Characterization of Heavy Metals Atmospheric Deposition for Assessment of Environmental Quality in Urban and Surrounding Areas

CLAUDIA STIHI[1,2]*, CRISTIANA RADULESCU[1,2]*, IOANA DANIELA DULAMA[2]*, OANA CATALINA BUTE[1,2], IOAN ALIN BUCURICA[2]

[1]Valahia University of Targoviste, Faculty of Sciences and Arts, 2 King Carol I Blvd., 130024, Targoviste, Romania

[2]Valahia University of Targoviste, Institute of Multidisciplinary Research for Science and Technology, 13 Sinaia Alley, 130004 Targoviste, Romania

The atmospheric deposition of Cu, Cd and Pb in urban and surrounding areas was investigated by using mosses as bioindicators. A total of 92 moss samples were collected from central and south-west parts of Romania. The content of Cu, Cd and Pb was determined by graphite furnace/flame atomic absorption spectrometry. Median values for Cu (8.217 mg/kg dw), Cd (1.299 mg/kg dw) and Pb (29.844 mg/kg dw) are high compared to other European countries. The evaluation of the sampling sites contamination was made using the contamination factor. Sites with a severe contamination with Cd and Pb were identified.

Keywords: heavy metals, moss, GFAAS/FAAS, contamination factor

The atmospheric deposition of heavy metals is receiving more attention by the scientists all over the world. The increase of heavy metal concentrations in the environment can affect the human health. The dust and particulate matter containing heavy metals [1,2] can get into the human body through breathing and can lead to various diseases [3, 4]. The mosses are recommended as good bioindicators of metal pollution in the atmosphere [5] because of the accumulation of heavy metals directly from precipitation and dry deposition, the uptake of metals from the substrate being insignificant.

Many studies were performed to assess the atmospheric deposition of heavy metals by moss biomonitoring technique together with different analytical methods [6-8].

In this study we investigated the atmospheric deposition of three toxic heavy metals, Cu, Cd and Pb using mosses collected from urban and surrounding areas in the central and south-west parts of Romania. The concentrations of the analyzed heavy metals were determined using the graphite furnace/flame atomic absorption spectrometry (GFAAS/FAAS). The pollution level of the sampling sites was evaluate using the contamination factor (CF) [9, 10].

Experimental part

Sampling was performed in a relatively dry season in July-September 2010 in 92 sampling sites. Sampling sites were not evenly distributed due to geographical positions. The moss samples were collected at least 300 m from the main roads, populated areas and industries and at least 100 m from the small roads and houses [11]. Two moss species were used, *Pleurozium schreberi* and *Hylocomium splendens,* moss species which are the most frequently sampled species at European level for heavy metal air pollution biomonitoring [11, 12]. For each sampling site were recorded the longitude and latitude using the global position system (GPS). The distribution of the sampling sites is shown in figure1.

After the sampling all the moss samples were cleaned, to remove foreign matter, dried to constant weight at 40°C for 48h and milled to a fine powder. For GFAAS/FAAS analysis around 0.4g of dried moss powder were digested

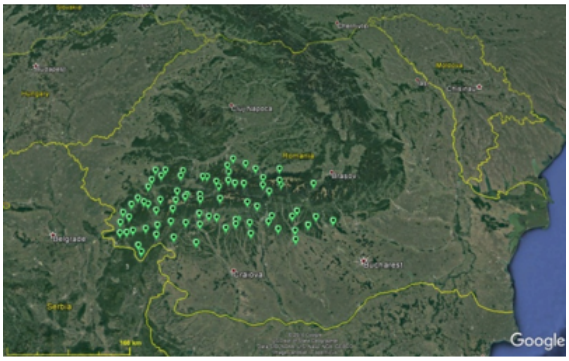

Fig. 1. The distribution of the sampling sites

in the Teflon digestion vessels by adding 7 mL HNO_3 (65%, m/V) and 2 mL H_2O_2 (30%, m/V) and using a Speedwave MWS-2 Berghof microwave digestion system. After cooling the digested solutions were filtered and transferred into 25 mL calibrated flasks. The contents of Cu, Cd and Pb were determined using a GFAAS/FAAS Avanta GBC spectrometer.

