

CENTRE FOR ECOLOGY AND HYDROLOGY
(Natural Environment Research Council)
Defra Contract AQ0810
CEH Project No. C03077

Report on Nitrogen in European Mosses
Work package 4
The UNECE International Cooperative
Programme on Vegetation

Spatial trends in nitrogen
concentrations in mosses
across Europe in 2005/2006

Harry Harmens, David Norris, David Cooper
Jane Hall and the participants of the moss survey

ICP Vegetation Programme Coordination Centre
Centre for Ecology and Hydrology
Environment Centre Wales
Deiniol Road, Bangor
Gwynedd LL57 2UW
United Kingdom

Email: hh@ceh.ec.uk

September 2008

Executive Summary

Background

The European moss biomonitoring network was originally established in 1990 to estimate atmospheric heavy metal deposition. The moss technique is based on the fact that carpet forming, ectohydric mosses obtain most trace elements and nutrients directly from precipitation and dry deposition with little uptake from the substrate. The technique provides a surrogate, time-integrated measure of element deposition from the atmosphere to terrestrial systems. It is easier and cheaper than conventional precipitation analysis as it avoids the need for deploying large numbers of precipitation collectors with an associated long-term programme of routine sample collection and analysis. Therefore, a much higher sampling density can be achieved than with conventional precipitation analysis.

Since 2001, the European moss survey has been coordinated by the ICP Vegetation¹ Programme Coordination Centre at the Centre for Ecology and Hydrology (CEH) Bangor, UK. The ICP Vegetation was established in the late 1980s to consider the science for quantifying the impacts of air pollutants on vegetation. It reports to the Working Group on Effects (WGE) of the Convention on Long-range Transboundary Air Pollution (LRTAP). The WGE monitors and reviews the effects of atmospheric pollutants on different components of the environment and health. Thus, the ICP Vegetation provides information for the review and possible revision of the Protocols of the LRTAP Convention.

The European moss survey has been repeated at five-yearly intervals and the most recent survey was conducted in 2005/6. For the first time 16 countries determined the nitrogen concentration in mosses (at almost 3,000 sites), as a pilot study in selected Scandinavian countries had shown that there was a good linear relationship between the total nitrogen concentration in mosses and atmospheric nitrogen deposition rates. The aims of the 2005/6 survey were to establish whether mosses can be used as biomonitors of atmospheric nitrogen deposition across Europe, identify the main polluted areas and produce European maps.

Methodology

As in previous surveys, moss samples were collected according to a standardised protocol and the total nitrogen concentrations were determined in the last three years' growth segments using either elemental analysis (dry ashing) or the Kjeldahl method (wet ashing). *Pleurozium schreberi* was the most frequently sampled species (41.3%), followed by *Hylocomium splendens* (19.0%), *Hypnum cupressiforme* (18.1%), *Scleropodium purum* (15.5%) and other species (6.1%). For quality assurance purposes moss reference material was included in the analyses and where necessary, correction factors were applied to outliers. The reported data were checked for anomalies and the format standardised. A European map was produced using ArcMAP, part of ArcGIS, an integrated geographical information system (GIS) and was based on the EMEP² 50 x 50 km² grid, displaying the mean total nitrogen concentration for each cell.

¹ The International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops

² Cooperative Programme for Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe

Spatial trends in Europe

The lowest total nitrogen concentrations in mosses were observed in northern Finland and northern parts of the UK, the highest concentrations were found in central and eastern Europe. The spatial distribution of the nitrogen concentration in mosses was similar to that of the total nitrogen deposition modelled by EMEP for 2004, except that the nitrogen deposition tended to be relatively lower in eastern Europe. However, the relationship between total nitrogen concentration in mosses and modelled total nitrogen deposition, based on averaging all sampling site values within any one EMEP grid square, shows considerable scatter. Some of this scatter can be explained by the fact that in the majority of EMEP grid squares mosses were only sampled at one to three sites. Actual nitrogen deposition values vary considerably within each EMEP grid cell due to for example topography, vegetation, local pollution sources and climate. The apparent asymptotic relationship shows saturation of the total nitrogen in mosses above a nitrogen deposition rate of ca. $10 \text{ kg ha}^{-1} \text{ y}^{-1}$. However, when the total nitrogen concentration in mosses was plotted against site-specific nitrogen deposition values in for example Switzerland, a strong positive linear relationship was observed.

Conclusions

The total nitrogen concentration in mosses can potentially be used as a surrogate to estimate total nitrogen deposition and identify areas with high nitrogen deposition at a high resolution. Due to the high local variation in nitrogen deposition, the relationship between nitrogen deposition and the nitrogen concentration in mosses will be most robust when deposition rates are measured at the moss sampling sites. The relationship is expected to be species-specific and might dependent on other factors such as nitrogen speciation, the contribution of wet and dry deposition to the total nitrogen deposition, the concentration of nitrogen in precipitation and local climate. These relationships and influencing factors require further investigation in order to improve the application of mosses as biomonitors of atmospheric nitrogen deposition at the European scale.

Future challenges

To enhance the coverage across Europe more countries are encouraged to submit data on the nitrogen concentration in mosses in the next European survey, planned for 2010. Including nitrogen analysis in future moss surveys allows the determination of temporal trends in nitrogen concentrations in mosses and comparison of these trends with temporal trends in total nitrogen deposition. Species-specific differences in nitrogen concentrations in mosses under field conditions should be investigated in more detail. Participants are encouraged to sample mosses near national or EMEP monitoring stations to investigate in greater detail the relationship between measured atmospheric nitrogen deposition and the nitrogen concentration in mosses. The spatial variation in nitrogen concentration in mosses across Europe should be analysed in greater detail to identify the main causes of this variation. Finally, an investigation is required into how the results of the moss survey can be used in an integrated assessment of effects of nitrogen on ecosystems and subsequently the identification of ecosystems at risk from nitrogen pollution. This would provide useful information for the critical load approach adopted by the LRTAP Convention.

