

Dedicated to Professor Marin Ivaşcu's 80<sup>th</sup> Anniversary

## ATOMIC AND NUCLEAR METHODS APPLIED IN THE STUDY OF HEAVY POLLUTING ELEMENTS

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*Abstract.* This paper is a short review of the results obtained in a biomonitoring research activity, which were published by the authors. Mosses and lichens, collected from Dambovită County Romania, were analyzed by Neutron Activation Analysis (INAA), Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Energy Dispersive X-Ray Fluorescence (EDXRF) to determine the content of different heavy metals. The concentrations of Cr, Fe, Mn, Ni and Zn were determined by INAA. The concentration of Fe in samples was determined using all the methods and was obtained a very good agreement, in statistical limits, which demonstrate the capability of these analytical methods to be applied on a large spectrum of environmental samples with the same results.

*Key words:* moss, lichen, biomonitoring, pollution, heavy metal.

### 1. INTRODUCTION

Dambovită County is located in the South of Romania and its main sources of heavy metal pollution are: stainless steel works (Targoviste), cement and related materials production (Fieni), glass and lighting sources production (Targoviste, Fieni), chemicals materials production (Targoviste, Doicesti), coal mining and thermal power station (Doicesti), oil exploration (Targoviste, Moreni, Gaiesti), etc.

The aim of this work is the assessment of air pollution level with heavy metals in some areas of the Dâmbovița County by using the biomonitoring method with mosses and lichens analyzed by atomic and nuclear methods. Many studies which were dedicated to the biomonitoring method [1, 2] showed its possibilities to provide significant results regarding the quality of the environment. Studies about moss properties [3–8, 15] and lichens as bio-monitors [9–13, 16, 21, 22], but also about the comparison of their characteristics as bio-monitors [11, 13, 14] reveal the fact that they have certain advantages such as: the capacity to accumulate dust particles from air, the stability of accumulation in time, the low cost of monitoring etc.

The moss and lichens groups are amenable to biomonitoring because they are widespread, easy to handle and they lack a cuticle and root system thus reflecting directly atmospheric heavy metal deposition. It is important during metal biomonitoring programs that background concentrations are established. The design of a monitoring program was involve: sampling locations, sample collection, heavy metals to be analyzed, multi-element determination using INAA – Neutron Activation Analysis [17, 18, 19], AAS – Atomic Absorption Spectrometry [18, 19], ICP-AES – Inductively Coupled Plasma-Atomic Emission Spectrometry [23, 24], EDXRF – (Energy Dispersive X Ray Fluorescence [26, 27], techniques and data analysis.

## 2. EXPERIMENTAL

### 2.1. SAMPLES AND SAMPLING

The mosses *Sphagnum species* have been considered especially suitable for monitoring heavy metal pollution due to the high cation-exchange capacity of their cell walls. Very useful results have been obtained with this type of moss in flat and spherical moss-bags.

In order to optimize the assessment of atmospheric pollution in an industrial area using active biomonitoring a novel sampling design was introduced, and transplants the moss *Sphagnum girgensohnii* were deployed in parallel in order to study the uptake of a series of trace elements from the air over a defined time period. The site selected for this experiment was Dambovita County, Romania.

Samples of *Sphagnum girgensohnii* were collected from the region of Dubna town, Russia (56.44 N, 37.09 E, altitude 120 m), in the frame of our protocol of collaboration with JINR-Dubna. This geographical zone is characterized by swamp landscape and extreme continental climate. Standard moss-bags of about 3 g moss

(dry-weight, unwashed, cleaned, air dried) were putted in nylon nets (10 × 10 cm in size). Three moss-bags were hung in parallel by means of a T-shaped support system made of wood. Moss *Sphagnum girgensohnii* was hanged in bags at 17 different locations (Table 1), in February 2006, and analyzed by NAA, AAS and ICP-AES methods, respectively, after 1, 2 and 3 months of exposure to precipitation and wind.

Table 1

Sample locations

| Samples code | Transplant localization sample |
|--------------|--------------------------------|
| 1            | Moroieni                       |
| 2            | Fieni                          |
| 3            | Pucioasa                       |
| 4            | Voinești                       |
| 5            | Gheboieni                      |
| 6            | Moreni                         |
| 7            | Doicești                       |
| 8            | Viforâta                       |
| 9            | Teiș                           |
| 10           | Târgoviște N-V                 |
| 11           | Târgoviște V                   |
| 12           | Târgoviște E                   |
| 13           | Adâncă                         |
| 14           | Ulmi                           |
| 15           | Picior de Munte                |
| 16           | Morteni                        |
| 17           | Tărtășești                     |

Another collected species of moss was *Hylocomium Splendens*. Also was collected some lichens samples as: *Xanthoria Parietina*, *Parmelia Furfuracea* and *Peltigera Canina*.

