BIOMONITORING OF ATMOSPHERIC TRACE ELEMENT DEPOSITION BY MOSS AND USING ENAA: SOURCE IDENTIFICATION USING FACTOR ANALYSIS

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Abstract: *R-mode factor analysis is developed to identify and locate the emission sources of chemical elements present in mosses collected at 341 sites in Romania. Firstly, a matrix of correlation coefficients was computed for the set of observations. Factor analysis is applied to the data matrix of element concentrations. Signals for the following six sources reproducing the concentration relationships observed in mosses are identified: (1) mineral dust, (2) a Ni-Co signal that is related to both Ni-smelters and ferrous industries, (3) general pollution, (4) marine sources (I, Br and Se), (5) vegetation component (Sr, K, Cs, Rb, Ba and Zn), and (6) a Ca crustal (Ca, Mg) signal. Further an estimation of the survey's quality was proved by procedures of clean-up of the data set and source isolation. Consequently the soil contributions were removed and a second-generation data set is achieved. Additional factor analysis investigations were performed on the four origin regions related with data sets to examine the variations in regional deposition patterns from one survey to another. Then the factor score profiles of samples combined with the meteorological conditions are used to produce the probability maps of source locations. The results obtained in this paper show that air toxics released by the industrial sources speed up the pollution in all ecosystems and become a potential risk on the unpolluted regions.*

Factor analysis has been widely used in geochemical study of moss data in order to assess the atmospheric pollution over large areas. It is a well known multivariate statistical technique used in studying the interrelationships among variables which belong to large data basis and to explaining the information content in terms of a few features.

The present study was carried out in the framework of the project "The assessment of environmental pollution in Romania" (1996 - 2009) as part of the European convention *Air Pollution International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops.*

In this paper the application of factor analysis for identifying potential sources of elements in surveyed mosses is described.

MATERIAL AND METHODS

Sampling

The widespread epiphytic moss species suitable for biomonitoring purposes in Romania are *Hylocomium splendens*, *Pleurozium schreberi* and *Hypnum cupressiforme*. The species considered could be found almost all over the territory. It has been operating a sampling network of the three moss species, located on a regular grid (e.g. 20 x 20 km^2). The monitored area included more than 57 % of the Romanian territory. As reflected in sampling performed, *Hylocomium splendens – HS* (found in 71 % of the sites) and *Pleurozium schreberi - PS* (found in 33 % of the sites) were more common in coniferous forests while *Hypnum cupressiforme - HC* (present in 58 % of the sites) was more abundant in mixed forests and low altitude areas (Table 1).

Table 1

Some moss surveys in Romania

Region	*HS*	*PS*	*HC*	Total samples	Sites	Period
West of Romania		21	57	78	69	Summer 2003
South of Romania	10		42	52	43	May to Sept., 2000
Transylvania Plateau	71			71	71	Summer 1999
Southern and Western Carpathians	73	56	64	193	73	May to August, 1998
Eastern Carpathians	88	34	35	157	85	Summer 1995
Total samples/sites	242	90	101	551	341	

The upper three fully developed segments of each *Hylocomium spendens* plant and corresponding green or green-brownish parts of the other moss species representing the last 2-3 years growth were prepared for the analysis following the European guidelines. The same experimental material was subjected both to INAA and FAAS. The QA and QC of the surveys and analytics were carefully accomplished.

Factor analysis

A statistical multivariant correlation analysis of each element concentration in the presence of the all others in suites of related samples was done to estimate communality of variation at different sampling sites. Then the correlation matrix was computed. Solving the eigenvalue problem, the initial factors by R-mode factor analysis were estimated. To make them more meaningful an orthogonal rotation by the varimax method was applied to minimize the medium loaded elements in the extracted factors and to maximize low and high loadings of the elements. In the last step of this procedure factor scores have to be computed between the initial values and the extracted factors.

The data sets based on biomonitor pollution approaches surveying the atmospheric deposition commonly include a number of soil associated elements (e.g. Al, Fe, Sc, Cr, Th, REEs).

The gain obtained by application of this approach on moss data consists in clean-up of the data set by removal firstly of the soil-dust component, then the vegetation component and possible sea influence, then to separate between pollution components (i.e. different types of industries, agriculture, traffic, etc.). In the last step of the procedure a second generation data set is achieved, for which new survey variances were computed. In the FA interpretation of the data, soil-associated fractions are computed and removed from the data set.

In the moss survey done, the associated general pollution factor was isolated from the survey data set and used to build the second generation specific data set.

In data interpretation various information on the monitored sites, geochemical, from local industrial activity, etc. are used.

