogenic association of elements. The geographical distribution of Factor 1 is shown in Fig. 2a. Aluminum (Al), As, Fe, Ti, Cs, La, Th and U are typical crustal elements and their content in the mosses can be associated with mineral particles released to the atmosphere mainly by wind erosion. Mineral particles originating from the soil usually increase concentrations of these elements in areas with sparse vegetation, arid climate, or exposed mineral soil (Chakrabortty and Pratkar 2006). The dry weather with low rainfall and large areas of cropland in Moldova substantially contribute to distribution of mineral particles and subsequent accumulation by moss species. However, high values for Fe, Cr, As, V and U, around Chisinau and Balti also indicate a certain influence from anthropogenic sources. Arsenic (As) and U, which are emitted into the atmosphere mainly from coal combustion, show a higher content near Chisinau where Combined Heat Power Plant No.1 and No. 2 are located. Vanadium (V), in turn, is associated with burning of heavy fuel oil for heating and electricity production (Spiric et al. 2013), and shows a high level near the Balti Combined Heat Power Plant North.

The increased content of Fe and Cr in mosses samples collected near Chisinau and Balti most probable could be associated with industrial activity of SA Moldovahidromas near Chisinau and SA Moldagrotechnica in Balti, as well as with the other small industrial enterprises, and with coal combustion (Cucu-Man et al. 2004; Cucu-Man 2006).

The second factor, F2, which includes Cl–Se–Sr (Table 3; Fig. 2b), is most likely of terrestrial origin as it indicates an element supply to moss from soil occurring in periods when the topmost layer of soil is saturated with water during snowmelt, heavy rains, etc. According to Lucaciu et al. (2004), this transfer is facilitated by the absence of a protective litter/humus layer between moss and the mineral soil. Again, the Chisinau area seems to be more sensitive from this point of view as here the human influence on the land is significant.

Table 3, the third factor (F3) was dominated by the Pb–Sb–Zn association, a typical anthropogenic one (Fig. 2c). Lead results from industries and from the combustion of leaded gasoline (Spiric et al. 2013). Indeed, increased Pb content has been found in the densely populated and industrialized parts of RM (Chisinau, Rezina, Ungheni), while the highest values were registered in the Causani-Stefan-Voda zone. Antimony (Sb) is a toxic trace element, commonly enriched in coals and related with fossil fuel combustion. Moreover, Sb can be associated with ceramics, glasses, plastics, and synthetic fabrics production

Table 2 A comparison between the experimental values of some elements potentially related with an anthropogenic activity as obtained in the present study and literature data

