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ATOMIC AND NUCLEAR METHODS APPLIED IN THE STUDY OF HEAVY METAL POLLUTION

I. V. POPESCU[1,6,8,9], M. Frontasyeva[2], C. Stihi[1,6], A. Ene[3], S. Cucu-Man[4], R. Todoran[5], O. Culicov[2], I. Zinicovscaia[2], My Trinh[2], S.S. Pavlov[2], C. Radulescu[1,6], A. Chilian[6,7], A. Gheboianu[6], R. Bancuta[7], Gh. Cimpoca[1,6,9], I. Bancuta[6], I.D. Dulama[6], L.G. Toma[6], A. Bucurica[6], G. Dima[1,6], R. Drasovean[3], A. Sion[3], S. Condurache-Bota[3], R. Buhaceanu[4], D. Tarcau[4], D. Todoran[5]

Abstract. *The aim of this study was to assess the air quality in Romania using terrestrial moss, to reveal highly polluted critical regions in the country in order to permanently survey the degree of atmospheric pollution and to contribute to the European moss survey 2010/11 conducted under the auspices of the UNECE ICP Vegetation covering some "white areas" in the map of atmospheric deposition of heavy metals in Europe. Within the bilateral project JINR- Romania, "Nuclear and related analytical techniques for Environmental and Life Sciences", moss samples were collected during the summer/autumn of 2010 at 303 sites in Romania: in the Carpathian Mountains, Transylvanian plateau, and Moldavia province, following internationally accepted guidelines. Nuclear analytical technique Neutron Activation Analysis (NAA, JINR-Dubna, Rusia) and Atomic Absorption Spectroscopy (AAS-Valahia University of Targoviste, Romania) were used to determine the concentration of minor and trace elements in moss samples collected in 2010 from Romania. The results for mean, median and geometric mean are compared with those previously obtained in 1990, 1995 and 2000 campaigns and the maps of the distribution of heavy metals were realized. 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, Mo, Ag, Cd, In, Sb, I, Cs, Ba, La, Ce, Sm, Eu, Tb, Hf, Ta, W, Au, Hg, Pb, Th, and U) were determined by NAA (JINR-Dubna) of which three of them (Cu, Cd, Pb) were determined by AAS (Valahia University of Targoviste) Romania [1]. Pearson correlation coefficients (r) were calculated.*

Keywords: air quality, terrestrial moss

[1]Valahia University of Targoviste, Faculty of Sciences and Arts, Sciences Department, 2 Carol I St., 130024, Targoviste, Romania.
[2]Joint Institute for Nuclear Research, Frank Laboratory of Neutron Physics, 141980 Dubna, Moscow Region, Russia.
[3]Dunarea de Jos University of Galati, Department of Chemistry, Physics and Environment, Faculty of Sciences and Environment, 111 Domneasca St., 800201 Galati, Romania.
[4]Alexandru Ioan Cuza University, Faculty of Chemistry, 11 Carol I St., 700506, Iasi, Romania.
[5]Technical University of Cluj-Napoca, North University Center, 62A Victor Babes St., 430083, Baia Mare, Romania.
[6]Valahia University of Targoviste, Multidisciplinary Research Institute for Sciences and Technologies, 13 Sinaia St., 130004, Targoviste, Romania.
[7]Valahia University of Targoviste, Doctoral School on Engineering Sciences, 35 Lt. Stancu Ion St., 130105, Targoviste, Romania.
[8]"Horia Hulubei" National Institute for Physics and Nuclear Engineering, 30 Reactorului St., P.O.BOX MG-6, Bucharest-Magurele, Romania.
[9]Academy of Romanian Scientists, Romania.

1. Introduction

The heavy metals in mosses biomonitoring network was originally established as a Swedish initiative. The idea of using mosses to measure atmospheric heavy metal deposition is based on the fact that carpet forming, ectohydric mosses obtain most trace elements and nutrients directly from precipitation and dry deposition; there is little uptake of metals from the substrate. The technique of moss analysis provides a time-integrated measure of heavy metal deposition from the atmosphere to terrestrial systems. It is easier and cheaper than conventional precipitation analysis as it avoids the need for deploying large numbers of precipitation collectors with an associated long-term programme of routine sample collection and analysis. In recent decades, mosses have been applied successfully as biomonitors of heavy metal deposition across Europe. Heavy metal concentrations in mosses provide a complementary, time-integrated measure of the spatial patterns and temporal trends of heavy metal deposition from the atmosphere to terrestrial systems, at least for the metals cadmium and lead.