Acknowledgements

We would like to thank the UK Department for Environment, Food and Rural Affairs (Defra, contract AQ0810), the UNECE (Trust Fund) and the Natural Environment Research Council (NERC) for funding the collation and dissemination of data for the 2005/6 European moss survey. We thank all participants for their contribution to the 2005/6 European moss survey (see below for details).

We gratefully acknowledge the contribution of Eero Kubin, who made moss reference material available to all participants for quality assurance purpose and thank Eiliv Steinnes for further processing of the moss reference data (Harmens *et al.*, 2008). We also thank all national funding bodies who have provided financial support to participants of the survey.

The main persons providing nitrogen data for each country for the 2005/6 survey were (see Annex 1 for further details):

Harald G. Zechmeister (Austria)
Ludwig De Temmerman (Belgium)
Lilyana Yurukova (Bulgaria)
Ivan Suchara (Czech Republic)
Siiri Liiv (Estonia)
Eero Kubin, Juha Piispanen (Finland)
Sébastien Leblond (France)
Winfried Schröder, Roland Pesch (Germany)
Renate Alber (Italy)

Marina Frolova (Latvia)
Blanka Maňková (Slovakia)
Zvonka Jeran (Slovenia)
José A. Fernández Escribano, Jesús M. Santamaría, Laura González-Miqueo (Spain)
Lotti Thöni (Switzerland)
Mahmut Coşkun (Turkey)
Harry Harmens (United Kingdom)

Contents

Executive Summary

Acknowledgements

1. INTRODUCTION.....	1
BACKGROUND.....	1
AIMS	2
2. METHODOLOGY	3
MOSS SPECIES	3
FIELD SAMPLING	4
CHEMICAL ANALYSIS	4
QUALITY CONTROL	4
MAPPING.....	4
3. SPATIAL TRENDS IN NITROGEN CONCENTRATIONS IN MOSSES.....	5
4. DISCUSSION AND CONCLUSIONS	9
CONCLUSIONS.....	12
5. FUTURE CHALLENGES	13
6. REFERENCES.....	14
ANNEX 1. PARTICIPANTS IN THE 2005/6 NITROGEN IN MOSSES SURVEY	17

1. Introduction

Background

The European moss biomonitoring network was originally established in 1990 to estimate atmospheric heavy metal deposition (Rühling, 1994). The moss technique is based on the fact that carpet forming, ectohydric mosses obtain most trace elements and nutrients directly from precipitation and dry deposition with little uptake from the substrate (Tyler, 1970). The technique provides a surrogate, time-integrated measure of metal deposition from the atmosphere to terrestrial systems. It is easier and cheaper than conventional precipitation analysis as it avoids the need for deploying large numbers of precipitation collectors with an associated long-term programme of routine sample collection and analysis. Therefore, a much higher sampling density can be achieved than with conventional precipitation analysis. Although the heavy metal concentration in mosses provides no direct quantitative measurement of deposition, this information can be derived by using regression approaches relating the results from moss surveys to precipitation monitoring data (e.g. Berg and Steinnes, 1997; Berg *et al.*, 2003).

During 2001, responsibility for the coordination of the European moss survey was handed over from the Nordic Working Group on Monitoring and Data, Nordic Council of Ministers, to the ICP Vegetation Programme Coordination Centre at the Centre for Ecology and Hydrology (CEH) Bangor, UK. The ICP Vegetation was established in the late 1980s to consider the science of the effects of air pollution on vegetation. It is one of seven ICPs/Task Forces that report to the Working Group on Effects (WGE) of the Convention on Long-range Transboundary Air Pollution (LRTAP). The WGE monitors and reviews the effects of atmospheric pollutants on different components of the environment (e.g. forests, fresh waters, vegetation, buildings) and human health (Working Group on Effects, 2004). Thus, the ICP Vegetation provides information for the review and possible revision of the Protocols of the LRTAP Convention.

Table 1.1. Countries that submitted nitrogen data for the 2005/6 European moss survey.

Austria	France	Slovenia
Belgium	Germany	Spain
Bulgaria	Italy	Switzerland
Czech Republic	Latvia	Turkey
Estonia	Slovakia	United Kingdom
Finland		

The European moss survey has been repeated at five-yearly intervals and the number of participating countries has expanded greatly since 1990 (Rühling, 1994; Rühling and Steinnes, 1998; Buse *et al.*, 2003; Harmens *et al.*, 2008). The most recent European survey was conducted in 2005/6 with 28 countries participating, sampling mosses from about 6,000 sites across Europe. The survey provides data on concentrations of ten heavy metals (arsenic, cadmium, chromium, copper, iron, mercury, nickel, lead, vanadium and zinc) in naturally growing mosses. In 2005/6, many countries also submitted data on the concentration of aluminium and antimony. For the first time 16 countries (Table 1.1) also determined the

nitrogen concentration in mosses (at almost 3,000 sites), as a pilot study in selected Scandinavian countries had shown that there was a good linear relationship between the total nitrogen concentration in mosses and atmospheric nitrogen deposition rates (Harmens *et al.*, 2005). The general suitability of mosses as indicators of atmospheric nitrogen deposition has been shown in a number of studies (e.g. Pitcairn *et al.*, 1995, 2006; Solga *et al.*, 2005; Salemaa *et al.*, 2008). Analysis of the nitrogen concentration in mosses collected for the heavy metals survey provided the opportunity to establish whether mosses can be used to biomonitor atmospheric nitrogen pollution at the European scale.

