CHAPTER 11

The Use of Moss-bags in Aerosol Monitoring

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ABSTRACT

Ideally, it would be desirable to characterize the atmospheric aerosol as follows:

(i) identify the aeolian dust component (derived from arid regions)
(ii) locate the areas of its origins
(iii) estimate its rate of deposition to the ground (including interception by vegetation)

Such information would assist in understanding the input–output dynamics in and around deserts including regional dust transport and indicate any dry-flushing effects on the productivity of vegetation receiving dust inputs.

Trace-element analysis has been used in elucidating items (i) and (ii) above, and for all those items above various kinds of traditional dry deposit gauges (e.g. filter paper pads) and dustfall collectors have been used.

This paper explores the possible use of specially cleaned samples of moss contained in flat, nylon-mesh envelopes (moss-bags) as substitutes for these gauges.

Moss-bags are very inexpensive to produce, can be sent easily by postal service to analytical laboratories and thus can be used in large numbers to make wide-scale synoptic surveys. They collect aerosol in terms of particle sizes and quantity per unit area with an efficiency closely similar to that of short grass sward, without the 'bounce-off', 'blow-off' or turbulence effects shown by certain types of dry-deposit gauge, which may tend to undersample, especially at higher wind-speeds.

Mosses have a high cation-exchange capacity and there is virtually no loss of metallic elements even under periods of intense rainfall. They can thus be used as total (wet and dry) collectors. This usefully avoids the need to carry out separate rainfall analyses to allow for the leaching of soluble trace-elements in dust-fall gauges following rain-episodes.

Evidence so far collected indicates that moss-bags orientated vertically to face various compass directions act somewhat like 'dipole aerials' so that, for pollutants at least, distant emission sources can be located. The possible utility of this for identifying the origins of transported dust is also discussed.

11.1 INTRODUCTION

Although dustfall buckets and various other kinds of dry-deposit (DD) and total-deposit (TD) collection devices have been widely used in the past to sample the atmospheric aerosol, recent improvements in direct air-filtration equipment, including isokinetic and high-volume samplers have proved capable of providing more unbiased estimates of atmospheric constituents. Additionally, the greatly increased sensitivity of modern chemical analytical methods has reduced the need for the large samples formerly required for analysis, thus further decreasing dependence on deposition samplers.

However, although the difficulties of relating the results obtained from deposit gauges to the actual concentrations of airborne constituents in the ambient atmosphere are well known, there are three principal reasons why deposit gauges still have a useful part to play in our understanding of aerial transport phenomena:

(1) They do not depend on the availability of electrical power supplies and although by no means a substitute for the direct measurement of air concentration (AC), they do at least give some idea of airborne constituents in remote places.

(2) Unlike AC gauges, they are not fixed volume samplers. Thus, in this respect they do not resemble the human lung and hence cannot be so conveniently related to medical studies as AC gauges can. However, they do reflect the nature and quantities of airborne constituents likely to be intercepted by the ground (including surface waters, soils and vegetation). Hence they are approximate measures of the atmospheric input of nutrients and pollutants to the food-chain. In this respect they relate usefully to agricultural, forestry, ecosystem and water-quality studies of chemical distribution.

(3) When investigating the fluxes of airborne materials from series of measurements in time and space, deposit gauges can often be more informative than AC gauges as they can show the net effects of aerial transport from one place to another.

When these features are seen in the context of aerosol-transport studies in arid zones, deposit gauges may be useful in studying: (a) the dry flushing effect on agricultural soils of airborne macronutrients and trace elements (K, Ca, Mg, N, S, Mn, B, Co, Cu, Zn, etc.) derived from deserts; (b) the genesis of aeolian soils and (c) the input/output dynamics of ground–surface materials in and around deserts.

The ensuing paper highlights some of the above-mentioned differences between AC, DD and TD methods and examines how far flat, nylon-mesh packets containing epiphytic or ombrotrophic moss (moss-bags) might be worth trying out as a convenient and inexpensive substitute for the more traditional type of deposit gauge and their possible use in future arid zone studies.

Unless otherwise stated, the type of deposit gauges being compared are as follows:

(a) *Total deposit gauge* (TD). This is like a rain gauge with a polythene funnel (the mouth is screened with 0.5 mm terylene mesh to exclude insects). It delivers deposited dust and precipitation into a polythene collecting bottle (Cawse and Peirson 1972).

(b) *Dry deposit gauge* (DD). This is essentially a flat horizontal pad of filter-paper protected above from rain by a sheet of perspex, but open to winds on all sides so that blown particles can deposit on the filter paper surface (Cawse and Peirson 1972).

(c) *Moss-bag* (MB). This is a flat 10 x 10 cm envelope of 2 mm nylon-mesh containing specially cleaned moss (usually *Sphagnum acutifolium* aggregate), evenly packed to occupy the whole surface area of the packet which is orientated horizontally or vertically to face a particular direction or hung freely suspended from a nylon thread.

All the gauges are normally positioned 150 cm above the ground surface. The air concentration sampler with which they are compared sucked air through a Whatman filter-paper at the rate of approx. 5 l/min (Cawse and Pierson, 1972).

11.2 MOSS-BAGS

11.2.1 Development of the method

Epiphytic mosses receive all their mineral nutrients from the air (Tamm, 1953), and therefore any metallic substance in the moss must come from this medium. Following this premise, Rühling and Tyler (1970) showed how varying metal concentrations in naturally growing epiphytic mosses in Sweden might reflect prevailing aerial metal burdens.

Investigations in the Lower Swansea Valley area (Goodman and Roberts, 1971) showed abnormally high levels of several heavy metals in the epiphytic moss *Hypnum cupressiforme*, both from natural populations and also in moss collected from clean areas and hung out in nylon mesh bags at atmospherically polluted sites. Elevated metal levels first appeared 10 km WSW (upwind) from Swansea. These rose to about 4–20 times the 'normal values' found in and around the city of Swansea and steadily fell off again to 'normal values' 25–30 km NNE (downwind of Swansea). This was the first study using moss-bags and the method was developed further and has been used extensively by the present authors and also by other workers.

Clean Sphagnum moss (*Sphagnum acutifolium* aggregate) is collected from rural areas in Wales, away from industrial activity. Following three washes in 0.5N HNO_3 for three days, the moss is soaked and washed three times in double-distilled water, surplus water removed and the moss mixed to obtain as homogenous a material as possible.