2. Sources and effects of heavy metals

Heavy metals are emitted mainly as a result of various combustion processes and industrial activities like metals works and smelters. The contribution of various sources to emissions of heavy metals across Europe has changed in recent decades. The most important emission sectors include:

- Metals industry (Al, As, Cd, Cr, Cu, Fe, Pb, Zn);
- Other manufacturing industries and construction (As, Cd, Cr, Hg, Ni, Pb);
- Electricity and heat production (Cd, Hg, Ni);
- Road transportation (Cu and Sb from brake wear, Pb, V, Zn from tires);
- Petroleum refining (Ni, V);
- Phosphate fertilisers in agricultural areas (Cd).

As well as polluting the air, heavy metals are deposited on terrestrial or water surfaces and subsequently build up in soils or sediments. Heavy metals are persistent in the environment and may bioaccumulate in food chains. Atmospheric deposition of metals has a direct effect on the contamination of crops used for animal and human consumption. In particular, leafy vegetables and fodder crops can accumulate heavy metals. Washing leafy vegetables before consumption reduces the risk of exposure by humans considerably.

3. Experimental

Within the bilateral project JINR-Romania, “Nuclear and related analytical techniques for Environmental and Life Sciences”, moss samples were collected during the summer/autumn of 2010 at 303 sites in Romania: in the Carpathian Mountains, Transylvanian plateau, and Moldavia province, following internationally accepted guidelines. Nuclear analytical technique Neutron

Activation Analysis (NAA) –IUCN Dubna and Atomic Absorption Spectroscopy (AAS)-Valahia University of Targoviste were used to determine the concentration of minor and trace elements in moss samples collected in 2010 from Romania.

Moss species: As in previous surveys, the carpet-forming mosses *Pleurozium schreberi* and *Hylocomium splendens* were the preferred species for analysis. Where necessary, other species were collected, *Hypnum cupressiforme* and *Pseudoscleropodium purum* being the next choice. Because the mosses were collected in a range of habitats and climatic conditions, it was necessary to collect a range of moss species. *Pleurozium schreberi* - was the most frequently sampled species, accounting for ca. 42% of the samples, followed by *Hylocomium splendens* or *Hypnum cupressiforme*, and *Pseudoscleropodium purum*.

4. Results

Table 1. Pearson correlation coefficients most element pairs.

	Al	As	Cd	Cr	Cu	Fe	Ni	Pb	Sb	V	Zn
Al	1.000										
As	0.318	1.000									
Cd	0.158	0.043	1.000								
Cr	0.821	0.350	0.200	1.000							
Cu	0.159	0.083	0.272	0.176	1.000						
Fe	0.826	0.387	0.148	0.901	0.125	1.000					
Ni	0.754	0.265	0.172	0.880	0.096	0.921	1.000				
Pb	0.137	0.228	0.291	0.221	0.210	0.204	0.199	1.000			
Sb	0.203	0.648	0.101	0.241	0.090	0.206	0.142	0.183	1.000		
V	0.977	0.309	0.148	0.820	0.157	0.840	0.761	0.142	0.189	1.000	
Zn	0.187	0.371	0.110	0.324	0.016	0.207	0.207	0.199	0.759	0.151	1.000

There are a strong correlation between Fe and Cr (r=0.901), Ni and Fe (r=921) and V and Al (0.977).

