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USE OF MOSSES AS BIOMONITORS OF ATMOSPHERIC DEPOSITION OF TRACE ELEMENTS

E. STEINNES
Department of Chemistry,
Norwegian University of Science and Technology,
Trondheim, Norway

Abstract

Some basic facts about the use of mosses as biomonitors of atmospheric trace element deposition are reviewed, and advantages and limitations of this approach are discussed, largely on the basis of experience from regular use of this technique in Norway over the last 20 years. Topics discussed include different versions of the moss technique, mechanisms and efficiences of trace element uptake, conversion of concentrations in moss to bulk deposition rates, and contribution from sources other than air pollution to the elemental composition of different elements. Suggestions are presented for further work in order to extend the use of mosses as biomonitors.

1. INTRODUCTION

Mosses have no root system, and pick up nutrients and other chemical substances mainly from wet and dry deposition. Moreover they have a high capacity to retain many trace elements. Mosses, and particularly species growing on the ground, have therefore shown to be suitable biomonitors of atmospheric deposition of trace elements. Since this approach was first proposed 30 years ago to monitor the deposition of lead [1] it has come into use in more than 15 countries in Europe [2], and the original applications focusing on a single or a few elements have been succeded by multi-element surveys where more than 30 elements have been studied simultaneously by techniques such as inductively-coupled plasma mass spectrometry [3] or epithermal neutron activation analysis [4]. In Norway the moss technique has been used regularly for the last 20 years in deposition surveys on a national scale [5-9]. In the present paper experience from this monitoring activity will be reviewed, and typical results for trace elements will be presented and discussed. Emphasis will be put on the possibility to calibrate moss concentration values versus bulk deposition data from precipitation analyses in order to convert relative deposition data, as normally obtained by moss analysis, to absolute deposition rates. Furthermore sources of trace element supply to mosses other than atmospheric deposition of pollutants will be discussed, and the significance of these sources for various elements will be assessed.

2. APPROACHES TO STUDY THE SUPPLY OF AIRBORNE TRACE ELEMENTS

The conventional way of studying rates of atmospheric deposition is to analyse precipitation samples collected over a given period of time and calculate deposition figures on the basis of the results of the chemical analyses. The samplers may be of the "bulk deposition" type, sampling all the time and thus also collecting dry-deposited aerosols during dry periods, or "wet-only" samplers which open automatically when a precipitation event starts and thus collect only wet deposition. These measurements are difficult because of the generally low levels of trace elements in precipitation. This means that a) the analyses are difficult and b) contamination problems during sampling and analysis may often be serious unless extreme care is taken to avoid them. Moreover the running of a precipitation sampling network will normally be restricted to a few stations. Thus the possibility of spatial distribution studies will be very limited.

Some of these problems can be overcome by the use of plants as biomonitors. Mosses and lichens, which absorb aerosols as well as substances dissolved in precipitation quite efficiently, have been most frequently used for this purpose. These biomonitors are easily collected, and the concentrations of trace elements in the moss or lichen is normally several orders of magnitude higher correspondingly smaller, and the sampling and analysis much easier and cheaper. The use of biomonitors therefore allows deposition surveys to be carried out simultaneously over large areas with a high spatial resolution. On the other hand the results are at best a relative measure of the atmospheric deposition of the elements in question, but this may be adequate for the study of temporal and spatial trends. What the results indicate is an integrated exposure over a certain period of time.

In Norway the moss *Hylocomium splendens* is used for trace element deposition monitoring on the national scale every 5 years. This moss species has a growth pattern that makes it easy to distinguish the annual incremental growth. The last 3 years´growth is taken for analysis, which means that the exposure period is well defined. Several other moss species also grow in a way that makes it possible to estimste the age of the sub-sample taken for analysis. Lichens absorb trace elements from the atmosphere with similar efficiency as mosses [10] but the age determination is often difficult or impossible. Lichens are therefore generally inferior to mosses as biomonitors of atmospheric deposition of trace elements.

Vascular plants have also been suggested as trace element biomonitors. In particular conifer needles or leaves of deciduous trees shed annually might seem convenient, since the exposure period in this case would be extremely well defined. A major drawback however is that it is normally not possible to distinguish beween fractions of an element in the sample supplied from the soil by root uptake and absorbed from the air - unless the surface layer is washed off and analysed separately [11]. Moreover comparative studies have shown that the retention of trace elements in conifer needles from the air is sometimes less than 10 % of that observed in moss growing at the same site [12]. It seems reasonable to assume that the waxy surface of needles (and some deciduous leaves) is a better retention surface for aerosols than for ions dissolved in precipitation.