Approximately 10–15 g (equivalent to about 2.0–2.5 g dry weight) is then sewn into flat 10 x 10 cm nylon mesh bags of approximately 2 mm mesh size (obtained from Henry Simon, type 18 GGN) so as to occupy the whole internal area of the bag. The bag is positioned in the centre of a circular loop of plastic-covered wire, held at the corners by four nylon threads each of which is tied to the loop.

After exposure to the air at the test site (usually on a bamboo cane at 150 cm above ground for 2–4 weeks) the bags are dried at 40 °C to constant weight. The surface area of moss is accurately measured and the moss then removed carefully into Kjeldahl flasks and weighed. Following wet digestion in 15 ml of a mixture of 'Aristar' grade nitric and perchloric acids (4 : 1 ratio), the solutions are boiled gently down to a few millilitres and made up to 25 ml volume.

The solutions are then analysed for metals by atomic absorption spectrophotometry using a Techtron model AA.3 (Mercury is analysed using a flameless technique).

After correction for the original metal content of unexposed moss, the amount of metal deposited and retained on the bag is calculated in terms of μg metal per cm^2 per month.

Further development work showed that the moss-bag appeared to be a useful, inexpensive, semi-quantitative indicator of metal pollutant levels and can be used to monitor relative changes in airborne metal burdens in space and time.

11.2.2 Using moss-bags to locate sources (April 1971, Isopleth survey)

In an experiment financed by the Natural Environment Research Council and the University of Wales, an array of moss-bags was set up in the Lower Swansea Valley, UK, at a network of sites, for a period of one month (10 April–11 May 1971). At each site, four bags were freely suspended 2 m above the ground-surface; two bags contained *H. cupressiforme* and the other two contained *Sphagnum acutifolium* aggregate. At the end of the period, bags from 80 sites were analysed in order to discover how far:

(a) meaningful spatial patterns of metal distribution would emerge;
(b) the results from the *Hypnum* and *Sphagnum* bags were comparable.

The results showed that regular patterns of metal distribution could be clearly discerned, allowing sites with similar metal values to be joined by isopleth lines giving a type of 'contour map' of intercepted airborne metal levels.

Magnesium isopleths showed a tendency to increase parallel to the coast as the sea is approached, an example of the, by now, well documented marine source of airborne magnesium. Other metals fell into two distinct groups. One group, nickel and cobalt showed a roughly concentric zonation of isopleths with the highest values centred close to a nickel refinery. The other group zinc, lead, and cadmium showed a broadly similar pattern with the highest values centred some 4.5 km farther south, close to a zinc smelter. The copper isopleths had a double centre,

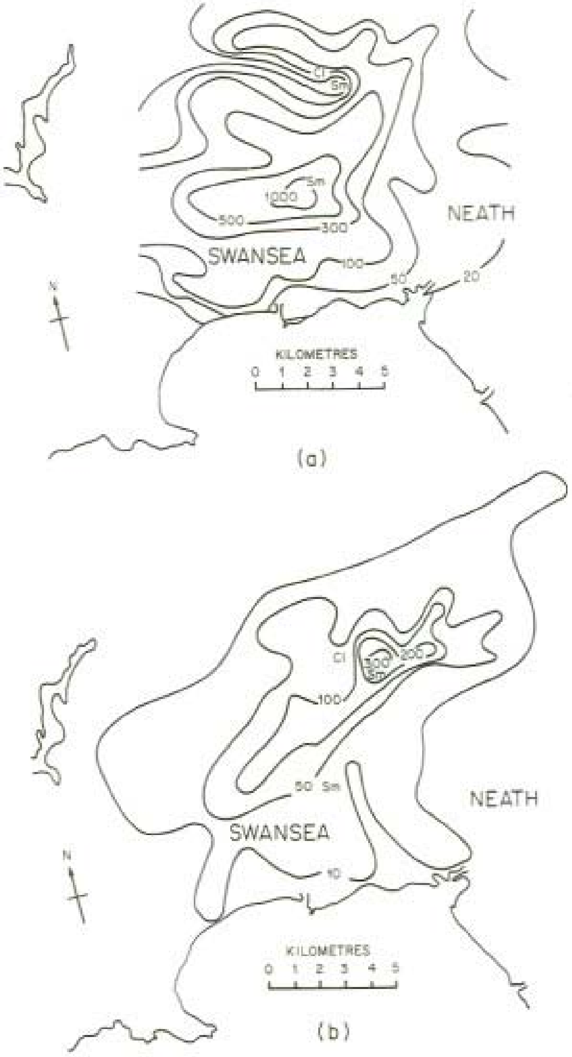

Figure 11.1 (a) Lead and (b) Nickel deposition onto Sphagnum moss-bags exposed during April 1971 (expressed as ng cm^{-2} day^{-1})

indicating some copper output by both works. The results clearly showed that metal emissions as: (a) wind-blown dusts from the old contaminated soils and waste-tips of former industry; (b) urban smoke; (c) vehicle exhausts and (d) other industries; were of far less significance than anticipated when compared with output from the two ongoing industries. Figures 11.1(a) and 11.1(b) show isopleth maps for Pb and Ni respectively.

The above conclusions emerged irrespective of whether the moss-bags contained *Hypnum* or *Sphagnum*. The level of each metal at each site, obtained from a *Hypnum* filled bag, compared closely with that obtained from a *Sphagnum* filled bag. All *Hypnum* data, taken site by site, correlated in a highly significant way with the corresponding *Sphagnum* data indicating that closely similar isopleth pictures of metal distribution are obtained irrespective of which moss is used.

11.2.3 Using moss-bags to follow airborne-metal changes with time (December 1971, Isopleth survey)

The use of moss-bags as a relative measure of the geographical distribution of metals around an emission source – changes in space – can be paralleled by their use to follow changes with time.

A good example was provided when in mid-May 1971 the zinc smelter in the Lower Swansea Valley mentioned above, closed down following industrial restructuring by the company concerned. The nickel works, 4.5 km north of the zinc smelter, continued to operate as usual. The effect of this shutdown on metal burdens in the area was monitored by regular sampling. In particular a second large-scale moss-bag survey using the same sites as in April 1971 was carried out in December (10 December–7 January 1972).

Although December patterns for the geographical distribution of all the elements were basically similar to those of April 1971, i.e. centred around the two metal works concerned, there were marked quantitative differences.