A standard reference material SRM 1571 - orchard leaves (National Institute of Standards and Technology-NIST production) was used to provide the quality control of AAS measurements. The standard reference material was prepared using the same sample preparation procedure and AAS measurements were performed using the same instrumental parameters. The measured concentrations of Cu, Cd and Pb were within the recommended values and the recovery of the elements ranged between 95.8 and 104.2%.

Results and discussions

The results of the descriptive statistics analysis of Cu, Cd and Pb concentrations in mosses collected from the central and south-west parts in Romania are presented in the table 1. The order of the elements in analyzed moss samples, according with their abundance was Cd<Pb<Cu. The coefficient of variation (CV) for Cd (46.882%) indicates a moderate variation in concentration of that metal. A weak variability (CV<25%) exists in the concentration Cu and Pb.

* *emails: claudia.stihi@valahia.ro; cristiana.radulescu@valahia.ro; dulama_id@yahoo.com*

Element	Minimum	Maximum	Mean	Median	St.Dev.	CV(%)
Cu	0.231	29.360	9.036	8.217	0.823	6.805
Cd	0.207	7.977	1.755	1.299	0.615	46.882
Pb	9.983	57.894	30.118	29.844	4.168	13.965

Table 1
THE DESCRIPTIVE STATISTICS OF Cu, Cd AND Pb IN MOSSES (N=92) (mg/kg d.w)

Element	Median			
	Romania	Bulgaria [10]	Albania [10]	Macedonia [10]
Cu	8.217	7.01	3.96	3.54
Cd	1.299	0.21	0.11	0.22
Pb	29.844	8.0	2.42	4.61

Table 2
THE COMPARISON OF MEDIAN VALUES OF Cu, Cd AND Pb CONCENTRATIONS (mg/kg d.w.) IN MOSSES FROM ROMANIA, BULGARIA, ALBANIA AND MACEDONIA

The obtained median values of the Cu, Cd and Pb concentrations in mosses samples collected in the frame of this work were compared with those of other Balkan countries which reported results of elemental content of the same moss species, like Bulgaria, Albania and Macedonia [12]. For all analyzed elements a higher median values were obtained in this work (table 2).

By using as background concentrations the median values for Cu, Cd and Pb concentrations in mosses collected from Norway in the frame of the international programme UNECE ICP Vegetation programme – 2010/2011 moss surveys [12], we determine the contamination factor (CF) [9] as the ratio of the concentration of each element in the study areas, with values of background concentrations.

Using the scale of contamination [9] the sampling sites were classified in uncontaminated sites (CF<1), suspected contamination sites (1<CF<2), slight contamination sites (2<CF<3.5), moderate contamination sites (3.5<CF<8) and severe contamination sites (8<CF<27).

The maps of the spatial distribution of CF calculated Cu, Cd and Pb are presented in figures 2-3. For Cu only few moderate contamination sites were found (fig. 2). One site with a severe contamination with Cd was found (fig. 3). Concerning the contamination with Pb many sites were found with a severe contamination (fig.4). It should be noted that the sites with a severe contamination were situated almost of a mining industry areas (Uricani, Petrosani), agricultural sites (Bogati, Albota) or close to the urban waste incinerations stations.

Fig. 2. The map of spatial distribution of contamination factor (CF) calculated for Cu

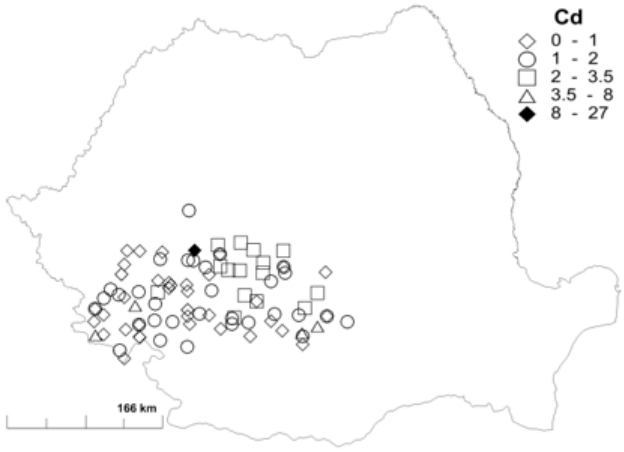

Fig. 3. The map of spatial distribution of contamination factor (CF) calculated for Cd