Organic surface soils concentrate many trace elements from the atmosphere very efficiently, and can therefore be used to monitor long time integrated exposure of these elements. Peats [13, 14] and natural surface soils from boreal forests and other ecosystems in temperate regions [15, 16] have been used quite successfully for this purpose. A main interfering problem in the latter case is contribution from mineral matter in the soil, but there are ways of overcoming this problem [17], in particular if the underlying subsoil is analysed simultaneously. Peat cores can be conveniently used to monitor temporal trends of atmospheric deposition of trace elements [18], and is an interesting alternative to snow and ice cores and lake sediments, neither of which are generally applicable.

3. MOSSES AS MONITORS OF ATMOSPHERIC DEPOSITION

3.1. Classification of mosses for biomonitoring

Mosses have been used for biomonitoring in a number of different ways which may lead to rather different results, and some kind of classification seems necessary at this point.

The large-scale mapping excercises are normally done by means of *indigenous* (i.e. naturally growing) mosses. An alternative possibility is to use moss *transplants*, e.g. in the form of "moss bags" [19]. In this approach a sample of "clean" moss, either collected from a very clean area or cleaned with dilute acid before use, is left at the sampling site for a given exposure period. This approach has been mainly used in local studies with rather high pollution levels. In cases with high exposure of either heavy metals or gaseous pollutants the indigenous moss populations may have been exterminated, and the use of transplants may be the only possibility.

Epigeic mosses (growing on the ground) are preferred in the regional surveys in northern and central Europe. Where mosses grow on the top of a substrate mainly consisting of organic soil and decaying plant debris, this is clearly preferable to using *epiphytic* mosses growing on trees. In the case of mosses collected from trunks or branches of trees it is very likely that the incoming flux of trace elements from the atmosphere - wet or dry deposition - will be substantially modified by the canopy before reaching the moss, and it is also conceivable that trace elements supplied to the tree from the soil through the root system and eventually leached e.g. from leaf surfaces will form part of the exposure of the moss. In warmer climates however the use of epigeic mosses may be rendered impossible because they grow more or less directly on the mineral soil and hence pick up soil particles to a great extent. In such cases other solutions must be found, and one possibility would be to use epiphytic species growing on stumps. In any case, when collecting mosses in forest sampling under the canopy of trees should be avoided as far as possible.

Two groups of epigeic mosses have been most commonly used for moss surveys:_*Feather mosses* such as *Pleurozium schreberi* and *Hylocomium splendens,* and peat mosses such as *Sphagnum fuscum.* Peat mosses possess the advantage of growing on a pure organic substrate, minimising the problem of soil contamination, but the habitat of a given species of *Sphagnum* moss normally does not show the kind of even geographical distribution necessary for a regional survey. The two above epigeic species are both very common in the boreal zone and can be used interchangeably in monitoring studies because they absorb many trace elements with very similar efficiency [20].

Lichens to be used for trace element monitoring can be classified in as similar way as done above for mosses. The advantages and problems associated with the various classes are likely to be similar for lichens as for mosses.

3.2. Uptake efficiency for trace elements in mosses

Trace elements may be absorbed on the moss from the atmosphere either as soluble chemical species in wet deposition or contained in particles from dry deposition. Part of the trace element content of particulates may eventually be released by weathering and reabsorbed by the moss. The uptake efficiency for a given element differs between different moss species [21], and large differences in uptake efficiency are evident for different element in the same moss species [20]. Presumably the "uptake efficiency" is also different for the same element from wet and dry deposition, and it seems reasonable to assume that the particle size distribution is another significant factor. Whereas uptake efficiencies for particulate-bound trace elements are generally poorly known, the knowledge is better regarding the uptake of dissolved elements in ionic form. Ions may be subject to active uptake into cells or attached on the moss surface by physical and chemical forces. Methods are available to distinguish between intracellular and surface-bound fractions of elements [22]. As far as the surface bound fraction is concerned, little is known about the binding mechanisms, but the fact that different metals show rather large differences in their retention capacities [20] indicates that both simple cation exchange on negative surface charges and complex formation with ligands on the moss surface are involved. Laboratory studies with uptake of selected metals to moss from artificially made precipitation samples, and at realistic metal concentrations in the solution, indicated that the moss behaves somewhat similar to a commercial cation exchanger [23]. The sorption of Pb and Cu was stronger than of Zn and Cd. The uptake was less from precipitation with significant content of marine salts, which may be due to competition from marine cations such as Mg, or possibly partial metal complexing by the chloride ion. Uptake was significantly reduced when the precipitation pH dropped appreciably below 4.0.