The average retention of nickel and cobalt by moss-bags doubled during the December period. There appeared to be a 'heaping-up' effect of Ni and Co isopleths around the nickel works (Figure 11.2(b)). This may have been caused by: (a) increased production at the works (considered unlikely); (b) the prevailing winter weather being less favourable for the dispersion of aerial particulates; and/or (c) the damper weather causing increased interception on the moss-bags because they stayed moist for longer periods. This latter phenomenon, i.e. wet moss-bags being more efficient interceptors, was demonstrated by Chamberlain and Clough in wind-tunnel experiments with moss-bags and is similar to what would happen with moist ground vegetation. Changes in wind speed and direction were largely discounted as being of any importance because apart from a slight increase in westerly and north-eastern winds in December, wind-rose data for the April period were substantially the same as those for the December period.

In sharp contrast to this increase, zinc, lead, and cadmium levels fell in December, by factors of × 4–10, to much less than the April levels (Figure 11.2(a)). According to these results, the area was no longer affected by appreciable fall-out of zinc, lead and cadmium and the removal of the swamping effect of this emission source enabled subsidiary emission sources to be located, e.g. wind-blown dusts from the old metal-rich wastes of former industry now contributed discernibly to the isopleths. This can be seen as a 100 ng isopleth 1 km North of Swansea (Figure 11.2(a)).

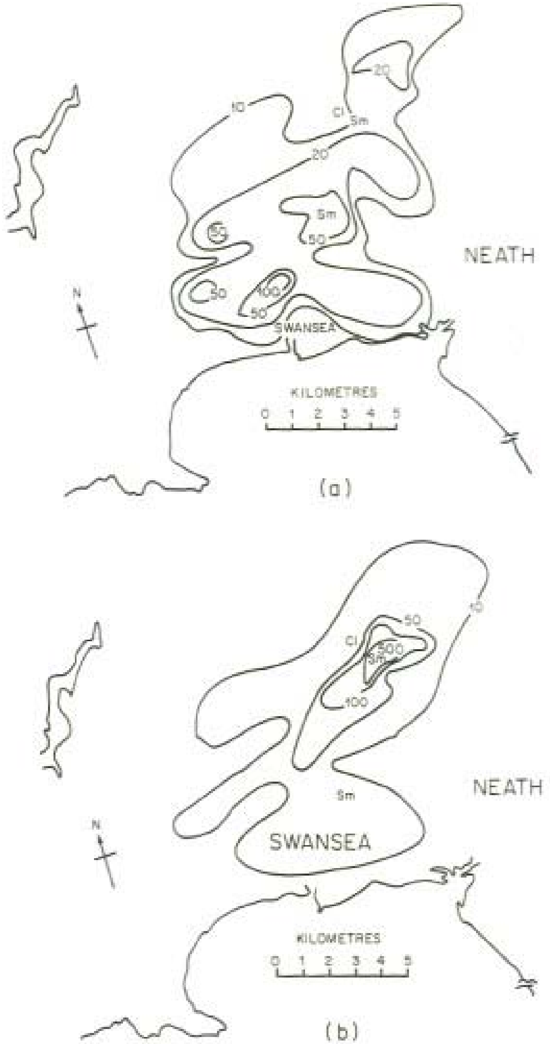

Figure 11.2 (a) Lead and (b) Nickel deposition onto Sphagnum moss-bags exposed during December 1971 (expressed as ng cm^{-2} day^{-1})

The copper isopleth map now lost is double centre; the single effective centre now being close to the nickel works.

A further feature of great interest was that the moss used had a very high cation exchange capacity. Thus, elution of solutions of metallic elements through columns of moss retained virtually all the dissolved metal on the moss. Likewise, moss-bags exposed to drenching rain (both natural and simulated) retained both the metallic elements already deposited on the bags and also the soluble metals in the rain itself.

In view of their cheapness, and the likelihood of their behaving like a grass sward as regards particle interception (Clough, 1974), moss-bags might be suitable for routine network sampling and monitoring. A special advantage is that these can easily be sent in polythene bags by letter post to a central analytical laboratory. This makes them more convenient to handle than TD bottles. However, further information on the behaviour of moss-bags as a deposition gauge is required. It is natural to ask:

(a) How they relate to the existing more traditional methods (TD, DD and AC)?
(b) How they and the traditional gauges relate to interception by ground vegetation?

11.3 COMPARISON OF MOSS-BAGS WITH OTHER GAUGES

During the period 1 June 1972–31 May 1973 a study of metal deposition on to moss-bags (MB), total deposition (TD), dry deposition (DD) gauges and measurements of air concentration (AC) were made at nine sites in South Wales sponsored by the Welsh Office. The Natural Environment Research Council sponsored a study of a further seven sites (six in the UK and one in the Netherlands). MB measurements were made by the present authors and the other measurements (TD, DD, and AC) by AERE Harwell. The following seven metals were analysed for all gauges: Co, Cu, Fe, Mn, Ni, Pb, and Zn. This enables comparisons to be made between airborne metal deposition on to moss-bags and the other three gauges. In addition, the relationship between metal retention by moss-bags and a grass sward was examined.

11.4 FACTORS INFLUENCING AIRBORNE METAL DEPOSITION ON GROUND VEGETATION AND SAMPLING GAUGES

Extensive work has been carried out by Chamberlain and Clough (Chamberlain, 1966a and b; Chamberlain and Chadwick, 1972; Clough, 1973, 1974) using a wind tunnel to investigate the behaviour of airborne particles during their deposition on receptor surfaces (trays of grass sward, trays of moss, moss-bags and the filter paper surfaces of dry deposit gauges). This showed that the proportion of airborne particles retained by the receptive surfaces of the grass sward and the three types of gauge depends upon:

(a) The retentive characteristics of the receptor surface ('hairiness', wetness, or stickiness).
(b) Factors affecting the delivery of particles to the receptor surfaces (wind speed, turbulence).

In the following summary it must be borne in mind that, as indicated in the Introduction 11.1 above, AC gives a rough estimate of lung burden whilst TD, DD and

MB all provide approximate guides to food chain burden *via* vegetation interception.