Ref.	Moldova (present work)		Moldova (Cucu-Man 2006)		Romania, 2010 (Harmens et al. 2013)		Romania, 2010 (Harmens et al. 2013)		Norway (Steinnes et al. 2011)	
n	33		13		78		330		464	
Elem	Med	Range	Med	Range	Med	Range	Med	Range	Med	Range
Na	308	151–2110	–	–	350	127–5880	510	102–6150	123	11–864
Mg	328	182–905	–	–	372	86–3980	461	51–3980	1335	502–3128
Al	0.31	0.16–1.72	–	–	0.23	0.03–2.7	0.33	0.02–3.44	0.03	0.005–0.46
Cl	104	46–373			342	72–2070	263	17–2860	–	–
K	0.71	0.26–1.16	–		0.84	0.52–1.54	0.88	0.35–2.57	0.39	0.18–0.87
Ca	0.99	0.53–1.70	–	–	0.87	0.26–0.78	0.75	0.09–4.07	0.28	0.09–0.85
Sc	0.6	0.3–3.3	–	–	0.4	0.05–5.3	0.6	0.05–11	–	–
Ti	232	103–1300	–	–	238	29–1840	307	19–3490	25	4–260
V	5.5	2.9–29	4.3	6.4–29	3.8	0.4–42	4.6	0.4–49	1.4	0.3–25
Cr	7.2	2.0–33	3.1	1.1–18	4.3	0.7–35	5	0.7–62.2	0.6	0.2–49
Mn	120	42–401	–	–	240	39–699	202	15–1000	292	19–2653
Fe	0.21	0.10–0.92	–	–	0.14	0.03–1.43	0.17	0.03–2.95	0.03	0.003–2.47
Co	0.8	0.4–4.7	–	–	0.6	0.1–7.4	0.8	0.1–13	0.2	0.03–39
Ni	4.7	2.3–17	2.9	2.0–16	2.9	0.8–17.8	3.1	0.4–36	1.2	0.15–856
Cu	15	5.9–28	10.7	8.0–25	15	4.2–161	18	0.2–627	4	1.4–443
Zn	37	20–79	38	20–141	33	4.6–80	42	0.6–1440	31	7.4–368
As	0.8	0.4–4.1	0.9	0.6–2.4	0.6	0.15–6.7	0.7	0.1–51	0.01	0.02–4.8
Rb	10	4.3–31	–	–	9.1	2.5–57	13	2.5–84	13	1.3–72
Sr	41	20–125	–		28	7.7–102	33	6.6–128	15	1.9–72
Cd	0.39	0.2–0.95	0.3	0.2–0.9	0.6	0.3–2.3	1.2	0.13–24	0.08	0.009–1.9
Sb	0.2	0.1–1.1	–	–	0.16	0.04–0.5	0.2	0.01–16	0.06	< 0.001–1.1
Cs	0.3	0.15–1.6	–	–	0.25	0.05–4.4	0.3	0.01–16	0.15	0.01–1.7
Ba	61	25–137	–	–	63	14–334	72	12–488	25	4–325
La	2.2	0.9–11.7	–	–	1.5	0.2–14	1.9	0.2–70	0.3	0.043–5.6
Ce	4.4	1.9–27	–	–	2.5	0.3–25	3.4	0.3–141	0.6	0.09–9.5
W	0.2	0.1–1.1	–	–	0.12	0.04–0.7	0.17	0.003–1.7	0.2	< 0.003–4.9
Pb	12	5.4–27	10.8	5.3–30	21	2–55	31	2.2–120	1.5	0.33–21
Th	0.65	0.27–3.8	–	–	0.4	0.06–4.9	0.5	0.05–21	0.1	< 0.02–1
U	0.23	0.1–1.25	–	–	0.12	0.01–1.1	0.15	0.01–6.7	0.02	< 0.001–0.37

In an absence of confident data regarding a normal distribution, we have used instead of the mean value the average value. For a better comparison, only the elements reported in literature are presented

All contents expressed in mg/kg excepting Al, K, Ca and Fe whose content is expressed in % dw

Table 3 Matrix of the first three factors loading

Elem.	F1	F2	F3	Elem.	F1	F2	F3	Elem.	F1	F2	F3
Na	**0.76**	0.25	0.52	Cr	**0.92**	0.13	0.34	Sr	0.1	**0.71**	0.39
Mg	**0.93**	0.11	0.08	Fe	**0.95**	0.1	0.25	Cd	−0.25	−0.27	0.48
Al	**0.96**	−0.07	0.08	Co	**0.88**	0.21	0.40	Sb	0.55	0.13	**0.62**
Cl	−0.14	**0.79**	−0.06	Ni	**0.86**	0.08	0.46	Cs	**0.96**	0.09	0.20
K	0.48	0.32	−0.14	Cu	0.54	0.25	0.36	La	**0.90**	0.16	0.32
Ca	0.48	0.44	0.59	Zn	0.27	0.14	**0.77**	Pb	0.26	−0.13	**0.69**
Ti	**0.97**	−0.05	0.03	As	**0.86**	0.14	0.42	Th	**0.9**	0.18	0.36
V	**0.95**	−0.09	−0.02	Se	−0.14	**−0.68**	0.07	U	**0.82**	0.24	0.45

