FURTHER PROMOTION OF THE USE OF MOSSES AND LICHENS FOR STUDIES OF ATMOSPHERIC DEPOSITION OF TRACE ELEMENTS

EILIV STEINNES

Department of Chemistry, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

Abstract:

Some recent and ongoing studies related to the use of mosses as biomonitors of atmospheric metal deposition are briefly reviewed. Issues discussed in particular are the conversion of concentration in moss to absolute deposition values, introduction of a second-generation ICP-MS instrument for moss analysis, determination of stable lead isotope ratios in mosses for source apportionment, and temporal trends of lead and cadmium deposition in Norway. A novel nuclear technique for the determination of fluorine in mosses surrounding an aluminium smelter is presented.

1. INTRODUCTION

Biomonitoring of air pollutants using mosses has been employed in Norway for the last 25 years employing nuclear as well as non-nuclear methods of analysis. Nationwide metal deposition surveys based on the moss technique were carried out in 1977, 1985, 1990, and 1995, each time including about 500 sites. These studies form an integral part of the national monitoring system for long range transported pollutants. In addition considerable research has been carried out in order to critically assess the moss technique. A summary of this extensive work was presented in a previous report (1). In the following text current work in the author's laboratory will be briefly described and some plans for the future will be discussed.

During the last decade collaboration has been started with scientists in a number of countries, particularly in eastern Europe, in order to implement the experience from the Norwegian studies in areas where such studies were not done before. Some of these studies will be described by other participants at this meeting (2,3), while others will be mentioned in the following.

2. METHODS

In the routine monitoring in Norway using the moss technique ICP-MS has been the preferred analytical technique since 1990 since it is able to provide reasonably good data for most elements of primary interest in this work. Among the ten elements in focus eight (V, Cr, Fe, Ni, Cu, Zn, Cd, Pb) normally do not represent any problem. Considering the two remaining elements the determination of As is sometimes difficult because of interference from $^{40}Ar^{35}Cl$ at mass 75. This problem is now about to be solved due to the introduction of a new field sector ICP-MS instrument with a mass resolution far superior to that of the previously used quadrupole istrument. In the case of Hg erratic results were obtained by ICP-MS, and atomic fluorescence has therfore been routinely used for this element.

Except for collaboration projects where JINR, Duibna has been involved, neutron activation analysis has not normally been used in our recent moss projects. An interesting exception is a study of fluorine pollution around an aluminium smelter in western Norway where a method employing epithermal irradiation and cyclic activation was shown to be

suitable for the determination of F in mosses and surface soils. The method is based on measurement of 26.9 sec ^{19}O produced by (n,p) reaction in ^{19}F.

3. RECENT INVESTIGATIONS

3.1. Conversion of concentrations in moss to absolute deposition values

Since 1990 parallel studies of metal deposition have been performed in Norway using respectively the moss technique and conventional bulk precipitation sampling. In 1990 deposition values for some metals from precipitation collected at 6 stations were compared with concentrations of the same elements in moss (*Hylocomium splendens*) near the same stations, and calibration curves were drawn (5). A very high correlation was observed for lead, whereas for other metals the relations were not so clear. In 1995 the experiment was repeated, this time with 13 precipitation stations (6), and with sampling of both *Hylocomium splendens* and *Pleurozium schreberi*, the two mosses employed in the joint European moss surveys. Significant positive correlations were found for V, Fe, Co, As, Y, Mo, Cd, Sb, Tl, and Pb. Concentrations of most of the 48 elements studied were quite similar in the two moss species, but the data may indicate that particles of geogenic origin were more effectively trapped in *Hylocomium splendens*. No variations were observed in the concentrations of the studied elements over the sampling season.

3.2. Temporal trends in atmospheric deposition of Pb and Cd in Norway

Over the years the analytical methods used in the nationwide moss surveys in Norway have varied to some extent, and it was suspected that this might be a source of uncertainty when using these data to study temporal trends in atmospheric deposition in different regions. This suspicion was particularly strong for Pb and Cd, which were determined by respectively flame AAS, graphite furnace AAS, and ICP-MS in different surveys. Moreover the lack of suitable reference materials in the early surveys made it difficult to assess the accuracy of these data. Therefore samples from 1977, 1985, 1990, and 1995 collected at the same site at 70 different geographical locations in Norway were re-analysed for Pb and Cd by graphite furnace AAS. The samples were analysed in random order, and the accuracy of the analyses checked against certified reference materials. From the results it is obvious that data from some of the previous surveys are either systematically high or low. In one case the Pb level was as much as 25% low (7).

3.3. Source apportionment of lead in mosses by stable isotope ratios.

Moss samples from 7 different sites taken at different times were analysed for the stable lead isotope composition using thermal ionization mass spectrometry (8). It was apparent from the data that the lead deposited in different parts of Norway was at least partly derived from a different mixture of sources. Whereas the $^{206}Pb/^{207}Pb$ ratio varied considerably over time in the south-western part of the country, it was distinctly different and very constant during the same period in the far north. The project is now extended in time and space, and the new data so far appear to support the conclusions drawn from the more limited material.

4. FUTURE WORK

4.1. Year 2000 moss survey in Norway

The 2000 moss survey in Norway will be run in a similar way as previous nationwide surveys, and the data will also be submitted to the joint European survey as before. A part of the material will be analysed by both ICP-MS instrument types mentioned above, and the feasibility of the new sector field instrument for this kind of survey will be tested.
In addition to the nationwide study the Norwegian Pollution Control Authority has asked for more detailed monitoring around some local pollution sources.

4.2. Atmospheric deposition in the catchment of Prut, a border river between three countries

Within the framework of the "NATO Science for Peace" program a study of heavy metals in the river Prut will be performed. The river Prut catchment is shared between three countries: Romania, Ukraina, and the Republic of Moldova, and the prosject is a co-operative effort between our laboratory and colleagues in Iasi (Romania) and Chisinau (Moldova). As a part of this project an attempt will be made to determine the atmospheric supply of the metals in question to the catchment by moss analysis. Since it is not yet clear that the naturally growing mosses in the area are suitable for this purpose, it may be necessary to use transplanted mosses.

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