It should be emphasized at the outset, however, that the deposit gauges (TD and DD above) were not originally designed to simulate a grass-surface, but to provide a useful measure of deposition behaviour of the various elements in the atmospheric aerosol (Cawse and Pierson, 1972). Similarly, the moss-bag gauge was designed to simulate deposition to natural populations of moss growing epiphytically on walls or trees (Goodman and Roberts, 1971). However, since these are the *only* convenient, inexpensive methods available to us for estimating deposition to ground vegetation, it is clearly desirable to determine how they relate to one another and, as far as possible, to discover how well they reflect interception by grass swards or other ground vegetation.

(1) Despite the apparent design differences in these three gauges (TD, DD, MB), the physical principles governing deposition on their retentive surfaces are basically the same as those controlling interception by a grass sward.

(2) The physical properties which make deposition surfaces efficient interceptors of airborne particles are 'hairiness', wetness or stickiness. The DD filter paper, which is kept dry and is relatively smooth, would not be expected to trap particles as efficiently (V_g)* as grass which is 'hairy', and periodically wet. Moss-bags, which get periodically wet to about the same extent as the grass at the site where the moss-bag is exposed, and are relatively far more hairy than grass, would be expected to trap particles more efficiently than grass. Because of its terylene mesh cover, the filter funnel of the total deposit gauge may possibly be more efficient than the filter paper of the dry deposit gauge. It is usually assumed that dry deposition on the filter paper of the dry deposition gauge (DD) is equivalent to that on the rain funnel of the total deposition gauge (TD) for equal projected horizontal areas.

(3) Particles of different sizes are not retained on any of these deposition surfaces with equal efficiency. Thus, for filter-paper, larger particles (c. 10 μm) and the smallest (c. 0.1 μm) are retained most efficiently (high V_g), with intermediate sized particles showing a sharp minimum in the proportion retained at c. 0.5 μm diameter (low V_g). This gives a pronounced V-shaped curve for the proportion of particles retained with increasing particle size. Grass swards and moss-bags have a closely similar particle size retention curve which is somewhat the same as that for filter paper but more U-shaped, i.e. there is a flattened trough at the minimum between particles of 0.1–2.0 μm – an important size fraction in air.

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*The proportion of airborne particles retained is normally expressed as velocity of deposition V_g:

$$V_g = \frac{\text{quantity } (\mu\text{g or ng}) \text{ deposited per cm}^2 \text{ of ground surface/second}}{\text{quantity } (\mu\text{g or ng}) \text{ contained in 1 cm}^3 \text{ of ambient air}}$$

Velocity of deposition is the summation of the processes of sedimentation, impaction and diffusion (i.e. dry deposition).

This differential retention of the various particle sizes by TD, DD and MB means that there can be no simple fixed relationship between air-concentration and deposition to ground vegetation or deposition on a gauge. In this respect the gauges would be a better reflection of vegetation retention than would be provided by the air-concentration gauge which draws an unbiased sample of airborne metals independent of prevailing wind speeds.

(4) The proportion of particles in the aerosol retained by the deposition surface in a wind tunnel is strongly increased with increasing wind speed. Since wind speed increases logarithmically with height above ground, the gauges placed at 150 cm height will be exposed to more wind than the grass sward.

Wind speeds above 500 cm/sec. (11 mph, Beaufort 3, gentle breeze), at 150 cm, may cause particles c. 30 μm to bounce off the filter paper of the DD gauge or to blow off again if already deposited earlier under less windy conditions. This effect is not so important at normal sites where particles are usually <10 μm, but could be very important at breezy sites close to an emission source. It is negligible for moss-bags but could reduce the deposition on to DD. By contrast, the air-concentration gauge sampling at a constant rate (c. 5 1/min.) is independent of wind speed.

(5) Although it is very difficult to quantify the integrated effects of the physical features of the receptor surfaces and wind speed upon retention efficiency, it is possible to make a very rough estimate from these wind tunnel observations as follows.

The filter paper dry deposit gauge would most likely *underestimate* input to a grass sward by a factor of 2–10. The *vertical* moss-bag placed at right angles to an emission source would be likely to *overestimate* input to a grass sward by a factor of 5–8. Thus, the methods might be expected to differ by a factor within the range x 10–80 as between moss-bags and the AERE dry deposition gauge, with a central tendency of *c.* x 30.

(6) There is evidence that doubling the wind speed in a wind tunnel approximately doubles the proportion of 0.5–2.0 μm particles retained by a filter paper pad, moss-bag or grass sward. Because the physical characteristics of the moss-bag or grass sward make them highly retentive compared with filter paper (x 20–30), doubling the metal input to grass or moss-bags represents a very large arithmetic increment compared with a relatively small increment to filter paper.

(7) Both moss-bags and the total deposit gauge suffer from the disadvantage that relative to a grass sward, although there is a scaling factor [see (5) above] operating for dry deposition, it is most likely that no scaling factor operates for metal deposition in rain, i.e. the quantity of metals received in rain/cm^2 of receptor surface is about the same for filter paper, moss-bags, and grass sward. Thus, if metal input from washout is rather variable and large, both gauges could give very misleading results. Since washout of industrially derived metals is believed to contribute only a small and relatively constant percentage to total deposition (10–20%), this problem is not thought to be a severe one in

practice, particularly for the moss-bag which overestimates dry deposition. However, the only way to overcome it thoroughly would be to use dry and total gauges together or pairs of moss-bags, side by side, which are exposed to and sheltered from rain.

11.5 FIELD TRIALS

These experimental findings in the wind tunnel need verification by field trials and in particular suggest the following questions:

(a) Do the results in the field indicate that all gauges are sampling the prevailing airborne metals much as they do in the wind tunnel, i.e. AC drawing an unbiased sample of all particle sizes and thus giving metal results somewhat different from MB, TD, and DD (all three of which undersample in the intermediate particle size range 2.0–0.1 μm)?
(b) Do the MB, TD, and DD metal results suggest that they each sample the various particle sizes to about the same extent, i.e. similar degrees of undersampling of intermediate particles (similar sampling quality)?
(c) Do moss-bags collect more metal/unit area than DD or TD, and TD more than DD in a given time period (sampling quantity)?
(d) If so, is this a fixed ratio (MB/TD; MB/DD; TD/DD, etc.) irrespective of month or site?
(e) Does metal deposition in a moss-bag bear any relation to deposition on to a grass sward in the field?