RESULTS AND DISCUSSIONS

Signals for the following six sources reproducing the concentration relationships observed in mosses are identified: (1) mineral dust, (2) a Ni-Co signal that is related to both Ni-smelters and ferrous industries, (3) general pollution, (4) marine sources (I, Br and Se), (5) vegetation component (Sr, K, Cs, Rb, Ba and Zn), and (6) a Ca crustal (Ca, Mg) signal. The new second generation element loadings are presented in Table 2. The R-mode factor analysis applied to the pollution component separated enough accurately between different industrial signals. There were identified following factors:

- a general pollution signal, that accounted for 55.3% of total variance and presents high loadings of Zn, Pb, Cd and Ni;
- a non-ferrous component, highly loaded with Ni, Cr and Co that explains 24.4% of variance;
- a combustion component due to high-temperature sources that signs for 15.3% of variance loaded with As, V, Sb and Se.

Table 2

Factor loadings in second generation data set

Factor / Component	F11	F12	F13
Zn	**0.80**	0.32	0.35
Pb	**0.78**	0.37	0.30
Cd	**0.74**	0.41	0.13
Ni	**0.56**	**0.75**	0.28
Cr	0.36	**0.74**	0.43
Co	0.24	**0.71**	0.49
As	0.21	0.33	**0.80**
V	0.10	0.25	**0.73**
Sb	0.24	0.51	**0.62**
Se	-0.13	0.03	**0.53**
Ba	0.47	0.21	0.35
Eigen value	6.8	3.0	2.0
Variance (%)	55.3	24.4	15.3
Cumulative Var. (%)	55.3	79.7	95.0

To add in source identification and localization the isoplets for some heavy metals were drawn and used in data interpretation (Figs. 1-4).

The general air pollution on the Romanian territory was generated mainly by local various industrial branches. For example, the spatial distribution of sources for some pollutants is described here.

Cadmium. Large-scale elevated cadmium levels were found in the following three areas in Romania. The higher values recorded in Alba district areas can be attributed to a complex ore (Cu, Pb and Zn) smelter from Baia de Aries and Cu smelters in Zlatna and Rosia Poieni.

In the northern part of the country, the pollution is mainly caused by the combustion of fossil fuel. In north and north-western part of Eastern Carpathians, the higher levels observed are connected with intensive mining of Co, Pb and Zn and Mn. A further important factor in this region is the domestic burning of coal. Local sources of airborne cadmium are the zinc-lead smelter in Copsa mica and the thermal power station in Sangeorgiu de Padure-Fantanele. The elevated levels observed in the South are related to the oil exploitation and refining from this area.

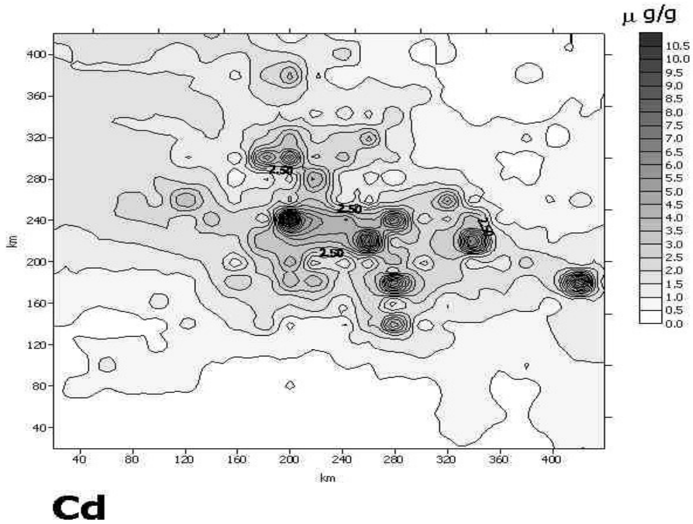

Fig. 1. – Geographical distribution of Cd concentration in moss surveys

Nickel. The iron and steel works in Resita, Otelu Rosu, Nadrag, Calan and Hunedoara emit nickel in air up to 11.3 μg/g along a large area. Elevated levels were found in Petrosani and Motru-Rovinari coal basins and in Tirgu Jiu regions and yield from coal burning. Another source of airborne nickel is the thermal power station in Rogojelu (situated down from Targu Jiu).

The highest concentrations observed in north-western part of the country are released by smelting in Baia Mare and by coal burning in the lignite Barcau Basin. The high emissions of nickel from Valea Prahovei (15.5 μg/g) and Buzau regions (13.7 μg/g) correlates strongly with that of vanadium and are related to local oil refineries.

Arsenic. The highest levels of arsenic were found in the north-western part of Romania, where there is a large number of complex ore (e.g. Cu, Pb and Zn) mines (at Baia Sprie, Baiut, Ilba, Nistru and Cavnic). The largest source of As emissions from this region is Baia Mare center, known for its traditional Cu, Pb and Zn smelting, Au and Ag processing and H_2SO_4 fertilizers manufacturing. Situated down from this region, the Barcau basin is polluted by lignite mining in Chiesd, Sarmasag, Ip, Borumiaca, Popesti, Voievozi and Varviz-Varzari.