The main anthropogenic sources for oxidised forms of nitrogen are transport, industry and energy production, estimated to contribute up to 70% of oxidised nitrogen emissions (Bragazza *et al.*, 2005). Additional sources include soil emission, particularly under high nitrogen inputs. Emission sources of reduced forms of nitrogen are primarily related to agricultural activities such as animal husbandry and the application and production of fertilizers. Another important source of nitrogen emission is forest fires (Jovan and Carlberg, 2007). Passive biomonitoring of atmospheric nitrogen deposition using mosses could be a step forward towards a higher spatial resolution in determining nitrogen deposition.

Aims

The main aims of the European nitrogen in moss survey were to:

- establish whether mosses can be used as biomonitors of atmospheric nitrogen deposition across Europe, and if so, to:
 - provide, in the form of maps, spatial information on the distribution of total nitrogen concentrations in mosses across Europe;
 - identify main polluted areas.

2. Methodology

Moss species

As in previous surveys, the carpet-forming mosses *Pleurozium schreberi* and *Hylocomium splendens* were the preferred species for analysis. Where necessary, other species were collected, *Hypnum cupressiforme* and *Scleropodium purum* being the next choice. Because the mosses were collected in a range of habitats from the sub-arctic climate of northern Scandinavia to the hot and dry climate in western Turkey, it was inevitable that a range of moss species were collected (Figure 2.1). *Pleurozium schreberi* (Brid.) Mitt was the most frequently sampled species, accounting for 41.3% of the samples, followed by *Hylocomium splendens* (Hedw.) (19.0%), *Hypnum cupressiforme* Hedw. (18.1%), and *Scleropodium purum* (Hedw.) (15.5%). Other moss species constituted only 6.1% of the mosses sampled. The sampling density varied a lot between countries and in some countries mosses were only sampled in selected regions (Figure 2.1).

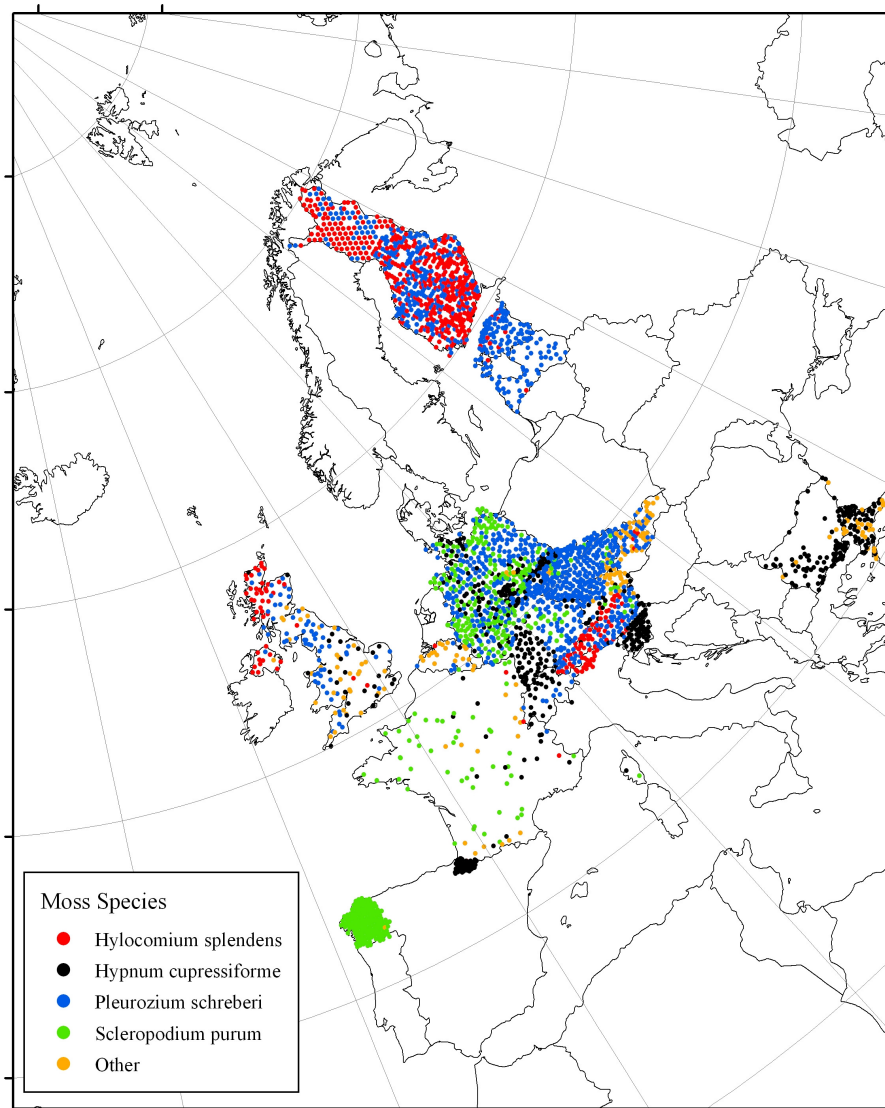


Figure 2.1. Moss species collected at each sampling point for N analysis (2928 sites in total).

Field sampling

The distribution of the collection sites throughout Europe can be seen in Figure 2.1. Moss sampling was according to the guidelines set out in the experimental protocol for the 2005/6 survey (ICP Vegetation, 2005). The procedure was similar to that used in previous European moss surveys. Each sampling site was located at least 300 m from main roads and populated areas and at least 100 m from any road or single house. In forests or plantations, samples were collected as far as possible in small open spaces to preclude any significant effect of canopy drip. Sampling and sample handling were carried out using plastic gloves and bags. Each sample was a composite of about five sub-samples. Dead material and litter were removed from the samples and only the last three years' growth of moss material was used for the analyses. Samples were refrigerated, deep-frozen or dried at room temperature and stored under those conditions until chemical analysis.