11.5.1 Comparing the qualitative characteristics of different gauges

This can be done most conveniently by correlating the quantities of all seven metals (Co, Cu, Fe, Mn, Ni, Pb, and Zn) retained by any two types of gauge in any month or at any site. As an example, it is possible at Windermere in January 1973 to compare the content of the seven metals analysed for in moss-bags with the amounts of the corresponding metals retained by the total deposition gauge. If the level of each metal from the moss-bag has the same fixed ratio to the level of the corresponding metal from the total deposit gauge (every metal value from the moss-bag is, say, 3.5 times greater than the value of the corresponding metal from the total deposit gauge) all metal values will lie along a straight line when graphed. Their closeness of fit to linearity will be given by '*r*' ($r = 1.0$ for a perfect fit to a straight line). This can be most easily recognized by the degree of statistical significance: xxxx ($p < 0.001$) = very good fit; xxx ($p < 0.01$) = good fit; xx ($p < 0.02$) = acceptable fit; x ($p < 0.05$) = statistically linear but not regarded as acceptable in this study. In this way, tests can be made at each site for each month comparing metal values on any pair of gauges, e.g. MB v TD; MB v DD; MB v AC; TD v DD; TD v AC; DD v AC. If the results normally fall along a straight line, this is

TABLE 11.1 Summary of Significance Levels of Correlation Coefficients (r) between Various Gauge Pairs for All Seven Metals and All Sites and Months

Significance levels	MB/TD	MB/DD	TD/DD	MB/AC	TD/AC	DD/AC
xxxx	86	90	85	25	32	24
xxx	17	12	12	50	45	50
xx	3	4	5	16	13	17
x	5	3	2	7	7	5
N.S.	6	7	12	18	19	20
N.D.	0	1	1	1	1	1
Total	117	117	117	117	117	117

Notes: xxxx; xxx; xx; x = r statistically significant at $P < 0.001$; 0.01; 0.02; and 0.05 respectively.
N.S. = not significant; N.D. = not determined

taken to mean:

(a) Each suspended particle contains one or other (more rarely two or three together) of the different metals and both gauges under comparison are thus sampling the various particle sizes and hence the metal aerosol in a conformable manner (i.e. similar amounts of over or undersampling various size fractions).

(b) The different analytical techniques used to measure the same element (in this case, atomic absorption spectrophotometry for moss-bags, by the authors, and neutron activation analysis, X-ray fluorescence and colorimetric methods for TD, DD, and AC, by AERE Harwell) are systematically compatible.

Table 11.1 summarizes the significance of correlations from the nine sites in S. Wales (seven for a 12-month period and two for six months each) and also from Windermere (grid reference SD 362974; seven months) Styrrup (grid reference SK 606989; eight months) and Petten (Netherlands; six months).

The results show a high degree of linearity in all comparisons involving MB, TD, and DD all of which are distinctly more linear than comparisons of any of these with AC.

This is what would be expected if MB, TD, and DD are sampling in a similar qualitative manner but not in quite the same way as AC. It is assumed that this result is caused by the unbiased sampling of AC as contrasted with the other gauges which tend to undersample at intermediate particle sizes to about the same extent.

11.5.2 Quantitative sampling characteristics of the gauges

What the above results do not show is whether the actual ratios of metals retained by each pair of gauges is the same from month to month and site to site. As an example, if metal levels on the moss-bag are, say, 3.5 times greater than those on the TD gauge for February 1974 for Styrrup, will this factor be the same for all other months and all other sites? Or will it change from month to month and site to site? Thus, although we know that gauge comparisons between MB, TD, and DD are linear, we do not know whether the slope of the line stays constant or changes from site to site or month to month, or depending which types of gauge are being compared. The following factors are thought to be most likely to influence the slope:

(a) Sampling rates of the two gauges being compared, especially as influenced by increasing wind speeds.
(b) Proximity of sampling site to main metal emission sources.
(c) Relative importance of aerial diffusion processes versus wind transfer for the various particle sizes of the metallic aerosol.
(d) Frequencies and strength of the various wind directions.
(e) Angle of moss-bag orientation in relation to main metallic emission sources.
(f) Frequency of rain showers.

These may interact in such a complex way that it seems unlikely that ratios will be constant.

Table 11.2 summarizes information on slopes (given as geometric means of monthly linear regression coefficients) for eight of the sites in Wales and shows that ratios vary widely from site to site and depending on which gauge pair is being compared. The fall in ratios generally observed when reading from left to right of the table are expected from the different effective sampling rates of the gauge, which in decreasing order, are: $\mathrm{MB} \gg \mathrm{TD} \geqslant \mathrm{DD} \gg \mathrm{AC}$.

TABLE 11.2 Geometric Means of Regression Coefficients for Metal Content of Various Gauge Pairs

GAUGE COMPARISON SITE	MB/AC	MB/DD	MB/TD	TD/AC	TD/DD	DD/AC
Port Talbot	48.86	13.74	7.12	6.86	1.93	4.80
Trebanos	7.87	4.50	2.90	3.08	1.55	2.17
Kidwelly	6.95	4.74	4.57	1.88	1.43	1.31
Skewen	7.65	5.41	4.26	1.78	1.37	1.30
Penmaen	4.02	4.21	1.62	2.64	2.67	0.97
Mount Pleasant	3.24	2.48	0.93	3.54	2.70	1.29
Llansamlet	2.61	2.65	2.14	1.44	1.35	1.06
Clydach	2.60	2.14	0.91	3.16	1.91	1.17

TABLE 11.3 Regression Coefficients for Metal Content of Various Gauge Pairs

	VMB/HMB	VMB/AC	HMB/AC	VMB/DD	HMB/DD	VMB/TD	HMB/TD	TD/AC	TD/DD	DD/AC
Port Talbot	3.2	74.6	24.1	16.4	5.2	8.5	2.7	8.6	1.9	4.6
Trebanos	2.1	13.3	6.1	5.3	2.5	4.7	2.1	2.7	1.4	2.4
Penmaen	1.7	9.4	5.2	15.4	9.1	5.4	3.2	1.7	2.9	0.6

Note: Vertical moss-bags (VMB) were orientated at right angles to prevailing metal sources to give maximum 'dipole' effect. Receptor surface area is the same for all wind directions in horizontal moss-bags (HMB).