Another area highly polluted with As in Western Carpathians region can be explained by the existence of complex ore (Cu, Pb and Zn) smelter from Baia de Aries and Cu smelters (at Zlatna and Rosia Poieni), coal burning power plants in Mintia Deva, Calan and Hunedoara, H_2SO_4 fertilizer plant in Copsa Mica and chemical plants from Turda, Ocna Mures and Tarnaveni.

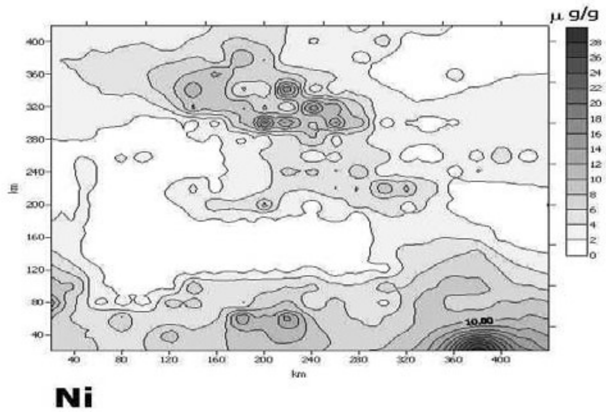

Fig. 2. — Geographical distribution of Ni concentration in moss surveys

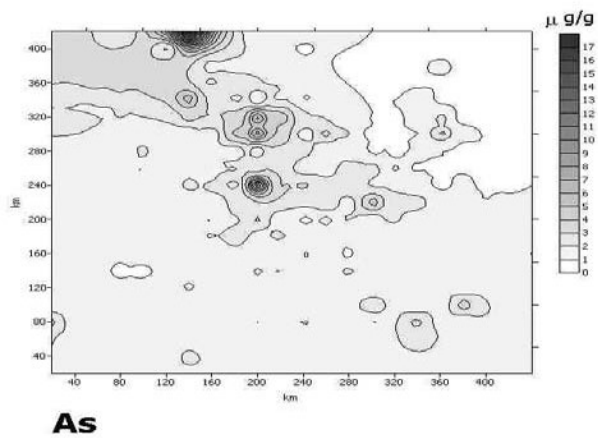

Fig. 3. — Geographical distribution of As concentration in moss surveys

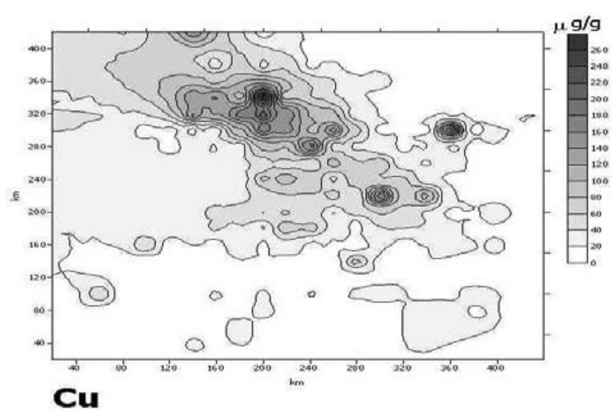

Fig. 4. — Geographical distribution of Cu concentration in moss surveys

In the north and north-western part of Eastern Carpathians several mines in Fundu Moldovei, Crucea, Lesu Ursului and Tarnita, respectively and four thermal power station situated along the Bistrita river can contribute to the high As values observed. The oil refineries in Moinesti-Darmanesti and Borzesti release into the air elevated levels of arsenic (up to 3.6 μg/g).

Copper. Airborne copper was accumulated in mosses near ore mining industry in Toroiaga, Lasu Ursului, Crucea and Fundu Moldovei in north of the country, in Balan (Eastern Carpathians) and in Rosia-Poieni, Baita, Deva, Moldova Noua and Sasca Montana in western part of the country and copper smelter in the town of Baia Mare.

CONCLUSIONS

The present research demonstrates the role of factor analysis in large -scaled surveys of air pollution based on biomonitoring approach.

Trace metal concentrations vary from region to another reflecting the initial emissions at different distances to the main sources. The highest levels signing for certain pollution sources were measured for As, Ba, Co, Cd, Cr, Cu, Fe, Ni, Se, Sb, V, and Zn on the investigated area. These trends are related to the industrial activities of the region.

The concentration values and trends in the present study are similar to those found by the other East-European countries participating in 2000 European moss survey. On the other hand, the trace metal levels were significantly higher in Romania compared with a background area in Norway.

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