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, Mo, Ag, Cd, In, Sb, I, Cs, Ba, La, Ce, Sm, Eu, Tb, Hf, Ta, W, Au, Hg, Pb, Th, and U) were determined by epithermal instrumental neutron activation analysis at the pulsed fast reactor IBR-2, FLNP, JINR, complemented by AAS for Cd, Cu and Pb in the Valahia University of Targoviste, Romania. Pearson correlation coefficients (r) [2,3], which is a measure of the linear correlation (dependence) between two variables X and Y, giving a value between +1 and −1 inclusive, where 1 is total positive correlation, 0 is no correlation, and −1 is total negative correlation, it is widely used in the sciences as a measure of the degree of linear dependence between two variables, and which is shown in Table 1 indicate very high positive correlation between the elements V-Al, Fe-Cr and Fe-Ni, high correlation between Al-Cr, Al-Fe, Al-Ni, Cr-Ni, V-Cr, V-Fe, V-Ni and Zn-Sb, and moderate correlation for Sb-As. We hypothesize that the metals which present moderate to strong correlation have common origin. Significant correlations are found for most element pairs; exception is made for Zn-Cd, Zn-Cu, Sb-Cu. As-Cu, As-Cd, Ni-Cu and Sb-Cd (Table 1). Correlation matrix for elemental concentration values in the investigated moss samples collected in Romania in the June-October 2010 campaign, are given in the table 1.

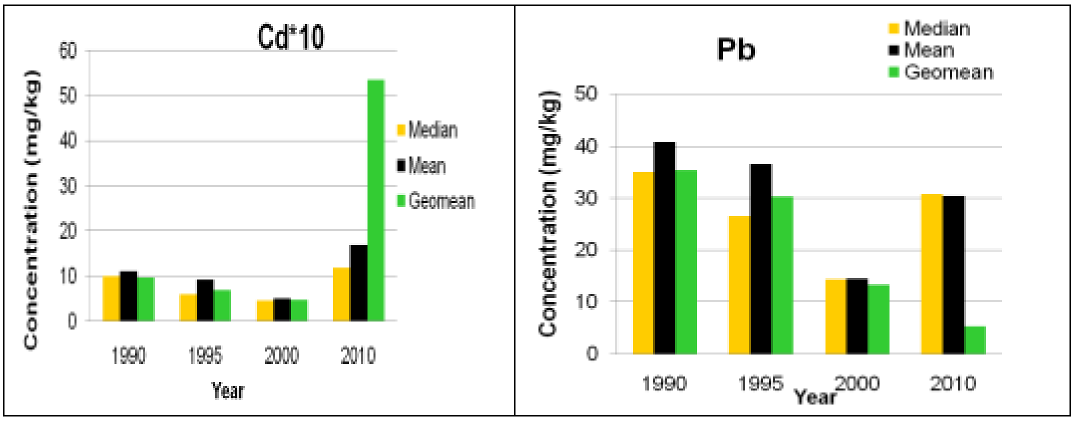

Fig. 1. Comparison of mean and median elemental concentration values (Cd, Pb) in mosses for different campaigns, in Romania.

High lead concentrations (determined by AAS in 2010) in mosses were reported in Romania, where the use of leaded petrol was banned completely only since January 2012. More, the presence of industrial areas, for instance metallurgical works or melting plants, located in Baia Mare, Magoaja, Letca, Cergau or Zagra and Copsa Mica, contributed to the high values of concentration of lead in mosses [4].

5. Conclusions

Moss biomonitoring provides a cheap, complementary method to deposition analysis for the identification of areas at risk from high atmospheric deposition fluxes of heavy metals and for monitoring changes with time.

For the priority metals cadmium and lead and the decline in average median concentrations in mosses across Europe is in agreement with that reported for modelled atmospheric deposition [1].

Despite the general European decline in concentrations in mosses between 2005 and 2010 (and also since 1990), in Romania there has been a growing trend of lead concentration in moss used as bioindicator in certain geographical areas.

Our study highlights the problems of air pollution in areas with intense economic activities under analysis.

R E F E R E N C E S

[1] http:icpvegetation.ceh.ac.uk/*heavy metals and nitrogen in mosses,* European survey **2010/11**.

[2] Galton, F. (**1886**) *Regression towards mediocrity in hereditary stature*, Journal of the Anthropological Institute of Great Britain and Ireland, 15: 246–263.

[3] Karl Pearson (June 20, **1895**) *Notes on regression and inheritance in the case of two parents,* Proceedings of the Royal Society of London, 58: 240–242

[4] Lucaciu, A., Moțoc, C., Jelea, M., Jelea, S.G. (**2010**). *Survey of heavy metal deposition in Romania: Transylvanian Plateau and western Carpathians Mountains,* University Politehnica of Bucharest Scientific Bulletin, Series A, 72: 171-178