The ratios also tend to fall from top to bottom of the table. The eight sites were arranged partly subjectively, in decreasing order of windiness (no wind data were available for several sites) as follows: Port Talbot ≫ Trebanos ⩾ Kidwelly > Skewen > Penmaen ⩾ Mount Pleasant ⩾ Llansamlet ⩾ Clydach. The decreasing slope with decreasing windiness is in accordance with expectation for all gauge comparison, involving AC which is a constant rate sampler whereas MB, TD, and DD are all expected to be wind sensitive. *This emphasizes the fact that MB, TD, and DD gauges cannot be used to determine air-concentration directly.*

The ratios MB/DD and MB/TD appear to show sensitivity to wind speeds, especially at the windiest site (Port Talbot) and one explanation for this may be that larger particles are being bounced off or blown off DD and TD gauges under the very breezy conditions of this more polluted site where large particles are most likely to be present.

Another important factor is that a number of experiments have shown that vertical moss-bags may seriously undersample all particle sizes when not orientated at right angles to the main metal emission source. This 'dipole' quality may be used to locate emission sources but the experiments showed that less-biased estimates of metal deposition can be obtained by using horizontally orientated bags. An indication of this is given (Table 11.3) by a comparative study of vertical and horizontal moss-bags which was made together with total deposition, dry-deposition and air-concentration during November 1972–May 1973, at some of the sites listed in Table 11.2 above. All regression coefficients shown in Tables 11.2 and 11.3 were calculated using the following units: VMB; HMB; TD and DD – μg metal/cm^2/month; AC – μg metal/m^3 air.

11.6 METAL ACCUMULATION ON MOSS-BAGS AND GRASS SWARD IN THE FIELD

A number of plastic seed trays containing clean (unpolluted) soil were sown with the grass *Festuca rubra* and allowed to grow in an uncontaminated environment.

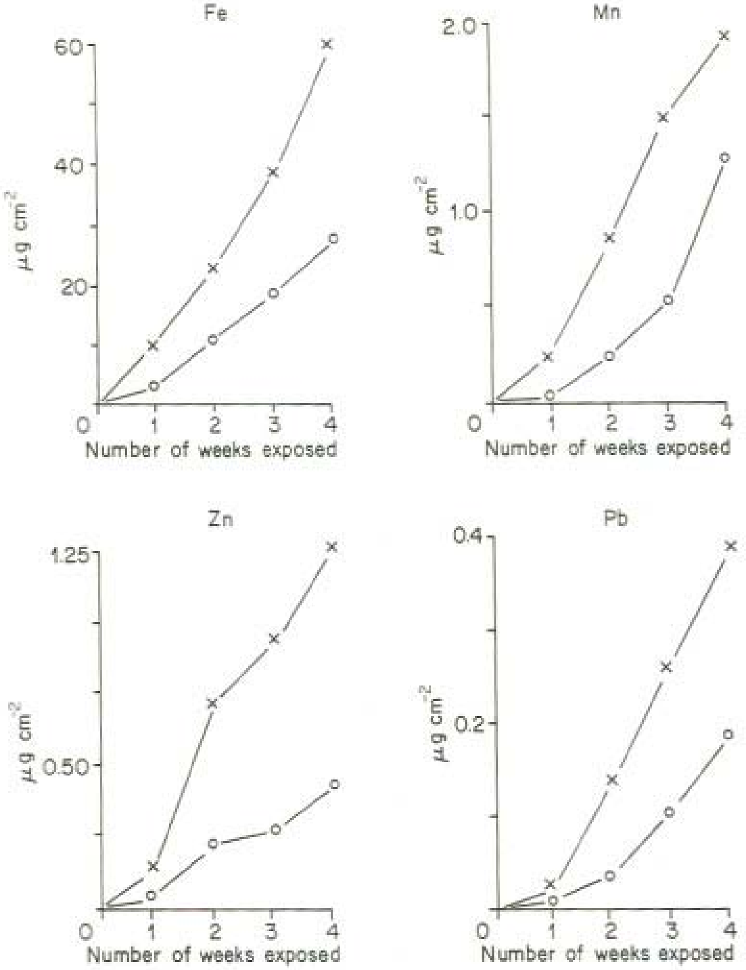

Figure 11.3 Weekly deposition of Fe, Mn, Zn, and Pb ($\mu g\ cm^{-2}$) as measured by moss-bag (x——x) and grass sward (o——o), exposed from 1–4 weeks at Port Talbot, South Wales. (Note vertical scale differences)

When the grass was about 6 cm high the trays were placed in a relatively polluted site together with a number of moss-bags suspended at the same height above the ground as the trays. Each week a fixed standard area of grass was cut from the centre of each tray to within 1 cm of the soil surface and the whole analysed. At the same time, moss-bags were removed and analysed. Figure 11.3 shows a comparison of weekly accumulation of Fe, Mn, Zn, and Pb per unit area of grass sward and moss-bag.

The moss-bags are roughly twice as retentive as the grass sward for these metals. This is in good agreement with the work of Clough (1974) who found that in wind tunnel experiments at the same wind speeds, moss-bags were about twice as retentive as grass swards. Further work over longer periods indicated clearly that grass tends to lose about 50 per cent of its intercepted trace-metals to the ground. This makes horizontal moss-bag retention about the same as grass under similar conditions.

11.7 EFFECTS OF WIND DIRECTION AND STRENGTH

If a metal is being emitted from a particular point source, winds blowing onto the sampling site from the direction of the source will deliver the airborne metal to the gauges. This could be quite important for larger airborne particles where diffusion processes are less important for transport but where the turbulent air in strong winds could carry the particles long distances from the source. Such considerations would indicate that the amount of metal accumulated by a gauge each month will be proportional to the number of miles of wind (i.e. frequency or duration each month x speed of wind) passing over the gauge from the direction of the emission source each month. No such correlation would exist for winds from other directions and a negative correlation for winds from the opposite direction, which would blow the metal away from the gauge. This situation should be particularly applicable to wind-sensitive gauges and to vegetation.

It was not possible to monitor wind direction and strength at each of the nine sites in S. Wales. Instead the present study relied upon observations of wind speed and direction made daily at the Penmaen site by Mr J. Powell and upon three hourly wind data collected on the coastal plain near the Port Talbot site (OS Ref. SS 789867) and kindly supplied by the Meteorological Office, Bracknell. In both cases, the data was arranged to give the number of nautical miles of wind passing over the meteorological stations Penmaen and Port Talbot from various points of the compass (reported as compass bearings in intervals of degrees) each month for the 12 month period. Each set of wind data was then correlated with the monthly metal accumulation on the gauges at the corresponding site. Correlation coefficients for moss-bags, total deposit and dry deposit gauges at Port Talbot and Penmaen are summarized in Tables 11.4 and 11.5. At Port Talbot, both moss-bag and total deposit gauges show that the higher the amount of metal deposited, the greater the number of wind miles received from the NW (260–340°). Winds from this direction pass over two large iron and steel works (lying at 290° and 310° respectively) and copper and nickel works (lying 310–320°). Negative correlations for moss-bags are observed with wind miles from the opposite direction. There appears to be a lead source in the SE (140–160°) at present unidentified. These results are in good agreement with expectation.

