SURVEY OF HEAVY METAL DEPOSITION IN ROMANIA: TRANSYLVANIAN PLATEAU AND WESTERN CARPATHIANS MOUNTAINS

Adriana LUCACIU[1], Cornelia MOȚOC[2], Marian JELEA[3], Stela Gabriela JELEA[4]

Acest studiu este similar unui procedeu anterior privind determinarea depunerilor atmosferice de metale grele, inițiată pentru prima data în România, în 1995. În acest articol se prezintă rezultatele obținute în urma colectării în 1999 si 2007 (în timpul verii) a 64 probe de muşchi din locațiile cele mai poluate ale unor regiuni din România. Scopul acestui studiu constă în a obține hărți de depunere atmosferică ale elementelor trasoare de metale grele şi de a pune în evidență sursele de poluare care afectează regiunile vestice ale tării noastre. Metalele grele au fost determinate prin metode de analiza cum ar fi ENAA şi FAAS. În vederea asigurării calității măsurătorilor s-au folosit materiale indicate de Agenția Internațională de Energie Atomică (IAEA).

This study is connected to an earlier survey of atmospheric heavy metal deposition started in 1995, for the first time, in Romania. In this paper the results obtained after collecting in 1999 and 2007 (during the summer) 64 moss samples from highly polluted area of some regions of Romania are reported. The aim of this study consists in obtaining the atmospheric deposition patterns of heavy metals trace elements and to reveal air pollution sources affecting the western regions of our country. The heavy metals were determined by using nuclear and non-nuclear methods, such as ENAA and FAAS. To ensure the quality of the measurements we used IAEA certified materials.

1. Introduction

Studies relating to atmospheric pollution generated by heavy metals or other toxic elements were, for the first time, started in 1995 in Romania [1]. We take advantage from the cooperation with foreign investigators belonging to different countries, such as Russia, Norway and others. Such investigations are now included in the International Program of Cooperation of O.N.U. regarding to atmospheric pollution effects on natural vegetation and culture plants.

[1] Senior research,Dept. of Life and Environmental Physics,"Horia Hulubei" National Institute for Physics and Nuclear Engineering Bucharest, Romania
[2] Prof., Faculty of Applied Sciences, University POLITEHNICA of Bucharest , Romania.
[3] Reader, Faculty of Sciences,North University of Baia Mare, Faculty of Science, Romania
[4] Reader, Faculty of Sciences,North University of Baia Mare, Faculty of Science, Romania

Several methods have been proposed for collecting and analyzing different samples in order to obtain information referring to the nature and extension of pollution. Most of them were expensive and unconvenient. At the end of 1960 a rather simple and moderate price procedure was proposed by Swedish scientists [2]. It consists in using different types of moss as biomonitors. This procedure was considered by the Economic Commission of O.N.U. and found to be the best to be used in all European countries.