Chemical analysis

For the determination of nitrogen sorted material (ca. last three years' growth) was dried at 40°C and concentrations were determined according to either the Kjeldahl method or via elemental analysis following the Dumas method (see Table 3.1 for details). Nitrogen concentrations are expressed as percentage nitrogen (based on dry weight).

Quality control

A quality control exercise was conducted for assessing analytical performance of the participating laboratories. Moss reference material M2 and M3, first prepared for the 1995/6 European moss survey (Steinnes *et al.*, 1997), were distributed amongst the laboratories. In addition, some laboratories used certified reference material for quality assurance. For determination of the elemental concentrations in the reference material, laboratories followed the same analytical procedure as used for the collected moss samples. The data obtained indicated good agreement between laboratories and analytical techniques, and recommended values for nitrogen were calculated for the reference material (Harmens *et al.*, 2008). In one laboratory the obtained values for M2 were outside the range of two standard deviations from the mean value. Therefore, a correction factor was applied to the nitrogen data received from that laboratory.

The accuracy of data submitted to the Programme Coordination Centre was assessed by inspecting them for extremes and by sending summarised data and the relevant draft maps to individual contributors for checking and approval before incorporating the final data into the maps and this report.

Mapping

The nitrogen map was produced using ArcMAP, part of ArcGIS, an integrated geographical information system (GIS) and was based on the EMEP 50 x 50 km² grid, which display the mean nitrogen concentration for each cell. Please note that the designations employed and the presentation of material in this report do not imply the expression of any opinion whatsoever on the part of the United Nations concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries.

3. Spatial trends in nitrogen concentrations in mosses

The lowest total nitrogen concentrations in mosses were generally observed in northern Finland and northern parts of the UK (Figure 3.1, 3.2, Table 3.1). In Finland there was a clear north-south gradient which continued into the Baltic States. In the UK, locally high concentrations were found in the Midlands and South-East. The highest concentrations were found in central and eastern Europe, in particular in Belgium, Germany, Slovakia, Slovenia and parts of Bulgaria and France. The minimum and maximum values for each country are shown in Table 3.1 and indicate that countries with low median values have locally high concentrations (e.g. the UK) and countries with high median values have locally low concentrations (e.g. Bulgaria), resulting in a considerable range of measured nitrogen concentrations in mosses in these countries.