Preliminary analysis of the gauges at Penmaen showed activity in the SE (70–140°) and NW (320–360°). Only these directions are reported in Table 11.5. Significant correlations for Fe and Mn, particularly for moss-bags, are seen from 70–140° and for Cu at 320–360°. The two iron and steel works referred to above

TABLE 11.4 Summary of Statistically Significant Correlations (r) between Monthly Wind-miles from Stated Compass Bearing and Monthly Metal Content of Gauges at Port Talbot

	Compass bearing (0° = N; 90° = E; 180° = S; 270° = W)											
	350-010°	020-040°	050-070°	080-100°	110-130°	140-160°	170-190°	200-220°	230-250°	260-280°	290-310°	320-340°
MOSS BAG												
Co	.	.	.	−N.S.	.	.	.	.	.	.	.	xxxx
Cu	.	.	.	−x	.	.	.	.	.	.	x	.
Fe	.	.	−N.S.	−x	.	.	.	.	.	.	xxxx	.
Mn	.	.	.	.	.	.	.	.	.	x	.	.
Ni	.	.	.	.	.	.	.	.	.	.	xx	.
Pb	.	.	.	.	.	xx	.	.	.	.	N.S.	.
Zn	.	.	.	−N.S.	.	.	.	.	.	.	.	.
TOTAL DEPOSITION												
Co	N.S.	xx	.	.	.	.	.	.	.	−x	x	N.S.
Cu	.	.	.	.	N.S.	x	.	.	.	.	.	.
Fe	.	.	.	.	.	N.S.	.	.	.	.	.	.
Mn	.	.	.	−N.S.	.	.	.	.	.	.	x	.
Ni	.	.	.	.	.	N.S.	.	.	.	.	xxx	.
Pb	.	.	.	.	.	.	.	.	.	.	xxxx	N.S.
Zn	xx	.	.	.	.	.	.	.	.	.	x	N.S.
DRY DEPOSITION												
Co	.	.	.	.	.	.	−N.S.	−x	−N.S.	.	.	.
Cu	.	.	.	.	.	.	.	.	.	.	.	.
Fe	.	.	−x	−xx	.	.	.	.	.	.	x	.
Mn	.	.	.	−N.S.	−N.S.	.	−N.S.	.	.	.	.	.
Ni	.	.	.	.	.	.	.	.	.	.	.	.
Pb	.	.	.	.	.	.	.	.	.	.	.	.
Zn	.	.	.	.	.	.	.	−N.S.	.	.	.	.

Note: x; xx; xxx; xxxx = r statistically significant at $P < 0.05$; < 0.02; < 0.01; < 0.001 respectively
N.S. = $r > 0.500$ but not statistically significant; – = negative correlation

TABLE 11.5 Summary of Statistically Significant Correlations (r) between Monthly Wind-miles from Stated Compass Bearing and Monthly Metal Content of Gauges at Penmaen

	Compass bearing (N = 0°; E = 90°; S = 180°; W = 270°)			
	30-70°	70-110°	110-140°	320-360°
MOSS BAG				
Co	.	.	.	.
Ni	.	.	.	.
Cu	.	.	.	xxxx
Fe	.	xxx	xx	.
Mn	.	xxx	xx	.
TOTAL DEPOSITION				
Co	.	.	.	.
Ni	.	.	.	.
Cu	−x	.	.	.
Fe	.	.	x	.
Mn	.	x	.	.
DRY DEPOSITION				
Co	.	.	.	.
Ni	.	.	.	.
Cu	.	.	.	.
Fe	.	.	x	−x
Mn	.	.	.	.

Note: x; xx; xxx; xxxx = r statistically significant at $P < 0.05$; < 0.02; < 0.01; < 0.001 respectively; − = negative correlation

lie between 70–90°. The Cu source to the NW is not known. The interesting feature of this site, selected as an uncontaminated 'background' site is the extent to which it is affected by industrial sources.

From the correlations presented above it may be concluded that the moss-bag is somewhat more responsive to the quantity of wind from the direction of an emission source of airborne metals than TD, and TD more than DD.

11.8 POSSIBLE USE OF MOSS-BAGS AS TOTAL PARTICULATE GAUGES

The results so far indicate that moss-bags may be useful in obtaining reasonably quantitative estimates of the total amounts of airborne metallic elements intercepted by a grass sward. It is of interest to consider whether they could be used to estimate total particle deposition. This cannot be done by direct weighing before and after exposure because in windy sites, small fragments of moss may become detached from the moss-bag and blow away during exposure.

TABLE 11.6 Observed Monthly Weights (μg) of 'Dust' in TD Gauge Compared with Estimates Based on Content of Various Metals respectively on Moss-bags (All Figures are per dm^2 Horizontal Deposition Surface)

Month 1976–77	Obs. 'Dust' in TD	Estimated 'dust' based on metal analysis					
		Fe	Mn	Pb	Ca	Mg	Mean
Aug.	40.7	47.0	68.0	34.0	22.0	70.0	48.2
Sept.	—	—	—	—	—	—	—
Oct.	54.0	95.0	52.0	67.0	54.0	65.0	66.6
Nov.	63.0	70.0	41.0	78.0	85.0	144.0	83.6
Dec.	48.5	60.0	42.0	46.0	35.0	60.0	48.6
Jan.	53.9	44.0	49.0	81.0	30.0	47.0	50.2
Feb.	38.9	60.0	40.0	37.0	26.0	31.0	38.8
March	30.4	46.0	37.0	39.0	39.0	34.0	39.0
Mean	47.0	60.0	41.0	55.0	42.0	64.0	52.4

However, if an array of moss-bags were exposed during the same period of time as one or two total deposit gauges, the TD gauges could be used to determine the concentration of various trace metals in the total-deposit material and by working backwards, the weight of dust intercepted by the moss-bag might be estimated from the total metal content of the bag itself. This of course assumes that the composition of the dust intercepted by moss-bag and TD gauge remains unaffected by the nature of each type of sampler. Data summarized in Table 11.1 above show this to be largely correct.