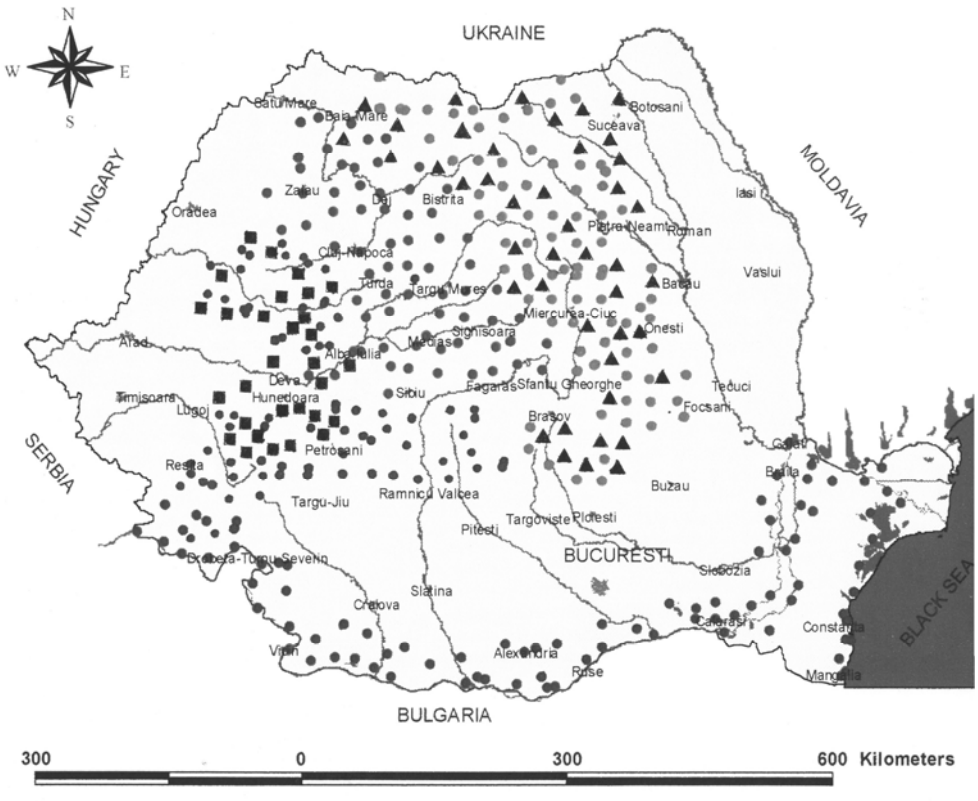

Fig.1. The map indicating locations of moss prelevations during the summer of 1999 and 2007
Legend: ■ Western Carpathians mountains • Transylvania plateau,Course of Danube river and Delta /over the Black Seea ▲ Eastern Carpathians mountains and North part of Transylvania

The first attempt to use moss biomonitorization was made in Romania in 1991 but it was constraint to a rather small area (Banat). This experience was followed by a systematic investigation performed in 1995, in Eastern Carpathians mountains and allowed us to obtain valuable information regarding the heavy metal depositions on 120 areas with a network of (20X20) km. Now this method

was extended and more than 74% of Romanian territory was investigated. Following the ideas of foreign organizations and considering the experience obtained during these years, when investigating pollution of our territory, we developed a systematic study based on the following objectives

1. Improving the procedure of sample prelevation in the most polluted regions of Romania.
2. Surveying the heavy metal polluted regions in correlation with atmospheric conditions and establishing the consequences of these toxic emissions on the environment.
3. Establishing the pollution degree generated by heavy metals in the most polluted area of Romania. These are the industrial regions existing in the vicinity of Baia Mare and Cop□a Mică where metal works, mineral plants, melting plants and copper works are found.
4. Obtaining a program containing valuable data in high polluted critical regions in order to survey permanently the degree of pollution, as it is done in other European countries.

In Fig.1 the map of Romania is presented and locations of moss prelevations during the summer of 1999 and 2007 are shown.

The aim of this paper was to improve the procedure of sample prelevations in order to make it as efficient as the Scandinavian one. As known the atmospheric pollution is dependent on geographical and teritorial position and also on its specific climate.

The results obtained in 1999 and 2007 when using moss biomonitoring on large area belonging to Transylvanian plateau and Western Carpathians Mountains are shown and the presence of different heavy metal elements is discussed.

2. Experimental method

Sample preparation. As it was mentioned before we used as biomonitors three types of mosses; they are termed Hylocomium splendens, Hypnum cupressiforme and Pleurozium schreberi. They were collected during the summers of the years 1999 and 2007 following the indications of Scandinavian scientists [2], including those considered by Markert [3]

The sampling sites were located at least 300 m from main roads and populated areas and at least 100 m from smaller roads or single houses. From each sampling site, 5 to 10 subsamples were taken within a 50 x 50 m area and mixed together.

Each sample has been collected with plastic gloves without talc and stored in clean plastic bags, marked with a specific number (code) and indicating the day, species of moss, weather conditions, vegetation cover, etc. The unwashed

green part of moss plant has been cleaned and dried at 40 ^{0}C before subjecting it to analysis. No further homogenization of the samples was performed [4].

Flame atomic absorption spectroscopy method analysis. This method was used for moss samples collected during the summer of 2007. Using a Perkin-Elmer AA-600 spectroscope we determined 10 elements of heavy metals. The measurements were performed at the Institute of Mining and Research of Baia Mare. Moss samples of about 1-5 g were introduced into a bottle of 10 ml containing concentrated nitric acid (HNO_3) and then put on a hot plate at $80-85^0 C$ for 18-20 h. After cooling down to room temperature, the samples were filtered and demineralized water was added up to a volume of 50 ml. The same procedures were followed when calibration standards and blanks were.

Neutron activation analysis. This method was used for most samples collected in the summer of 1999. Samples weighting 0.3 g were packed in aluminum cups used for long-time irradiation. Long-lived isotopes were determined using the Cd - screened channel Ch1 (epithermal neutron activation analysis, ENAA). The samples were irradiated for 5 days, re-packed, and then measured twice after 4-5 and 20 days of decay, respectively. The measurements lasted from 1 to 5 hours. The elements Cu, Cd and Pb were determined in Norway by flame atomic absorption spectrometry after subjecting the samples to the same procedure mentioned before. The characteristics properties of the irradiation channels of IBR -2 reactors from Frank Laboratory of Nuclear Physics (FLNP) of Joint Institute of Nuclear Research (JINR), from Dubna (Russia) are shown in *Table I*.