## 2.2. METHODS

**INAA (Neutron Activation Analysis)** was performed at the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia. Following exposure, the moss was removed from the nylon net, manually homogenized and dried in a thermostat oven at 400 C for 48 h. Conventional and epithermal NAA at the IBR-2 pulsed fast reactor FLNP JINR Dubna, Russia [3], were used to determine concentrations of following elements: Cr, Mn, Ni, Fe, Zn. Two kinds of analysis were performed: long irradiation for 100 hours in Ch.1 was used to determine elements associated with long-lived radionuclides Cr, Fe, Ni and

Zn) and short irradiation for 2 minutes in Ch.2 was used for short-lived radionuclides (Mn). Gamma-ray spectra were recorded four times using a high-purity Ge detector; after decay periods of 5 minutes and 10 minutes following the short irradiation, and after 5 days and 13 days following the long irradiation. The quantity of radioactive nuclides is determined by measuring the intensity of the gamma characteristic gamma-ray line in spectra.

**AAS (Atomic Absorption Spectrometry)** is the most widely utilized method today for quantitative element analysis. The detection limit in AAS is up to about one ppt under optimum experimental conditions. A material sample, in a liquid solution, is atomized, through rapid heat application and placed in the radiation path of several elements – specific light sources. The atoms of sample absorb the wavelength corresponding to their excitation energy, thus reducing the radiated energy. The concentration of element can be determined using the Lambert-Beer law [9], through wavelength dispersive measurement of this reduction. The absorbance is proportional with the element concentration. The Atomic Absorption Spectrometer used by us is an AAS-AVANTA GBC with hollow cathode lamp (HCL). Measurements were made separately for each element of interest from sample using the calibration curve – absorbance *versus* concentration.

**ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry)** method is based on the fact that the atoms and ions produced in the plasma are excited and emit light. The intensity of light emitted at wavelengths characteristic of the particular elements of interest is measured and related to the concentration of each element from samples.

The ICP-AES spectrometer used is a Baird ICP2070 – Sequential Plasma Spectrometer.

For the AAS and ICP-AES analysis, portions of about 0,4 g moss were decomposed with 4 mL of concentrated nitric acid in a microwave oven. The extracts were then filtered, and deionised water was added to a total volume of 25 mL. The presence of possible contaminants during the digestion process was controlled using blanks. Accuracy was checked by analysis of three replicates of reference material IAEA 336, lichen.

**EDXRF (Energy Dispersive X-Ray Fluorescence)** measurements were performed using an Elvax EDXRF spectrometer which including a solid state Si-pin-diode detector, thermoelectrically cooled, with a resolution of 180 eV at 5.9 keV (XK $\alpha$  line of <sup>55</sup>Fe isotope). The X-ray tube can be powered by voltages in range of 4–50 kV with 100 V steps and have a Be window of 140  $\mu$ m thickness. The processing software for the acquired X-ray spectra has the following possibilities: determination of energy peaks and their characteristics, identification of chemical elements, removal of the background, giving measurement errors etc.

For EDXRF analyses, the samples were prepared as follows: after drying, they were shredded, followed by placing them into the special plastic cylinders of the EDXRF spectrometer. The cylinders were covered with Mylar foil Fluxana having 2.5 mm thickness, through which the exposure to X-ray beam can be done.

### 3. RESULTS AND DISCUSSION

The analytical performance was checked by the regular analyses of the standard reference materials (SRM IAEA-336, lichen and moss) issued by the International Atomic Energy Agency [10].

The concentration values obtained in our study are presented in Table 2, together with the concentration values of elements in SRM IAEA-336 [10].