In work carried out at a very sheltered site, the Chelsea Physic Garden, London, UK, the weight of total deposit, sampled monthly for 8 months (including dissolved material in the precipitation collected by the TD gauge – without a terylene covered funnel) correlated significantly ($P < 0.001$) with Ca and Mg values respectively in moss-bags correspondingly exposed under both wet (completely open to the atmosphere) and dry (sheltered from precipitation by a horizontal sheet) conditions.

This suggested that it might be possible to estimate total particulate interception using moss-bags, as suggested above.

At the same site, the amount of particulate interception on moss-bags was calculated, based on a monthly comparison of the concentrations of Fe, Mn, Pb, Ca, and Mg respectively in the TD gauge and the total amount of each of these metals deposited on a moss-bag for each month. Table 11.6 compares these estimates based on each metal for the period August 1976–March 1977 with the total weight of material received by the TD gauge.

The first results look promising. The moss-bag gives deposition values approximately equal to the TD gauge. This is what would be expected in a very sheltered site. More results are needed before drawing firmer conclusions as to whether the approach might be worth trying under arid-zone conditions. As indicated earlier, it is unlikely that the moss-bag will lose dust in wind or rain-episodes and so it might be expected to perform adequately even under arid or semi-arid conditions.

11.9 CONCLUSIONS

Considerable research work has been done on interception of airborne particles by grass surfaces and other obstacles and despite their different designs, the physical principles governing deposition on all gauges (MB, TD, DD) are the same.

Laboratory work by Chamberlain (1966a,b) and Clough (1973) using wind tunnels has shown that 'hairiness' and wetness are important properties making objects efficient interceptors of airborne particles. Because grass sward and other ground vegetation, MB, TD and DD are all different for these characteristics, each will tend to retain airborne particles with different 'efficiencies' in terms of the proportion of airborne particles retained and also exhibit a tendency to retain particles of different sizes in different proportions compared with their occurrence in the air. Doubling wind speed was found roughly to double the proportion of particles retained on vegetation, MB, TD, and DD.

Because AC is quite independent of wind speed and extracts an unbiased sample in terms of the different particle size fractions, there can be no simple relationship between AC and deposition to ground vegetation or to MB, TD, and DD. *Thus, these latter gauges cannot be used to determine air-concentration directly.*

Metal retained on MB correlated well with metal retained by TD and DD at each site for each month. Correlations between AC and MB, TD, or DD were less good. This is taken as evidence for the fact that MB, TD and DD are all sampling the chemical composition of the aerosol in similar qualitative ways but not absolutely representatively, as done by AC. This may be caused by differential retention of different particle sizes. It is also evidence for the quantitative compatibility of the different chemical analytical techniques used by the authors for MB and AERE Harwell who analysed for TD, DD, and AC.

The metal ratios obtained from comparing gauge pairs showed that comparison of MB or TD or DD with AC gave ratios that were highest for windiest sites. This is as expected, the gauges being wind dependent whereas AC is a fixed rate sampler. Other comparisons gave ratios MB/DD, MB/TD, and TD/DD as expected from the greater proportion of airborne particles retained by MB than by TD and DD. Each of these last three ratios varies depending on month and site. Higher ratios were generally associated with the most exposed (and polluted) site (Port Talbot). One explanation might be that larger particles (*c.* 30 μm) of similar chemical composition to the smaller particles were being retained more efficiently on MB and to a lesser extent on TD or DD where they may bounce off or blow off. The way the moss-bag is presented to the air is also important, horizontal bags giving less biased results than vertical bags. This 'dipole' effect can be used to pinpoint metal emission sources.

Strong winds and rain episodes do not remove particles already deposited on the moss-bags. Soluble cations are held on the exchange-surfaces of the moss so that the soluble metal is not lost following rain.

Trays of the grass *Festuca rubra* placed at the same height above ground as horizontal moss-bags at Port Talbot and sampled weekly for a month accumulated about the same quantity of metals per unit surface area as did moss-bags. The grass leaves lost half of this amount of metal to the ground surface making moss and grass results similar to those found in the wind tunnel by Clough.

The results indicate that the moss-bag is a useful gauge providing informative metal deposition figures in terms of space and time. It is relatively inexpensive and can be used for extensive surveys. It is wind-sensitive like ground vegetation and other deposit gauges. Further critical studies, which would include wind direction and strength, and rainfall measurements are desirable to quantify further the moss-bag as a reliable index of metal input to a grass sward. The results obtained from the study described above indicate that such critical experiments would further validate the horizontal moss-bag as a reasonably accurate deposition gauge and the vertical bag as an indicator of emission sources.

Preliminary evidence indicates that it might be possible to use moss-bags as total 'dust' monitors in arid-zone conditions but this needs to be verified experimentally.

11.10 ACKNOWLEDGEMENTS

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REFERENCES

Cawse, P. A. and Pierson, D. H. (1972). An analytical study of trace elements in the atmospheric environment. *AERE – R7134* (HMSO Lond.).

Chamberlain, A. C. (1966a). Transport of *Lycopodium* spores and other small particles to rough surfaces. *Proc. R. Soc. Lond. (A)*, **296**, 45–70.

Chamberlain, A. C. (1966b). Transport of gases to and from grass-like surfaces. *Proc. R. Soc. (A)*, **290**, 236–265.

Chamberlain, A. C. and Chadwick, R. C. (1972). Deposition of spores and other particles on vegetation and soil. *Ann. Appl. Biol.*, **71**, 141–158.

Clough, W. S. (1973). Transport of particles to surfaces. *J. Aerosol Sci.*, **4**, 227–234.

Clough, W. S. (1974). The deposition of particles on moss and grass surfaces. *AERE – M2612* (HMSO Lond.).

Goodman, G. T. and Roberts, T. M. (1971). Plants and soils as indicators of metals in the air. *Nature, Lond.*, **231**, 287–292.

Ruhling, Å. and Tyler, G. (1970). Sorption and retention of heavy metals in the woodland moss *Hylocomium Splendens* (Hedw.), *Br. et Sch. Oikos*, **21**, 92–97.

Tamm, C. O. (1953). Growth, yield and nutrition in carpets of a forest moss (*Hylocomium splendens*). *Meddn. Statens Skogsforskninginst.*, **43**, 1.