Boldface numbers indicate significant ($p < 0.05$) loading factors

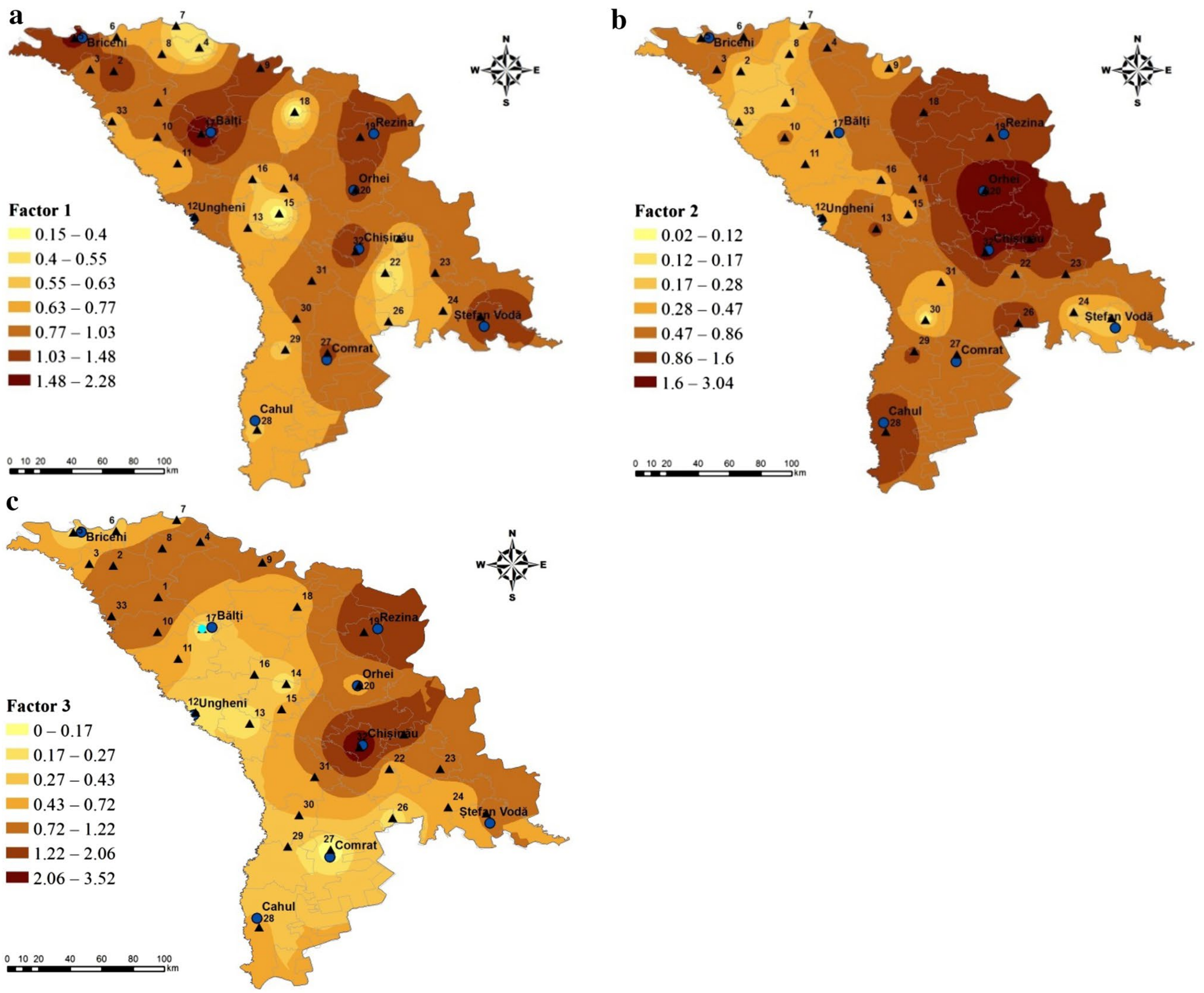

Fig. 2 Spatial distribution of Factor 1 (**a**), 2 (**b**) and 3 (**c**)

(Shotyk et al. 2005). Indeed, the highest Sb values were determined in Chisinau and Balti while the highest levels of Zn were in the vicinity of Rezina due to the influence of metallurgical industry located in Ribnita (samples were not collected in Transnistria).

To quantify the anthropogenic influence on the environment, diverse descriptors such as contamination factor C_F, the geo-accumulation index I_{geo} (Müller 1969), or pollution load index (PLI) (Tomlinson et al. 1980) were proposed during the past decades. In fact, all these indices, starting from the local values of the contamination factor C_F proposed different criteria to assay the human influence.

For instance, the geo-accumulation index I_{geo} for a given element depends on the contamination factor $C_F = {}^{c_M}/_{c_b}$ following the relation: $I_{geo} = \log_2\left({}^{C_F}/_{1.5}\right)$ where c_M is the content of the considered element in moss and c_b is the background or pristine value of the element (Gongalves et al. 1992). Depending upon their calculated values for a given element, both indices allow for a classification of an environment into several classes ranging from pristine, uncontaminated ones to heavily polluted ones.