Table 2

The mean values of elemental concentration determined in mosses, by three methods (NAA, AAS, ICP-AES), mg/kg± standard deviation

|    | Cr        | Mn     | Ni       | Zn       | Fe        |           |           |
|----|-----------|--------|----------|----------|-----------|-----------|-----------|
|    | NAA       | NAA    | NAA      | NAA      | NAA       | AAS       | ICP-AES   |
| 1  | 0.95      | 198.67 | 1.80     | 19.00    | 430.10    | 436.14    | 469.33    |
| 2  | 1.60      | 202.37 | 2.30     | 66.59    | 579.23    | 571.41    | 617.67    |
| 3  | 2.04      | 157.23 | 2.28     | 110.38   | 601.47    | 589.43    | 645.00    |
| 4  | 1.54      | 177.40 | 2.19     | 21.20    | 549.27    | 545.68    | 609.00    |
| 5  | 1.85      | 155.37 | 2.63     | 21.75    | 582.77    | 555.79    | 577.67    |
| 6  | 0.73      | 179.15 | 2.76     | 352.62   | 503.65    | 504.72    | 519.00    |
| 7  | 3.06      | 178.70 | 1.93     | 51.19    | 550.43    | 565.37    | 521.33    |
| 8  | 1.66      | 859.93 | 2.06     | 32.52    | 528.87    | 561.23    | 496.67    |
| 9  | 2.49      | 148.00 | 2.04     | 24.98    | 595.93    | 558.14    | 562.33    |
| 10 | 7.08      | 182.97 | 1.97     | 33.02    | 577.97    | 585.76    | 611.67    |
| 11 | 26.17     | 164.83 | 5.62     | 121.93   | 2056.33   | 1939.01   | 2038.33   |
| 12 | 13.08     | 274.97 | 3.61     | 63.31    | 1397.43   | 1286.72   | 1332.33   |
| 13 | 1.76      | 188.23 | 2.07     | 43.60    | 513.10    | 502.36    | 532.00    |
| 14 | 8.64      | 157.70 | 2.80     | 40.22    | 963.60    | 946.12    | 986.00    |
| 15 | 3.69      | 608.50 | 3.31     | 97.98    | 951.63    | 962.86    | 983.67    |
| 16 | 1.12      | 184.33 | 1.20     | 23.53    | 487.10    | 483.93    | 475.00    |
| 17 | 1.09      | 189.13 | 0.94     | 48.84    | 377.20    | 307.95    | 345.00    |
| *  | 1.06±0.09 | 246    | 3.5±0.35 | 30.4±1.4 | 430±10.75 | 430±10.75 | 430±10.75 |

\* SRM-IAEA. The mean standard deviation: 5–20 %.

In Figs. 1, 2, 3 and 4 are presented the variation of Cr, Mn, Ni and Zn concentrations in transplanted *Sphagnum girgensohnii* mosses [10].

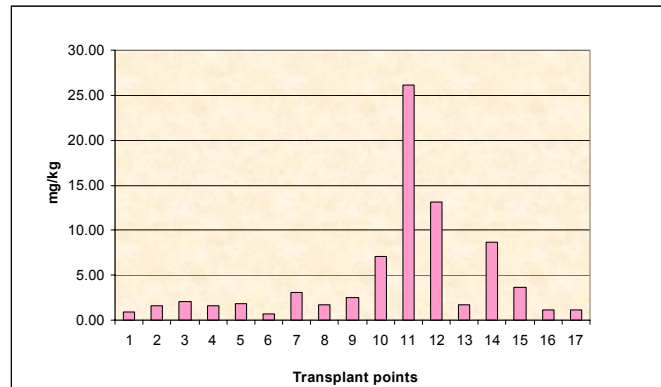


Fig. 1 – Variation of Cr concentration in mosses.

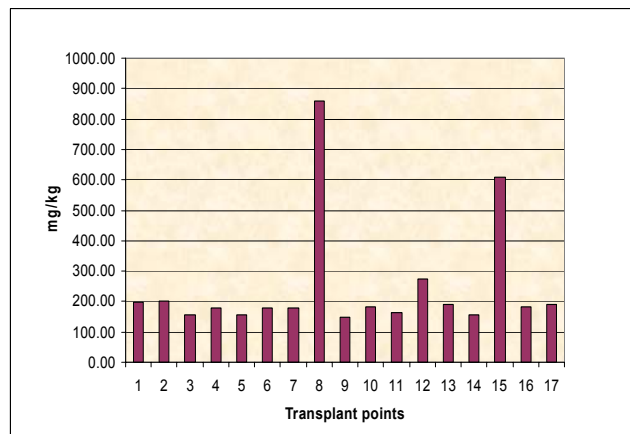


Fig. 2 – Variation of Mn concentration in mosses.

