AIR POLLUTION STUDIES USING PIXE AND ICP METHODS

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Abstract. In the present work the moss biomonitoring technique and the combination of two analytical techniques – Particle Induced X-ray Emission (PIXE) [3] and Inductively Coupled Plasma (ICP) [4] – were applied for assessing environmental situation from the point of view of air polluting along the transect from north to south of the Dambovita County. PIXE analysis at the Tandem Accelerator FN-8 of the National Institute of Nuclear Physics – Horia Hulubei of Magurele, Bucharest, allowed determination of P, S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Sr, Cd and Pb in samples. ICP analyses were made using a Baird ICP2070 – Sequential Plasma Spectrometer in Targoviste and we determined in samples the concentration of Li, B, Na, and Mg together with Cd and Pb. The obtained results will permit to determine the regional extent of heavy metals and toxic elements atmospheric pollution and to identify specially affected areas and local sources of

1. Introduction
Most methods in heavy metal monitoring employ mosses as bioaccumulators and involve sample collection followed by laboratory analysis techniques. The majority of studies have been multielement investigations and few have been restricted to a particular metal except where different methods of analysis were required. Since Burton's review in 1986 [1], approaches to moss monitoring of heavy metal deposition have changed little in principle. Refinements have been made in monitoring design, in terms of standardized sampling and reduction of error and variance. As may be expected new developments in chemical analysis have occurred. A major choice lies between using techniques which employ indigenous species or transplanted species. A successfully series of studies using mosses as bioindicators were initiated in the Steines group [2-5].

The main sources of air pollutants are industrial processes, thermal power stations, domestic heating systems and motor vehicles. All these sources are present in the territory of the Dambovita County, Romania. The main polluting regional industries 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).
The above mentioned industries are potential sources of such pollutants as: As, Cd, Cr, Cu, Fe, Ni, Pb, Si, Sb and Zn regularly determined in the European moss surveys. [6,7]. The most affected towns are Fieni, Doicesti, Moreni, Gaiesti and Targoviste in decreasing order regarding pollution with sedimentable powder. The cement factory in the town of Fieni is responsible for the third place in the list of the most polluted localities of Romania (Romanian Statistical Yearbook-2001: National Institute of Statistics).

For assessing environmental situation from the point of view of air polluting we applied moss biomonitoring technique in combination with two analytical techniques – Particle Induced X-ray Emission (PIXE) [8] and Inductively Coupled Plasma (ICP) [9].

2. Experimental section
Using PIXE and ICP methods we analyzed samples of Mnium undulatum. Sampling of mosses was carried out in the investigated area: the transect from north to south of the Dambovita County (fig. 1).

2.1. PIXE experimental procedure
Sample preparation procedure was: first, soil was washed off the samples in running water and then the samples were finely cut and dried at a room temperature in a clean box preventing further contamination. After that the dried mosses - with a constant weight have been grained. The obtained powder was mixed with 2 μg of Yttrium (internal standard) in 150 μl demineralized water and depicted on Mylar support.

PIXE measurements of target elements were made using a 3 MeV proton beam extracted from the Tandem accelerator FN-8. of the National Institute of Nuclear Physics – Horia Hulubei of Magurele, Bucharest

X-ray spectra were measured with a spectrometric chain with a Canberra Ge hyperpure detector with a 160 eV resolution at 6.4 keV of K line of iron. The x-ray spectrum analysis was made off-line, at Valahia University of Targoviste, using LEONE fitting program.;

2.1. ICP experimental procedure
Sample preparation procedure was: first, soil was washed off the samples in running water and then the samples were finely cut and dried at a room temperature in a clean box preventing further contamination. After that the dried have been grained. The obtained powders of mosses - 1.5 g- were digested with 15 ml of nitric acid in a 100 ml Erlenmeyer flask on a hot plate at 80° for 12 hours. After cooling to room temperature the samples were filtered and then mixed with demineralized water to a total volume of 100 ml.

ICP analyses were made using a Baird ICP2070 – Sequential Plasma Spectrometer in Targoviste at 40.68 MHz and a plasma gas Argon.

3. Results and discussion
PIXE analysis allowed determination of Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Sr, Cd and Pb in samples. In table 1 is reported the concentration of elements in mosses samples obtained by PIXE method.

ICP analysis allowed determination of Na, and Mg together with Cd and Pb. In table 2 is reported the concentration of elements in the same mosses samples, used in PIXE measurements, but obtained by ICP method.

The concentrations of heavy and toxic metals in mosses depend on the industrial activity of studied area. The high concentration of iron, zinc and copper in mosses from Fieni and Targoviste towns is explained by the existence of cement factory and steel industries (figure 1).

