THE RADIOCHEMICAL STUDIES OF MOSS PLANTS AND SOIL USING INAA AND AAS

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Abstract: This report presents the results of a regional survey of chemical contents of moss species and related topsoil, where the moss plants are growing, and uses them to derive estimates of atmospheric deposition. The moss and soil samples were analysed using the atomic absorption spectrometry and neutron activation analysis. Mean elemental concentrations varied between moss species sampled. This was partly due to the different locations from which they were sampled, and partly due to species differences in the rate of elemental uptake. Comparison of results with matched sites and moss species from the previous survey showed significant reductions in heavy metal concentrations of both Pleurozium schrebery and Hypnum cupressiforme.

The epiphytic mosses were tested to monitor the atmospheric deposition on a regular network in Europe from 1990s years and now are regularly used for monitoring purposes. Such mosses present enough reliable biomonitor qualities since they have a poor root system and then obtain most of their mineral nutrients as particulates and in solution directly from the atmosphere. Also they pose a great capacity to retain many chemical elements, to a large diapason of concentrations. Incipient studies of the heavy metal uptake by moss *Hylocomium splendens* done by Swedish scientists A. Ruhling and G. Tyler in 1970s years showed that the accumulation rates of the heavy metals followed this order: Cu, Pb>Ni>Co>Zn, Mn. The other Swedish scientist, H.B. Ross, determined in 1990 the uptake efficiencies in moss *Hylocomium splendens* for some elements presented in Table 1. A Norwegian scientist, E. Steinnes, determined in 1985 a large suite of heavy metal uptake efficiencies in mosses *Hylocomium splendens* collected in Southern Norway (Table 1).

Uptake efficiencies of moss Hylocomium splendens

Table 1

Element	٧	Cu	Cr	Zn	As	Se	Cd	Sb	Pb
Uptake efficiency (%) by Ross	40-60	50-85		46-70			40-50		
Uptake efficiency (%) by Steinnes	54		84	41	32	46	65	50	~100

The aim of the present study is to provide extended knowledge about correlations between chemical content in mosses and adjacent topsoil, in order to evaluate for which constituents mosses are reliable as biomonitors and to which extent. For this purpose the mosses belong to a moss survey done in Oradea's Plane in 2003 year were used. The chemical content of moss plants sampled was determined by neutron activation analysis and flame atomic absorption spectroscopy analytical methods.

This research is part of the project "Survey of Atmospheric Heavy Metal Deposition in Transilvania using moss biomonitoring technique" (2003-2009), applied by one of the authors (i.e. C. Oprea) in Bihor County.

MATERIAL AND METHODS

For sampling the guidelines reported in the protocol *Monitoring of Atmospheric Heavy-Metal Deposition in Europe Using Bryophytes 2000/2001* were used. Sampling was carried out during the summer of 2003 year. The moss species sampled were *Pleurozium schrebery* and *Hypnum cupressiforme*. The green part of the plant was separated and used further in the experiment.

The corresponding surface soils where the moss plants are growing in their natural habitat were sampled at the 0- to 5 cm depth.

The chemico-physical preparation of samples for analysis and the analysis procedures in the earlier studies of the author Oprea C. were detailed described.

A total of 39 chemical constituents were determined in analysed samples using both analytical methods.

Rahn. K.A. has proposed a graphical method for distinguishing plant material and soil from atmospheric deposition in biomonitors in 1997 and in 1999 applied it with success for determining major sources of elements in a mixed aerosol. We applied this method also to separate the moss component than that of soil nature and to characterize the main sources of elements in surveyed moss samples.

The definition of the enrichment factor for an element is the following:

$$EF = (X/Sc)_{moss}/(X/Sc)_{soil}$$

where X denote the element and Sc is the usual soil reference element.

RESULTS AND DISCUSSION

Graphical technique moss to soil

The results obtained by application of graphical technique to average moss and soil concentrations have selected between the best indicators sources of chemical element other than soil contribution (Fig. 2).

The element factors close to unity show geochemical similarities of these elements with sampled topsoil. The best indicators of non-soil sources are that of EF>3 and they correspond to chemical moss compounds as I, Cl, Cd, Br, As, Pb, Zn, Mn, Sb, Cu, Mo, K, Na, Ni, V, Ca, Hf and Sr, in that order.

According to their main origin sources, those elements can be divided by groups as follows:

- 1) I, Cl, Br, K, Na, Mg (long-range atmospheric transport from ocean environment);
- 2) Cd, As, Pb, Zn, Mn, Sb, Cu, Mo, Ni, Ca (regional general pollution due to anthropogenic activity (industry, urbanization, agriculture, tourism);
- 3) Ni, V (regional pollution due to oil industrial activity);
- 4) Cd, As, Pb, Zn, Mn, Sb, Cu, Mo, Ni, V, Ca, Hf (long-range atmospheric transport from Europe);
- 5) Sr, Cs, Ba, Rb, Zn, Cu, Ca (vegetal component transferred from living or dead vascular plants).