In a recent study [20] of relative uptake efficiencies for different air-pollution associated trace elements in *Hylocomium splendens* and *Pleurozium schreberi,* Pb and Tl were found to be most strongly bound among the elements studied. Relative to a Pb uptake defined as 1.00, the following approximate factors were observed: Mo, 0.75; V, Cd, 0.60; Sb, 0.25; As, Se, 0.15. The above elements showing low relative uptake are probably present mainly as anions in wet deposition. Experience from the national monitoring work in Norway however clearly indicates that the moss technique works well even for these elements with respect to temporal and spatial trends [6-9].

3.3. Conversion from relative to absolute deposition rates

Comparison of trace element concentrations in moss and bulk precipitation samples at six different stations in Norway [24] showed that calibration of concentrations in moss to bulk deposition could be done very well for some elements, thus converting relative deposition figures from moss surveys to absolute deposition rates. Examples are shown in Fig. 1 for Pb and Cu. For Pb the calibration curve goes through the origin, indicating that essentially all Pb in the moss was derived from atmospheric deposition. In the case of Cu the intercept with the ordinate axis indicates a "baseline" concentration of about 3 ppm in the moss not related to deposition. More recently the study

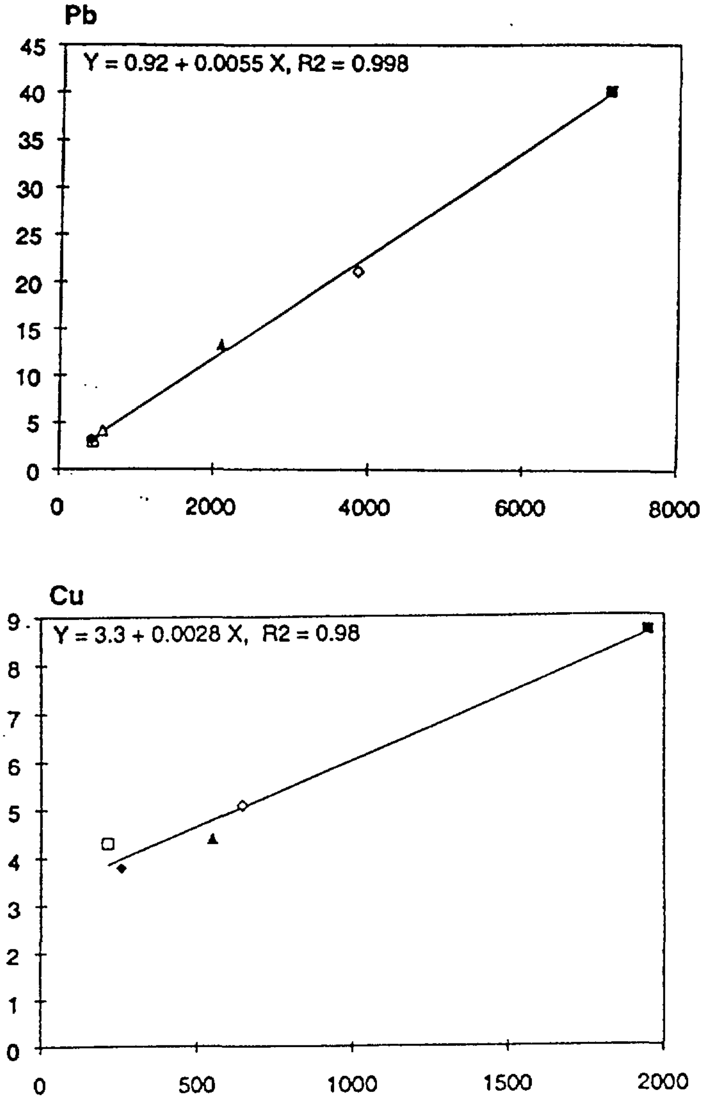

Fig.1. Calibration plots of trace element concentrations in Hylocomium splendens moss ($\mu g\ g^{-1}$) versus atmospheric bulk deposition ($\mu g\ m^{-2}$) from precipitation analysis. Modified from Berg et al. [24].

was extended to 13 stations, and satisfactory calibration relations were obtained also for elements such as As and Sb [20] earlier shown to have a low relative uptake in the moss.