The obtained concentrations of elements was compared with Norway background level [5] and we can say that the Fe, As, Cd and Pb concentrations are greater in Targoviste town.
### Table 1: Concentration (mg/kg) of elements obtained by PIXE method

| Samples          | Cl  | K   | Ca  | Fe  | Mn  | Ni  | Cu  | Zn  | As  | Sr  | Cd  | Pb  |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Şaua Strungă     | 18.25 | 38.00 | 191.00 | 14.00 | 43.00 | nd* | 3.60 | 9.00 | 0.00 | nd* | nd* | nd* |
| Fieni            | 32.00 | 311.00 | 824.00 | 1697.00 | 103.00 | 0.64 | 4.40 | 48.10 | 0.08 | 0.12 | 0.12 | 0.25 |
| Doicești         | 35.00 | 86.00 | 276.00 | 477.00 | 15.00 | 0.39 | 11.90 | 25.00 | 0.19 | 0.15 | 0.14 | 0.02 |
| Pucioasa         | 42.13 | 153.00 | 464.00 | 26.00 | 53.00 | 0.26 | 22.00 | 7.91 | 0.05 | 0.14 | 0.07 | nd* |
| Brânești         | 27.00 | 414.00 | 78.00 | 2320.00 | 75.00 | 2.12 | 32.50 | 19.00 | 0.09 | 0.15 | 0.10 | nd* |
| Targoviste South | 34.75 | 115.00 | 265.00 | 5507.00 | 30.00 | nd* | 20.25 | 25.30 | 0.09 | 0.17 | 0.14 | 0.05 |
| Ungureni         | 32.22 | 173.00 | 252.00 | 434.00 | 43.00 | nd* | 19.40 | 25.80 | 0.07 | 0.15 | 0.10 | 0.02 |
| Targoviste North | 33.25 | 201.60 | 318.00 | 2890.00 | 20.00 | 0.99 | 23.60 | 37.50 | 0.12 | 0.16 | 0.12 | 0.05 |
| Mircea Vodă      | 24.60 | 413.00 | 772.00 | 196.00 | 55.00 | 0.39 | 19.60 | 7.90 | 0.09 | 0.12 | 0.09 | nd* |
| Târtășești       | 19.72 | 166.00 | 175.00 | 411.00 | 27.00 | 0.65 | 7.99 | 3.19 | 0.08 | 0.10 | 0.07 | nd* |
| Racari           | 20.25 | 249.00 | 105.00 | 279.00 | 35.00 | 0.21 | 7.50 | 3.12 | 0.06 | 0.10 | 0.07 | nd* |
| Ilfoveni         | 13.64 | 177.00 | 203.00 | 138.00 | 32.00 | 0.25 | 12.55 | 13.25 | 0.09 | 0.13 | 0.10 | nd* |
| Titu             | 11.42 | 185.00 | 543.00 | 576.00 | 31.00 | 0.30 | 6.73 | 32.25 | 0.08 | 0.10 | 0.12 | 0.04 |
| Norway background level | 200 | 3000.00 | 1500.00 | 400.00 | 200.00 | 1.60 | 0.30 | 36.00 | 0.30 | nd* | nd* | nd* |

*not detected

### Table 2: Concentration (mg/kg) of elements obtained by ICP method

| Samples          | Na  | Mg  | Cd  | Pb  |
|------------------|-----|-----|-----|-----|
| Şaua Strungă     | 255.00 | 869.00 | 0.01 | 0.01 |
| Fieni            | 247.00 | 1253.00 | 0.13 | 0.23 |
| Doicești         | 271.00 | 1326.00 | 0.14 | 0.03 |
| Pucioasa         | 283.00 | 1452.00 | 0.05 | 0.01 |
| Brânești         | 268.00 | 1491.00 | 0.09 | nd* |
| Targoviste South | 301.00 | 1891.00 | 0.15 | 0.06 |
| Ungureni         | 269.00 | 1715.00 | 0.11 | 0.01 |
| Targoviste North | 315.00 | 1963.00 | 0.12 | 0.05 |
| Mircea Vodă      | 226.00 | 1237.00 | 0.08 | nd* |
| Târtășești       | 240.00 | 1124.00 | 0.07 | 0.01 |
| Racari           | 198.00 | 1084.00 | 0.06 | nd* |
| Ilfoveni         | 237.00 | 1627.00 | 0.10 | 0.01 |
| Titu             | 169.00 | 1396.00 | 0.12 | 0.04 |

*not detected
Figure 1 - Elements concentration in mosses (mg/kg) along from north to south Dambovita County

Figure 2. Cd and Pb concentrations obtained by PIXE and ICP methods

4. Conclusion
A certain conclusion which can be draw is that PIXE and ICP methods are complementary methods. The results obtained in this work by PIXE and ICP measurements for Cd and Pb concentrations are in good correlations (figure 2).

The obtained results will permit to determine the regional extent of heavy metals and toxic elements atmospheric pollution and to identify specially affected areas and local sources of pollution.

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