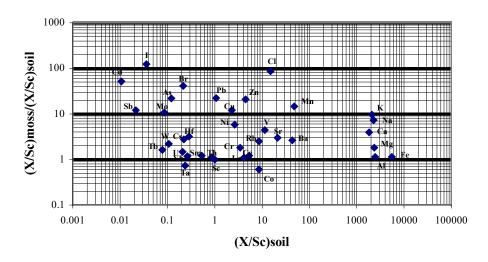


Fig 1. Enrichment factor of elements in mosses versus soil Moss species comparison

When it was possible, in some locations were recorded both *Pleurozium schreberi* and *Hypnum cupressiforme* species and this survey allowed a comparison between the two species elemental content. The moss concentrations were normalized and then the interspecies moss concentration ratios (R=c(PS)/c(HC)) were calculated and compared with those of previous surveys (Table 2). The R ratio varies between 0.6 and 1.1 for Mg, K, Ca, Cr, Fe, Co, Br, Rb, Sr, I, Ba. The most pollutants elements in the region as Cd, As, Zn, Pb, Ni, V, and Cl, were highly loaded in *Pleurozium schreberi* then *Hypnum cupressiforme*. *Hypnum cupressiforme* moss showed high loadings for the elements Mn, Sb, Mo and Sr.

R ratio for chemical element of the two sampled moss species

R	Elements
R<0.6	Mn, Sb, Mo, Sr
0.6 <r<1.1< th=""><th>Mg, I, Br, Cu, K, Na, Ca, Cr, Fe, Co, Ba, Hf, Rb, Se, U, Th, Cs, L, Ce, Sm, Ta, Tb, Yb, W</th></r<1.1<>	Mg, I, Br, Cu, K, Na, Ca, Cr, Fe, Co, Ba, Hf, Rb, Se, U, Th, Cs, L, Ce, Sm, Ta, Tb, Yb, W
R>1.1	Cd, As, Zn, Pb, Ni, V, Cl

CONCLUSIONS

The chemical content in epiphytic mosses *Pleurozium schreberi* and *Hypnum cupressiforme* living in surveyed area was determined to an extent of 39 inorganic constituents. The pollution tendencies that influenced the regional environment were reflected by the analysed moss and even soil samples. The most polluting elements occur in the moss from both local emissions as well s as a result of long-range atmospheric transport. The element concentrations in the two moss were compared and was established the best biomonitor of different elements, belonging to different origin sources.

REFERENCES

- Berg, O.; Røyset, O. Steinnes, E. 1995 Moss Used as a Biomonitor of Atmospheric Trace Element Deposition. Estimation of Uptake Efficiencies. Atmos. Environ 29:325-360.
- Galsomies, L.; Letrouit, M.A., Deschamps, C., Savanne, D., Avaim, M. 1999 Atmospheric Metal Deposition in France: Initial Results on Moss Calibration from the 1996 Biomonitoring. Sci. Tot. Environ. 232:39-47.
- 3. Halleraker, J.H.; Reimann, C., De Caritat, P., Finne, T.E, Kashulina, G., Niskaavaara, H., Bogatyrev I. 1998 Reliability of Moss (Hylocomium Splendens and Pleurozium Schreberi) as a Bioindicator of Atmospheric Chemistry in the Barents Region: Interspecies and Field Duplicate Variability, Sci. Tot. Environ. 218:123-139.
- Rahn, K.A. 1999 A Graphical Technique for Determining Major Components in a Mixed Aerosol. I. Descriptive Aspect. Atmos. Environ. 33:1441-1455.
- Rahn, K.A. 1997 A Graphical Technique for Distinguishing Plant Material and Soil from Atmospheric Deposition in Biomonitors. Proceedings of BioMAP-1997, Lisbon, Portugal, 21-24 Sept., 1997: 47-62.
- Ruhling, A. 1993 Atmospheric Heavy Metal Deposition in Europe Estimation Based on Moss Analysis. Nordic Council of Ministers, Copenhagen (NORD 1994:9).
- 8. **Steinnes, E., Rambæk, J.P., Hanssen, J.E. 1992** Large Scale Multi-Element Survey of Atmospheric Deposition Using Naturally Growing Moss as Biomonitor. Chemosphere, 25: 735-752.
- Steinnes, E. 1980 Atmospheric deposition of heavy metals in Norway studied by the analysis of moss samples using neutron activation analysis and atomic absorption spectrometry. J. Radioanal. Chem. 58:387-391.
- United Nations Economic Commission for Europe Convention on Long-Range Transboundary, 2000/2001 - Monitoring of Atmospheric Heavy-Metal Deposition in Europe Using Bryophytes 2000/2001. Air Pollution International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops ISBN 1 870393;pp 60.