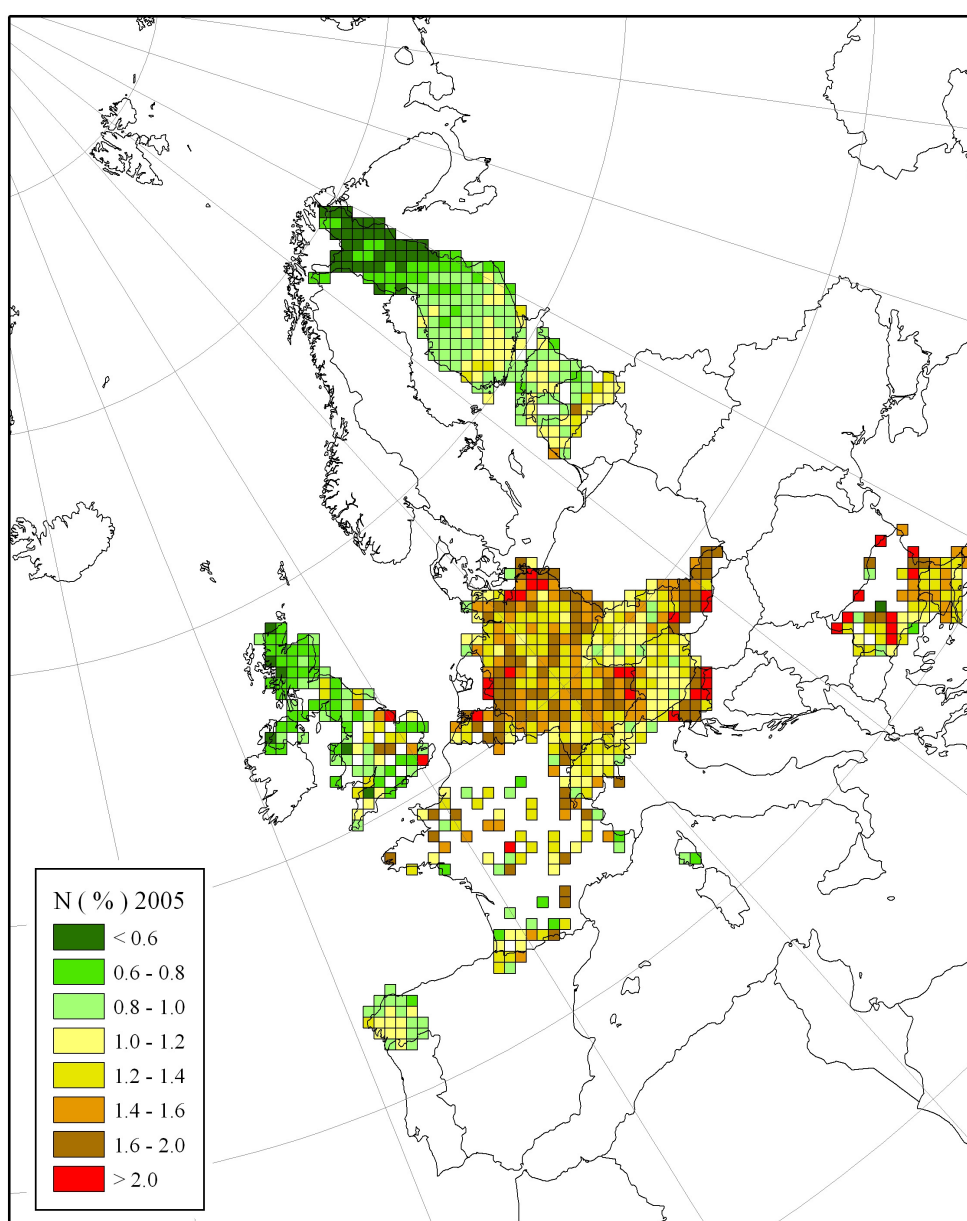


Figure 3.1. Mean concentration of nitrogen in mosses per EMEP grid square in 2005/6.

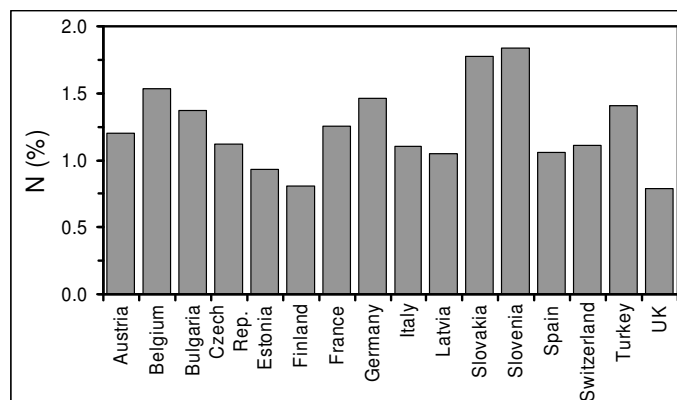


Figure 3.2. Median nitrogen concentration in mosses per country in 2005/6.

Table 3.1. Analytical technique used and summary of total nitrogen concentration (% dry weight) in mosses in each country.

Country - Region	Analytical technique ^a	Number ^b	Min ^c	Max ^d	Median
Austria	NA	212	0.70	2.15	1.20
Belgium	Kjeldahl	28	0.79	2.31	1.54
Bulgaria	Kjeldahl	105	0.34	2.94	1.37
Czech Republic	Kjeldahl	282	0.68	2.30	1.12
Estonia	Kjeldahl	111	0.63	1.66	0.93
Finland	Kjeldahl	693	0.38	1.79	0.81
France	NA	88	0.62	2.18	1.26
Germany	NA	725	0.78	3.36	1.46
Italy - Bolzano	NA	20	0.84	1.52	1.11
Latvia	Kjeldahl	49	0.80	1.65	1.05
Slovakia	NA	77	0.90	3.82	1.78
Slovenia	NA	57	0.82	2.82	1.84
Spain - Galicia & Navarra	NA & Kjeldahl ^e	207	0.61	2.30	1.06
Switzerland	Kjeldahl	30	0.78	2.12	1.12
Turkey	NA	74	0.78	2.01	1.41
United Kingdom	NA	170	0.44	2.45	0.79

^a NA = nitrogen analyser (dry ashing), Kjeldahl (wet ashing)

^b Number = number of samples

^c Min = minimum

^d Max = maximum

^e Galicia – NA (147 samples), Navarra – Kjeldahl (60 samples)

The spatial distribution of the nitrogen concentration in mosses is similar to the one of the total nitrogen deposition modelled by EMEP for 2004 (Figure 3.3), except that the nitrogen deposition tended to be relatively lower in eastern Europe. However, the relationship between total nitrogen concentration in mosses and modelled total nitrogen deposition, based on averaging all sampling site values within any one EMEP grid square, shows considerable scatter (Figure 3.4a). Some of scatter can be explained by the fact that in the majority EMEP grid squares mosses were sampled at only one to three sites. Actual deposition values vary considerably within each EMEP grid cell due to for example topography, vegetation, local pollution sources and climate. Indeed, the relationship improved and showed less scatter when based on data per grid cell averaged for at least five moss samples (data not shown). The apparent asymptotic relationship shows saturation of the total nitrogen in mosses above a nitrogen deposition rate of approximately $10 \text{ kg ha}^{-1} \text{ y}^{-1}$. In contrast, for Switzerland the relationship was significantly linear ($R^2 = 0.91$) using measured site-specific bulk nitrogen deposition rates (Figure 3.4b; Thöni *et al.*, in press). In the UK, the relationship between the total nitrogen concentration in mosses and habitat-specific estimated total nitrogen deposition rates was determined (Figure 3.5; Hicks *et al.*, 2008; Mills *et al.*, 2008). This relationship also showed a lot of scatter, reflected in the low R^2 value of 0.21. For each moss sampling point in the UK, the deposition data (averaged for 2003-2005) were extracted from the UK $5 \times 5 \text{ km}^2$ maps (Concentration Based Estimated Deposition (CBED), Smith *et al.*, 2000).