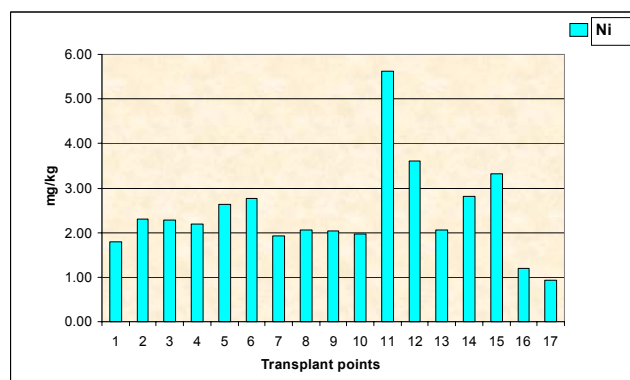


Fig. 3 – Variation of Ni concentration in mosses.

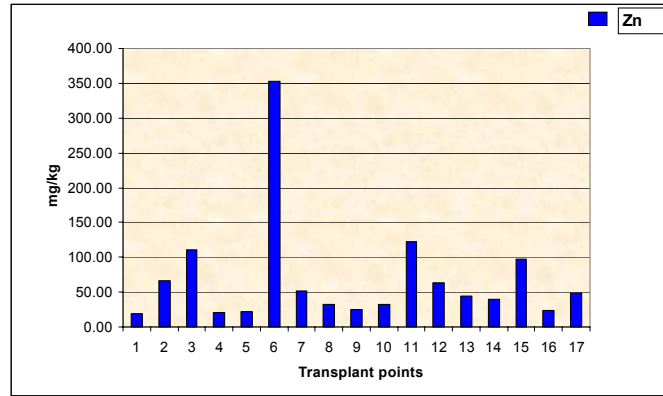


Fig. 4 – Variation of Zn concentration in mosses.

The concentration of Fe in *Sphagnum girgensohnii* mosses samples was determined by NAA, AAS and ICP-AES to perform a comparison of the experimental results. The obtained diagram on comparison results are presented in Fig. 5.

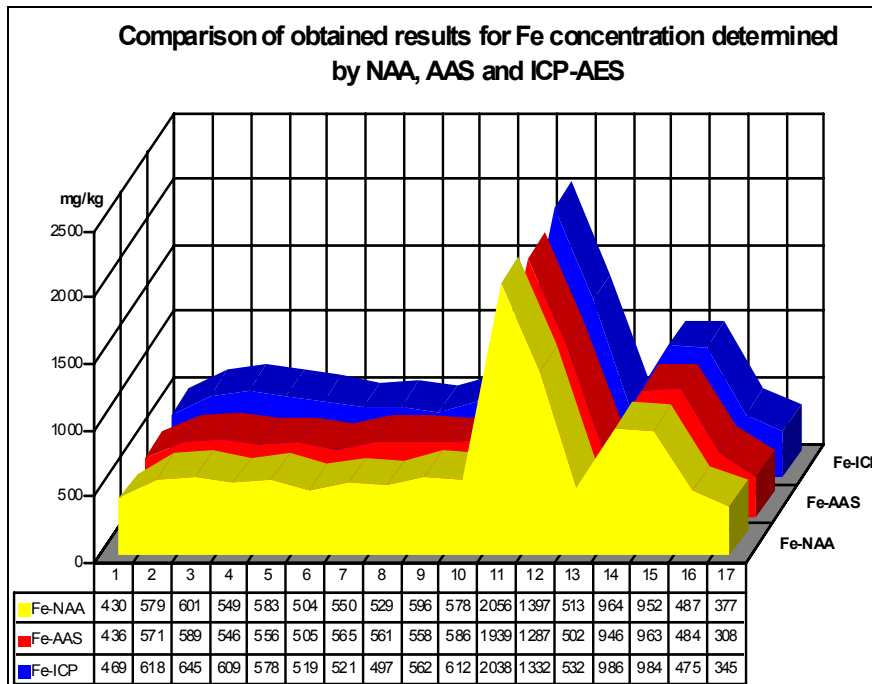


Fig. 5 – Comparison between obtained results for Fe concentration determined by NAA, AAS and ICP-AES.