While both I_{geo} and C_F regard individual elements, the PLI offers a more global characterization as it represents the n order geometric mean of an entire set of C_F regarding the contaminating elements as follows: $PLI = \sqrt[n]{\prod_{i=1}^{n} C_{F,i}}$, where n equals the total number of contaminating elements.

The PLI can also be defined for a reduced number of elements, but in our case, to get a more complete characterization of the environmental status we have taken into account all 9 elements related to industrial activity. All three indices were calculated for the entire RM, as well as

Table 4 Average values of the contamination factor C_F, geo-accumulation index I_{geo} as well as pollution load index (PLI) for the entire Republic of Moldova and the municipalities of Chisinau and Balti

Element	Moldova		Chisinau		Balti		Element	Moldova		Chisinau		Balti	
	C_F	I_{geo}	C_F	I_{geo}	C_F	I_{geo}		C_F	I_{geo}	C_F	I_{geo}	C_F	I_{geo}
Al	1.5	0.58	5.1	2.35	7.2	2.85	Zn	1.2	0.26	2	1.00	1.6	0.68
V	1.2	0.26	4.1	2.04	8.6	3.1	Sb	1	0.00	4.7	2.23	3.5	1.81
Cr	1.7	0.77	7.6	2.92	5.8	2.54	Pb	2	1.00	1.9	0.93	1.1	0.14
Fe	1.6	0.68	6.7	2.74	6.5	2.70	U	1.7	0.77	12.5	3.64	1.5	0.58
As	1.3	0.34	6.7	2.74	2.7	1.43	PLI	1.44		4.89		3.38	

for Chisinau and Balti (Table 4). According to the scales proposed by Fernández and Carballeira (2001) ($C_F < 1$ no contamination; 1–2 suspected; 2–3.5 slight; 3.5–8 moderate; 8–27 severe, and >27 extreme) and Müller (1969) (I_{geo} <0 no contamination; 0–1 slightly polluted; 1–2 moderately polluted; 2–3 moderately to severely polluted; 3–4; severely polluted; 4–5 severely extremely polluted, and I_{geo} >5 extremely polluted), both indices point toward moderate or moderate to severely polluted classifications for the entire country, with higher values for U in Chisinau. NAA determination of the U content in 17 soil samples collected from Romanesti and Cricova (Eastern Moldova) showed an average U content of 2.35 ± 0.49 mg/kg, similar to values reported for the upper continental crust (Rudnick and Gao 2003). In our study, the local increased U content in the vicinity of Chisinau could be due not only to the U existing in soil, but also to U being released into the atmosphere by power plants. The PLI classification similarly indicated moderate to severe pollution, especially in Chisinau where the main contribution comes from U (Table 4).

The concentrations of 41 elements were determined in 33 moss samples using NAA and AAS. Statistical analysis was performed on the obtained data resulting in three significant factors. The first factor appeared to represent a mixed geogenic–anthropogenic association of elements, the second factor was most likely of vegetation origin, and the third was most likely of anthropogenic origin. The main sources of pollution were considered to be thermoelectric plants (V, U, Sb, As), transport (Pb) and industry (Fe, Cr, Zn). Three different indices used to quantify the degree of contamination indicated moderate to severe industrial pollution that was localized around major urban and industrial centres—the municipalities of Chisinau and Balti. At the same time, our results showed little difference with respect to the previous moss biomonitoring study of 2006.

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References

Barandovski L, Frontasyeva MV, Stafilov T et al (2015) Multi-element atmospheric deposition in Macedonia studied by the moss biomonitoring technique. Environ Sci Pollut Res 22:16077–16097

Chakrabortty S, Paratkar GT (2006) Biomonitoring of trace element air pollution using mosses. Aerosol Air Qual Res 6:247–258

CLRTAP (2015) Manual on methodologies and criteria for modelling and mapping critical loads and levels and air pollution effects, risks and trends. UNECE Convention on Long-range Transboundary Air Pollution. http://icpvegetation.ceh.ac.uk. Accessed 26 June 2016

Cucu-Man SM (2006) Study of atmospheric deposition of heavy metals in Moldova using biomonitors. PhD Thesis, Alexandru Ioan Cuza University, Iassy (**in Romanian**).