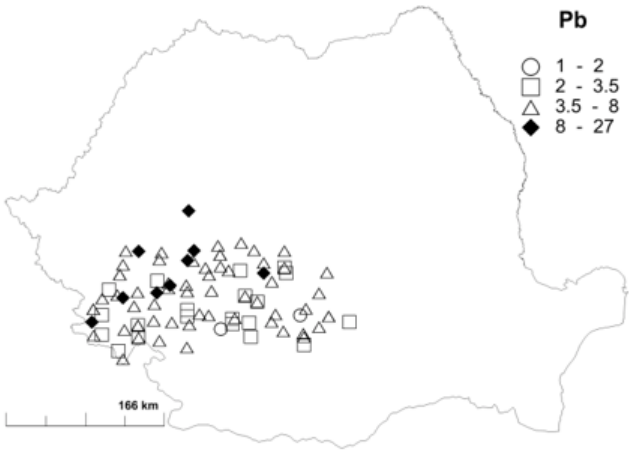

Fig. 4. The map of spatial distribution of contamination factor (CF) calculated for Pb

Conclusions

This study was conducted to assess the atmospheric deposition of Cu, Cd and Pb in areas from the central and south-west parts of Romania, using mosses as bioindicators.

The obtained results leaded reveal sites with a moderate contamination with Cu, and severe contamination with Cd and Pb. Certain local emitters were identified, like mining industry, agricultural activities and waste incineration stations. This study may serve for a future national human health risk assessments.

Acknowledgement: The research leading to these results has received funding from the research project Nuclear and related analytical techniques for Environmental and Life Sciences, based on 3869-4-08/ 10 and 4080-4-11/13 scientific protocols between Valahia University of Targoviste (UVT), Romania and Joint Institute for Nuclear Research (JINR), Dubna, Russia. We thank to all the collaborators who helped us at the sampling campaign.

References

1.RADULESCU, C., IORDACHE, S., DUNEA, D., STIHI, C., DULAMA, I., Romanian Journal of Physics, **60**, no. 7-8, 2015, p. 1171
2.DUNEA, D., IORDACHE, S., RADULESCU, C., POHOATA, A., DULAMA. I., Romanian Journal of Physics , **61**, no. 7-8, 2016, p. 1354
3.VENNERS, S.A., WANG, B., PENG, Z., XU, Y., WANG, L., XU, X. , Environmental Health Perspective, **111**, 2003, p. 562
4.DUNEA, D., IORDACHE S., LIU H.Y., BOHLER T., POHOATA A., RADULESCU C., Environmental Science and Pollution Research, **23**, no. 15, 2016, p. 15395
5.RÜHLING, A., TYLER, G., Water Air and Soil Pollution, **2**, no. 4, 1973, p. 445
6.QARRI, F., LAZO, P., STAFILOV, T., FRONTASYEVA, M., HARMENS, H., BEKTESHI, L., BACEVA, K., GORYAINOVA, Z., Science Pollution Research, **21**, 2013, p. 2506
7.HARMENS, H., NORRIS, D.A., SHARPS, (...), ZECHMEISTER, H.G., Environmental Pollution, **200**, 2015, p. 93
8.FERNANDEZ, J. A., CARBALLEIRA, A., Chemosphere, 46, 2002, p. 535
9.FERNANDEZ, J.A., CARBALLEIRA, A., Archives of Environmental Contamination and Toxicology, **40**, 2001, p. 461
10.QARRI, F., LAZO, P., BEKTESHI, L., STAFILOV, T., FRONTASYEVA, M., HARMENS, H., Environmental Science and Pollution Research, **22**, no. 3, 2015, p. 2258
11.HARMENS, H. et al, Heavy metals in European mosses: 2010 survey monitoring manual, ICP Vegetation Programme Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK, 2010
12.HARMENS, H, NORRIS, D., MILLS, G., et al, Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and long-term temporal trends in Europe, ICP Vegetation Programme Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK, 2013

Manuscript received: 10.01.2017