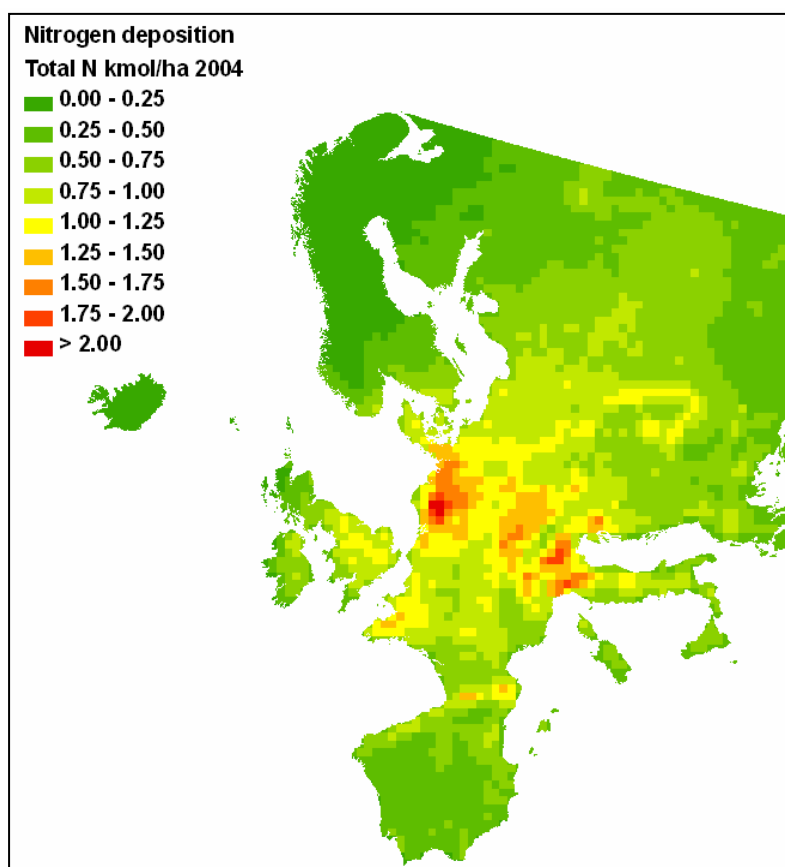


Figure 3.3. Modelled nitrogen deposition per EMEP grid square in 2004. Source of deposition data: EMEP.

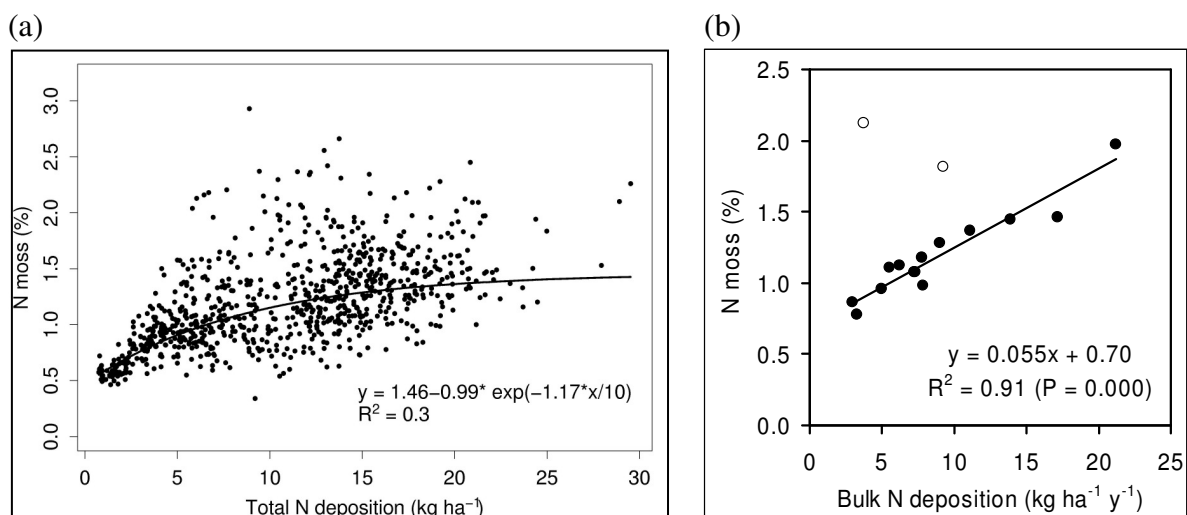


Figure 3.4. Relationship between EMEP modelled total nitrogen deposition (2004) and averaged nitrogen concentration in mosses (2005/6) per EMEP grid square across Europe (a) and the relationship between measured bulk nitrogen deposition rate and nitrogen concentration in mosses in Switzerland (b); the open symbols were excluded from the regression (Thöni *et al.*, in press).

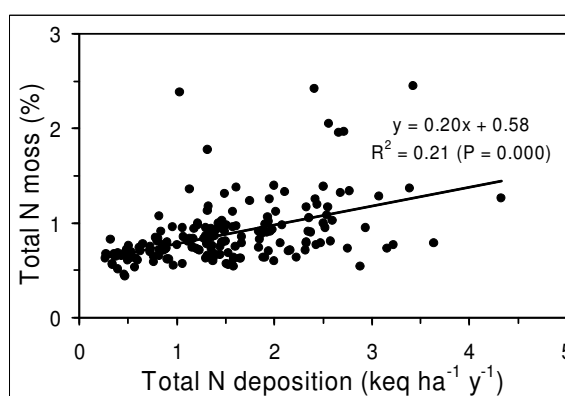


Figure 3.5. Relationship between the total nitrogen concentration in moss and habitat-specific estimated total nitrogen deposition (5 x 5 km² grid) in the UK.