4. PROBLEMS WITH THE USE OF MOSSES AS BIOMONITORS

Although the moss method has had considerable success in the past and the areas of application are currently extending, there are certain limitations that should not be overlooked when this method is used for biomonitoring of trace element deposition from the atmosphere. Some of these problems are discussed in the following. The discussion is specifically related to the application of naturally growing epigeic mosses. Many of the problems discussed are also relevant and may be even more serious when other biomonitoring approaches are used.

4.1. Contribution from sources other than air pollution

As discussed more in detail elsewhere [25] there are several other sources for mineral elements in mosses than the deposition of air pollutants from local and distant sources, which is the target of the biomonitoring work:

TABLE I. RELATIVE INFLUENCE FROM DIFFERENT FACTORS TO THE ELEMENTAL COMPOSITION OF MOSSES GROWING IN RURAL AND REMOTE AREAS (Cfr. Section 4.1).
+, ++, +++ : positive contribution, increasing importance.
-, - -, - - - : negative contribution (removal), increasing importance.

Element	Air pollution	Marine factor	Vegetation factor	Soil factor
Al				+++
V	++			+
Cr	+			++
Mn		- -	+++	
Fe	+			+++
Ni	++			++
Cu	++		+	
Zn	++	-	++	
As	+++	-		+
Se	++	++		
Br		+++		
Sr		+++		+
Cd	++		+	
Sb	+++			
Hg	++			+*
Pb	+++			

* Gaseous emission of Hg^0 from the soil may be absorbed in the moss.

a. Atmospheric supply of marine elements and other components from natural cycling processes. In coastal areas far from local pollution sources e.g. elements such as Br and Se in moss are likely to be derived mainly from this source [6].

b. The "Vascular pump", i.e. root uptake of elements into higher plants, in particular trees, and subsequent leaching onto the moss from living or dead plant tissue.

c. Windblown mineral dust from local soil. This can be a serious problem, in particular in areas with sparse vegetation such as the polar regions [26, 27].

d. Transport of soluble compounds from the soil into moss tissue, particularly during periods with excessive soil/water contact such as during snowmelt. Although mosses do not have a root system, influence from this source cannot be disregarded, in praticular in areas with low atmospheric deposition [28].

The relative contribution from these additional sources will differ substantially among the elements. In Table I experience from the Norwegian moss surveys with respect to the relative influence from different source categories is presented for 15 of the elements most frequently studied in connection with environmental pollution. From the table and the evidence it is based on it is obvious that e.g. the deposition of Mn cannot be studied by the moss method. Also for elements such as Fe and Zn there are considerable problems, unless the contamination level is very high.

4.2. Other disturbing factors

Although the contribution from other sources to the elemental composition of the moss is the main problem to be considered when evaluating the results of a moss survey, there are also other factors that should not be overlooked, such as:

- Differences in growth rate of the moss within the region.

- Re-distribution of snow by wind, contributing to irregular snowmelt patterns.

- Variable forest density, influencing the dry deposition to the moss.

- Variations in precipitation chemistry during the exposure period.

- Sensitivity of the moss to air pollutants (SO_2, metals, - -).

5. CONCLUDING REMARKS AND SUGGESTIONS FOR FURTHER WORK

Even though the problems discussed above to some extent influence the precision and accuracy of the moss technique to depict the atmospheric deposition and suggest some limitations to the use of this approach, it is clear that biomonitoring of trace elements has come to stay for the foreseeable future. It is hardly possible by any other approach to obtain such a detailed picture of variations in time and space within reasonable limits of cost. The calibration of the moss technique versus bulk deposition adds futher to the usefulness of the method.

A discussion of the feasibility of different analytical techniques for moss surveys is beyond the scope of the present paper. Still it is clear that nuclear and nuclear-like methods have played, and are presently playing, an important role in this work, in regular surveys as well as in the calibration of reference materials to be used in this work [29].

The use of the two epigeic feather mosses *Hylocomium splendens* and *Pleurozium schreberi* in large-scale biomonitoring studies has in most cases worked very well in the northern half of Europe because one species or the other can be easily found in most places. When moving this activity farther south, and eventually to other continents, these mosses may have to be replaced by other species of moss or lichen, and epigeic species may not any longer be the best choice. In order to extend the existing European deposition monitoring network beyond its present borders, it will be necessary to calibrate new species versus the present ones with respect to collection efficiency of important trace elements. It also appears advantageous to carry out calibrations against bulk deposition wherever a new biomonitor species is introduced for local or regional studies, in order to be able to estimate absolute deposition rates.

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