Table 1

Characteristics of the irradiation channels of JINR

	Neutron flux density / 10^{12}n cm^{-2}s^{-1}			
Irradiation site	Thermal	Resonance	Fast	T (^{0}C)
Ch1	Cd coated	0,23 ± 0.03	1.4± 0.16	70
Ch2	0.54 ± 0.06	0.12 ±0.014	0.64±0.04	60

Data processing and element concentration determination were performed on the basis of certified reference materials and flux comparators, using software developed in FLNP JINR. For long-time irradiation in Ch1, single comparators of Au (1μg) and Zr (10μg) were used [6-7]. The concentrations of elements yielding long-lived isotopes have been also determined using certified reference materials: SDM-sediment (International Atomic Energy Agency, Vienna), Montana Soil (NIST) and moss DK–1.

Table II

Element concentration in moss survey of 2007 year (mg/Kg). Error limit for the measurements is 15%.

2007	LAT.	LONG.	As	Cd	Co	Cr	Cu	Fe	Ni	Pb	Zn	V
M12	44^0 26' 12''	23^0 9' 47''	2.56	1.67	0.80	7.90	15.52	5139	1.25	13.24	129.60	10.08
M15	45^0 58' 22''	23^0 58' 26''	2.15	0.63	0.84	10.82	3.68	5168	1.32	11.76	152.80	17.20
M16	45^0 57' 17''	24^0 09' 21''	2.09	1.22	0.67	9.75	3.20	5876	1.31	14.32	148.00	12.64
M17	45^0 55' 38''	24^0 27' 16''	1.10	1.34	0.74	11.61	6.16	5616	1.17	22.13	188.00	4.96
M19	45^0 56' 11''	25^0 00' 47''	3.64	0.99	1.08	10.50	3.04	7992	1.44	10.50	162.40	15.20
N13	46^0 04' 22''	23^0 35' 50''	1.02	1.10	0.22	2.90	7.20	1256	0.70	18.32	40.00	3.84
N15	$46^0$06'00"	23^0 54' 32''	1.42	0.61	0.38	3.22	8.88	1660	0.77	25.20	41.60	4.72
N16	46^0 6' 56''	24^0 14'18"	1.01	0.17	0.28	3.53	4.64	1302	0.58	77.06	82.40	4.24
N17	46^0 5' 27''	24^0 29' 12''	1.01	0.90	0.20	4.72	7.60	1444	0.63	22.64	88.00	3.12
N21	46^0 07' 38''	25^0 33' 30''	1.36	1.07	0.51	2.33	5.84	2787	0.83	17.84	144.80	7.12
O16	46^0 11'01"	24^0 20' 08''	1.01	1.15	0.65	3.30	6.72	987	0.81	26.72	38.40	3.52
O18	46^0 20'00"	24^0 28' 25''	0.90	0.62	0.35	3.94	2.08	1574	0.67	6.24	46.40	7.04
P17	46^0 28' 06''	24^0 30' 48''	0.86	0.76	0.57	1.80	2.24	1758	0.72	4.96	41.60	4.96
Q14	46^0 36' 45''	23^0 45' 48''	1.06	0.49	0.39	10.77	1.76	1790	0.66	6.56	57.60	7.04
Q16	46^0 40'00"	24^0 08' 48''	1.00	0.18	0.38	3.42	7.04	970	0.78	21.52	40.00	4.40
Q17	46^0 38' 55''	24^0 21' 36''	0.65	0.18	0.36	8.33	6.48	1317	0.51	5.92	32.00	5.52
Q18	46^0 40' 32''	24^0 47' 22''	2.86	1.32	0.80	4.72	13.76	4833	0.15	26.72	99.20	14.08
T12	$47^0$09' 29''	23^0 05' 24''	1.90	0.99	0.31	3.54	24.32	1123	0.62	52.64	64.80	7.92
T13	47^0 09' 44''	23^0 24'00"	2.11	0.92	0.92	4.83	25.92	4822	1.04	33.68	139.20	23.04
T15	47^0 09' 22''	23^0 52' 41''	1.91	0.65	0.85	3.51	26.40	3786	1.02	31.68	103.20	16.48
T16	47^0 10' 48''	24^0 10' 24''	1.50	1.02	1.34	5.76	26.80	6918	1.33	30.16	135.20	20.56
T17	47^0 11' 21''	24^0 33' 24''	2.99	1.14	1.66	1.98	18.56	5017	1.31	24.48	116.00	13.92
U12	47^0 19' 28''	23^0 04'00"	3.56	1.43	2.22	2.88	22.40	8752	1.88	33.12	121.60	22.08
U13	47^0 21'0 5''	23^0 28' 48''	2.64	1.64	1.61	5.55	20.40	6068	1.26	29.60	79.20	18.80
U14	47^0 19' 28''	23^0 36' 48''	1.91	0.38	0.82	6.72	7.60	3715	0.78	31.84	63.20	12.64
U15	47^0 21' 54''	23^0 51' 12''	1.56	0.26	0.46	7.80	6.48	2046	0.54	28.96	24.80	10.24
U16	47^0 20'00"	24^0 16'00"	1.88	0.38	0.86	6.40	6.64	3782	1.08	28.88	33.60	11.12
V15	47^0 31' 54''	23^0 56'00"	0.82	0.35	0.18	11.80	8.64	1786	1.50	22.96	51.20	9.28
X12	47^0 38' 22''	23^0 03' 38''	1.06	0.20	0.10	15.08	6.40	1047	0.90	26.08	39.20	4.56
X13	47^0 40'00	23^0 15'00"	1.83	1.29	0.36	11.24	8.32	3636	1.57	18.24	66.40	13.12
X14	47^0 37' 36''	23^0 34' 12''	0.80	0.26	0.12	15.85	11.52	909	0.38	44.64	50.40	4.96