4. Discussion and conclusions

In general, the total nitrogen concentration in mosses shows a good resemblance with the EMEP deposition map, i.e. the lowest total nitrogen concentration in mosses were observed in northern Finland and northern parts of the UK, and the highest concentrations were found in central Europe. However, in eastern Europe the nitrogen concentrations in mosses were relatively higher than the EMEP modelled nitrogen deposition. A plot of the nitrogen concentration in mosses against EMEP modelled nitrogen deposition rates suggests an asymptotic relationship, with a lot of scatter in the data and possible nitrogen saturation in mosses occurring at deposition rates above approximately $10 \text{ kg ha}^{-1} \text{ y}^{-1}$. For the UK, a more or less linear relationship was observed based on modelled deposition data per $5 \times 5 \text{ km}^2$ grid (Hicks *et al.*, 2008; Mills *et al.*, 2008), but once again with a lot of scatter in the data. The relationship was slightly better when habitat-specific deposition data (e.g. for moorland and forests) were used rather than average deposition values.

At the local scale, the variation in total nitrogen deposition and concentration in mosses can be high, in particular in areas with local pollution sources (Sutton *et al.*, 1998), variations in aerodynamic roughness of vegetation (Fowler *et al.*, 1998) and orographic effects on wet deposition (Fowler *et al.*, 1988), which could explain a considerable part of the scatter observed in the relationship between more or less site-specific nitrogen concentrations in mosses and nitrogen deposition rates averaged over a large area, whether at 5×5 or $50 \times 50 \text{ km}^2$. Indeed, when the total nitrogen concentration in mosses was plotted against site-specific bulk nitrogen deposition values in Switzerland, a strong positive linear relationship was observed (Thöni *et al.*, in press). However, previous studies in Norway and Sweden have also shown strong positive linear relationships between total nitrogen concentration in mosses and EMEP modelled deposition data (Harmens *et al.*, 2005), which might be due to the absence of significant local pollution sources in many parts of these countries. In contrast to non-essential heavy metals, nitrogen is a nutrient for mosses and recycled between old and new developing tissue. Therefore, the background concentration of nitrogen in mosses is estimated to be ca. 0.5 – 0.6% (Figure 3.3a, 3.4; Pitcairn *et al.*, 1995; Harmens *et al.*, 2005), but could be as high as 0.7% in some areas (Figure 3.3b). The measured maximum concentrations were often three or more times higher than these background concentrations.

Apart from the different geographical scale affecting the relationship between atmospheric nitrogen deposition rates (averaged over a large area) and the nitrogen concentration in mosses (more site-specific), other factors might confound this relationship, such as:

1. *Effects of nitrogen and climate on moss growth rate.*

Lower plant species, in particular certain species of mosses and lichens, which obtain nitrogen largely from rainfall and other atmospheric inputs, are the most at risk from enhanced nitrogen deposition (Working Group on Strategies and Review, 2007). In general, moss biomass production is favoured by low to moderate nitrogen additions, but declines with high nitrogen exposure (Bragazza *et al.*, 2005; Curtis *et al.*, 2005; Solga *et al.*, 2005; Nordin *et al.*, 2006; Pitcairn *et al.*, 2006; Salemaa *et al.*, 2008). Some studies have shown that nitrogen addition does not stimulate moss growth, but can result in luxury accumulation of nitrogen (Bates, 1987; Skyre and Oechel, 1979). In some studies, the negative response to enhanced nitrogen deposition might have been confounded by simultaneous limitation of water availability, which is crucial for the growth of bryophytes. The ability of bryophytes to respond to added nutrients depends on the moisture availability (Bates, 1987) and the duration of the periods when the bryophytes are wet (Busby *et al.*, 1978). The growth rate of

mosses tends to be seasonal, being closely related with moisture levels and rainfall (Streeter, 1965). Mosses grow in the cool moist conditions of autumn and spring (Al-Mufti *et al.*, 1977; During, 1990) and hence nutrient uptake is also greatest at those times (Brown, 1982; Streeter, 1965; During, 1990). The local microclimate is likely to affect the moss growth rate and hence the nitrogen concentration in mosses.

2. Species-specific responses to nitrogen deposition.

Species-specific growth response curves to nitrogen were found as well as differences in the effective use of nitrogen for biomass production (Salemaa *et al.*, 2008). As a result, the observed linear nitrogen accumulation rate in mosses was species-specific. This indicates that mosses can be used as biomonitors of atmospheric nitrogen deposition, but that individual species responses should be taken into account. When plotting the total nitrogen concentration in mosses against EMEP nitrogen deposition data for each moss species individually, still a lot of scatter in the data was observed (data not shown). In the UK, the relationship between the modelled nitrogen deposition rate (5 x 5 km² grid) and the nitrogen concentration in mosses improved for some species but was worse for other species when plotted for each species individually (Hicks *et al.*, 2008; Mills *et al.*, 2008). Species-specific responses to nitrogen deposition is likely to affect moss species composition in ecosystems (Zechmeister *et al.*, 2007).

3. Nitrogen speciation, wet or dry deposition.

Atmospheric nitrogen deposition includes a wide range of compounds in the gas phase, in aerosols and in precipitation. The main compounds include nitrogen oxides, nitric oxide, nitrogen dioxide, nitric acid, ammonia, particulate nitrate, particulate ammonium and nitrate, ammonium and organic nitrogen in rain (Pitcairn *et al.*, 2006). The nitrogen concentration in mosses responds differently to wet and dry deposited nitrogen and appears to respond more to concentrations of nitrate and ammonium in precipitation than to total nitrogen deposition at wet deposition sites (Pitcairn *et al.*, 2006). The nitrogen concentration in mosses provides a good indication of nitrogen deposition at sites where deposition is dominated by dry deposition of ammonia, in particular in areas where a gradient of ammonia deposition exists, and is valuable in identifying vegetation exposed to high concentrations of ammonium and nitrate in areas dominated by wet deposition, such as hilltops. Regional studies in the UK have shown maximum nitrogen concentrations of 1.6% in wet deposition areas, despite relatively large inputs of nitrogen, whereas in gradient studies around livestock farms dominated by dry deposition, tissue nitrogen values of up to 4% were measured (Pitcairn *et al.*, 2006). Nordin *et al.* (2006) found that mosses take up predominantly ammonium, however, biomass production tended to be higher with nitrate fertilization, resulting in a lower nitrogen concentration in the moss due to growth dilution.