We can observe a good agreement, in statistical limits (about 5%), between the concentration values of Fe determined by NAA, AAS and ICP-AES methods. These results demonstrate the capability of these analytical methods of high sensitivity and precision to be applied on a large spectrum of environmental samples.

In Tables 3 and 4 there are summarized the concentrations of Cr, Cu, Fe, Ni, Pb and Zn obtained for *Hylocomium Splendens* mosses samples and *Xanthoria Parietina*, *Parmelia Furfuracea* and *Peltigera Canina* lichens samples.

The contamination factor CF [15], was determined by using the formula (1):

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

where  $C_m$  is the maximum value of measured element concentration and  $C_b$  is the background concentration.

Table 3

Statistical data on the concentrations obtained by AAS and EDXRF methods for mosses

| Element |                      | Concentration [ppm] |
|---------|----------------------|---------------------|
| Cr      | C <sub>m</sub> [ppm] | 1021.00±2.07        |
|         | C <sub>b</sub> [ppm] | 19.13±2.05          |
|         | CF                   | 53.37±3.63          |
| Cu      | C <sub>m</sub> [ppm] | 49.24±0.575         |
|         | C <sub>b</sub> [ppm] | 5.46±0.087          |
|         | CF                   | 9.018±0.24          |
| Fe      | C <sub>m</sub> [ppm] | 7012.00±1.01        |
|         | C <sub>b</sub> [ppm] | 728.15±66           |
|         | CF                   | 9.63±1.01           |
| Ni      | C <sub>m</sub> [ppm] | 38.74±1.684         |
|         | C <sub>b</sub> [ppm] | 2.11±0.002          |
|         | CF                   | 18.36±0.81          |
| Pb      | C <sub>m</sub> [ppm] | 157.76±5.788        |
|         | C <sub>b</sub> [ppm] | 2.5±0.17            |
|         | CF                   | 63.104±1.024        |
| Zn      | C <sub>m</sub> [ppm] | 158.00±4.04         |
|         | C <sub>b</sub> [ppm] | 6.25±0.377          |
|         | CF                   | 25.28±2.21          |



Table 4

Statistical data on the concentrations obtained by AAS and EDXRF methods for lichens

| Element |          | Concentration [ppm] |
|---------|----------|---------------------|
| Cr      | Cm [ppm] | 64.5±3.73           |
|         | Cb [ppm] | 5.8±0.6             |
|         | CF       | 11.11±1.79          |
| Cu      | Cm [ppm] | 34.08±2.3           |
|         | Cb [ppm] | 2.76±0.1.4          |
|         | CF       | 12.34±1.4.5         |
| Fe      | Cm [ppm] | 6071.29±4.73        |
|         | Cb [ppm] | 412.01±2.8          |
|         | CF       | 14.73±2,14          |
| Ni      | Cm [ppm] | 10.48±0.102         |
|         | Cb [ppm] | 0.76±0.062          |
|         | CF       | 13.78±1.25          |
| Pb      | Cm [ppm] | 75.12±6.85          |
|         | Cb (ppm) | 5.56±0.45           |
|         | CF       | 13.51±2.32          |
| Zn      | Cm [ppm] | 155.7±7.02          |
|         | Cb [ppm] | 4.7±0.351           |
|         | CF       | 33.12±3.96          |

The results reveal that the accumulation of Cr, Cu, Fe, Ni, Pb and Zn in moss samples is different comparative with the data obtained in lichen samples.

The contamination factor (CF) values can be interpreted as follows: for  $1 \leq CF < 2$  – without contamination; for  $2 \leq CF < 3.5$  – low contamination; for  $3.5 \leq CF < 8$  – moderate contamination; for  $8 \leq CF < 27$  – severe contamination; for  $CF > 27$  – extreme contamination. It is observed while the moss samples evidence a severe pollution only for Cr, the lichen samples evidence severe pollution for Zn and Ni. These differences are due to the different distribution of the two types of biomonitors in sampling areas, respectively to the different capacity to absorb heavy metals from air.

In the industrial sampling areas was observed a high level of pollution with heavy metals.

#### 4. CONCLUSIONS

The use of different sensitive analytical techniques as: Neutron Activation Analysis (INAA), Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Energy Dispersive X-Ray

Fluorescence (EDXRF) together with biomonitoring method can offer complete data concerning the heavy metals distribution in environment. By knowing the heavy metals concentrations in biomonitors it can be determine the contamination level of a polluted area.

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