The contributions of the interference from the reactions ^{56}Fe (n,p)^{56} Mn and ^{56}Fe(n,α)^{51}Cr were estimated as less than 0,1% for a given concentration of Fe. The high density of fast neutrons in the employed irradiation channels, provided favorable conditions for the determination of Ni by the ^{58}Ni(n,p)^{58}Co reaction.

3. Experimental results

The experimental results obtained when surveying the moss samples collected in 2007 are shown in *Table II.* In this table we give the code number of the sample, its position (determined by the latitude LAT and longitude LONG) and the concentration of the foreign elements.
For purposes of comparison we give into the *Table III* the percentages of the same elements obtained as a result of collecting moss samples on the same areas in 1999 and 2007 [8, 9].

Table III

Changes in the element concentrations (mg/Kg) in moss samples collected in different years (1999 and 2007). Error limit of the average values is 10%.

Element_99	As	Cd	Co	Cr	Cu	Fe	Ni	Pb	V	Zn
Range	0.60-119	0.23-55.40	0.32-7.05	2.72-51.90	18-2420	815-21300	0.58-3.12	40-1070	1.95-25.20	39.20-2950
Average	15.10	5.69	1.57	14.40	339	4600	1.12	404	9.91	498
Element_07	As	Cd	Co	Cr	Cu	Fe	Ni	Pb	V	Zn
Range	0.65-3.64	0.17-1.67	0.10-2.22	1.80-15.85	1.76-26.80	909-8752	0.15-1.88	4.26-77.60	3.12-23	24.80-188
Average	1.71	0.82	0.71	6.79	10.75	3471	0.96	25.78	10.44	85.87

4. Discussion

The presence of heavy metals in different regions of Romanian territory is a consequence of different local pollution sources; this explains why geographical positions and meteorological phenomena need to be taken into account if one had to explain such phenomena.

It is known that nickel and vanadium derive from crude oil combustion, petrol -refining or public electricity and heat production.

Copper, chromium and zinc sources are generated by road transportations, non-ferrous plants and by other manufacturing industries and constructions. This is the reason why in *Table II* pollution elements were determined in different locations (specified by the longitude and latitude) belonging to Transylvania and Carpathian mountains.

It is worth mentioning that in the north regions, high concentrations of Cu, Pb,Zn, Ni or As were noticed. These arise because high pollutions sources are

present in their vicinities; they are factories, metallurgical works or melting plants, located in Baia Mare, Magoaja, Letca , Cergau or Zagra and Copsa Mica.

When comparing the pollution results determined in Romanian territory with those obtained in other European countries we fond that the first ones are much higher. This fact has to be considered by the agencies interested in environment protection.

5. Conclusions

As a result of surveying, using biomonitorization, a rather large surface of Romanian territory during several years we had the possibility to get valuable information concerning the pollution phenomenon. We found that during these years depletion in the concentration of heavy metal pollutants was noticed. This is due to the new control methods of noxious emissions and to the closure of old factories and plants. The most polluted area of Romanian territory was determined and heavy metal pollutants can now be monitorized.

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