Cucu-Man S, Mocanu R, Culicov O et al (2004) Atmospheric deposition of metals in Romania studied by biomonitoring using the epiphytic moss *Hypnum cupressiforme*. Int J Environ Anal Chem 84:845–854

Culicov OA, Duliu OG, Zinicovscaia I (2016) Active *Sphagnum girgensohnii* Russow moss biomonitoring of an industrial site in Romania: temporal variation in the elemental content. Bull Environ Contam Toxicol 96:650–656

Dmitriev AYu, Pavlov SS (2013) Automatization of quantitative determination of element concentrations in samples by neutron activation analysis at the reactor IBR-2 FLNP JINR. Phys Part Nucl 10:58–64.

Fernández JA, Carballeira A (2001) Evaluation of contamination, by different elements, in terrestrial mosses. Arch Environ Contam Toxicol 40:461–468

Frontasyeva MV (2011) Neutron activation analysis for the life sciences. A review. Phys Part Nucl 42:332–378

Gongalves EPR, Boaventura RAR, Mouvet C (1992) Sediments and aquatic mosses as pollution indicators for heavy metals in the Ave River basin (Portugal). Sci Total Environ 114:7–24

Harmens H, Norris D et al (2008) Spatial and temporal trends in heavy metal accumulation in mosses in Europe (1990–2005), Centre for Ecology & Hydrology, Bangor, UK. http://nora.nerc.ac.uk/8672/2/HarmensN008672CP.pdf. Accessed 26 June 2016

Harmens H, Mills G, Hayes F et al (2009) Air pollution and vegetation: ICP Vegetation annual report 2008/2009NERC/Centre for Ecology & Hydrology, Bangor, UK. http://www.unfccc.int/resource/docs/natc/mdanc3.pdf. Accessed 26 June 2016

Harmens H, Norris D, Mills G (2013) Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and long-term temporal trends in Europe. Bangor, UK, NERC/Centre for Ecology & Hydrology. http://nora.nerc.ac.uk/502676/1/N502676CR.pdf. Accessed 26 June 2016

Lucaciu A, Timofte L, Culicov O et al (2004) Atmospheric deposition of trace elements in Romania studied by the moss biomonitoring technique. J Atmos Chem 49:533–548

Makholm MM, Mladenoff DJ (2005) Efficacy of a biomonitoring (moss bag) technique for determining element deposition trends on a mid-range (375 km) scale. Environ Monit Assess 104:1–18

Markert B (1992) Establishing of ‘Reference characterization plant’ for inorganic of different chemical plant species by finger printing. Water Air Soil Pollut 64:533–538

Müller G (1969) Index of geoaccumulation in sediments of the Rhine River. Geol J 2:109–118

Rudnick RL, Gao S (2003) Composition of the continental crust. In: Turekian HDHK (ed) Treatise on geochemistry. Elsevier, Oxford, pp 1–64

Ruhling A, Tyler G (1971) Regional differences in the deposition of heavy metals over Scandinavia. J Appl Ecol 8:497–507

Shotyk W, Krachler M, Chen B (2005) Anthropogenic impacts on the biogeochemistry and cycling of antimony. Met Ions Biol Syst 44:171–203

Spiric Z, Vuckovic I, Stafilov T, Kusan V, Frontasyeva M (2013) Air pollution study in Croatia using moss biomonitoring and ICP–AES and AAS analytical techniques. Arch Environ Contam Toxicol 65:33–46

Steinnes E, Berg T, Uggerud HT et al (2011) Atmostærisk nedfall av 1095 tungmetaller i Norge Landsomfattende undersøkelse i 2010. Stallig program for forurensningsovervåking, Rappotur 1109/2011, 1096 (**in Norwegian**)

Thinova L, Frontasyeva M, Vergel K et al (2014) Assessment of contamination with trace elements and man-made radionuclides around Temelin Nuclear Power Plant in Czech Republic. Rad Phys Chem 104:432–435

Tomlinson DL, Wilson JG, Harris CR et al (1980) Problems in the assessment of heavy-metals in the estuaries and the formation of the pollution index. Helg Mar Res 33:566–575

Wolterbeek HTh (2002) Biomonitoring of trace element air pollution: principles, possibilities and perspectives. Environ Pollut 120:11–21

Salaru G (2013) Third National Communication of the Republic of Moldova under the United Nations Framework Convention on Climate Change, Ministry of Environment of the Republic of Moldova, Chisinau. http://www.unfccc.int/resource/docs/natc/mdanc3.pdf. Accessed 27 June 2016