4. Altitude.

Conflicting results have been reported on the impact of altitude on the nitrogen concentration in mosses. Some studies have found a positive correlation between the nitrogen concentration in mosses and altitude (Pitcairn *et al.*, 2006; Holy *et al.*, submitted), whereas others found a negative correlation (Pesch *et al.*, 2007). Baddeley *et al.* (1994) observed an increase in nitrogen concentration in mosses with altitude at lower altitudes, followed by a decline at high altitudes.

Nitrogen critical load exceedances

Within the LRTAP Convention, the critical load approach has been developed to identify areas at risk from adverse effects of air pollution (LRTAP Convention, 2004; Working Group on Effects, 2004; Slootweg *et al.*, 2007). Modelled critical loads of nitrogen are based on the acceptable nitrogen concentration in soil solution, i.e. the critical value at which nitrogen starts to leach from the soil. Applying the mass balance method, the critical nitrogen load from deposition can then be calculated. In addition, empirical nitrogen critical loads for vegetation have been defined (Bobbink *et al.*, 2003), based on the effects of elevated nitrogen deposition on vegetation. Compared to modelled critical loads, empirical critical loads are generally higher for the most sensitive ecosystems (Slootweg *et al.*, 2007). Nevertheless, mapped exceedances of empirical and modelled critical loads show a good resemblance. Areas in western Europe are particularly at risk from critical load exceedance, as shown for example for modelled critical loads in Figure 4.1. Although the same areas also have high concentrations of nitrogen in mosses, in parts of continental and eastern Europe the nitrogen concentrations in mosses are relatively higher than the critical load exceedance. Poikaolainen *et al.* (2008) indicated that mosses could prove to be useful in determining the nitrogen critical loads for terrestrial ecosystems in low deposition areas such as Finland. In order to be able to use the nitrogen concentration in mosses as indicator of areas at risk from adverse effects of nitrogen deposition on ecosystems, a relationship between the nitrogen concentration in mosses and ecosystems effects needs to be established. This requires further investigation.

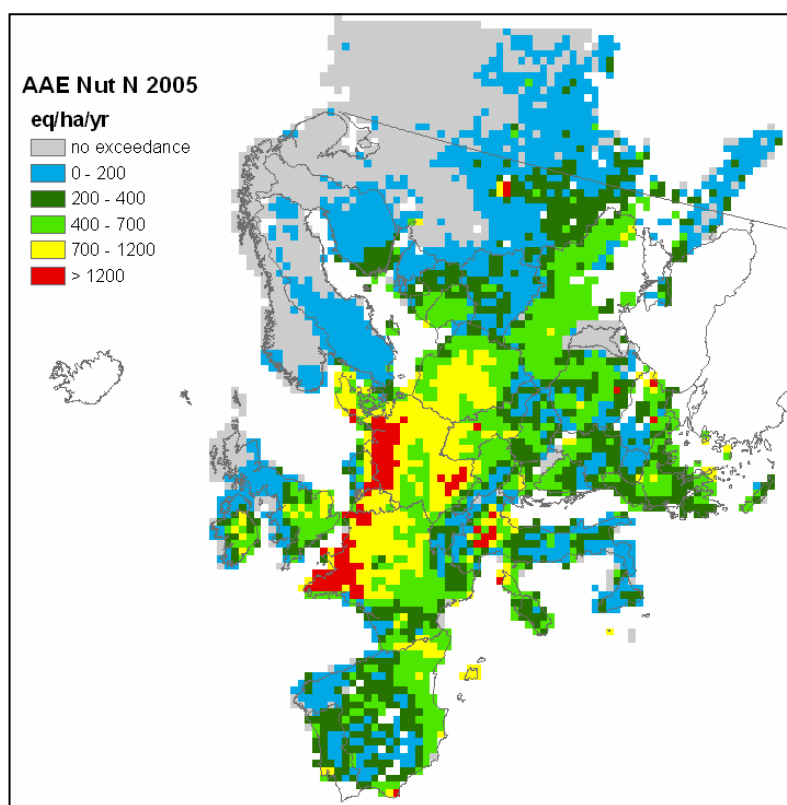


Figure 4.1. Average accumulated exceedance (AAE) of modelled critical loads of nitrogen (Nut N) in 2005. The size of the coloured squares reflects the area exceeded. Source data: ICP Modelling and Mapping, Coordination Centre for Effects.

Conclusions

The total nitrogen concentration in mosses can potentially be used as a surrogate to estimate total nitrogen deposition and identify areas with high nitrogen deposition at a high resolution. Due to the high local variation in nitrogen deposition, the relationship between nitrogen deposition and the nitrogen concentration in mosses will be most robust when deposition rates are measured (rather than modelled) at the moss sampling sites. The relationship is expected to be species-specific and might dependent on other factors such as nitrogen speciation, the contribution of wet and dry deposition to the total nitrogen deposition, the concentration of nitrogen in precipitation and local climate. These relationships and influencing factors require further investigation to improve the application of mosses as biomonitors of atmospheric nitrogen deposition at the European scale.

5. Future challenges

Nitrogen was determined for the first time in the European moss survey by selected European countries. To enhance the coverage across Europe more countries are encouraged to submit data on the nitrogen concentration in mosses in the next European survey, planned for 2010 (Harmens *et al.*, 2008). Including nitrogen analysis in future moss surveys allows the determination of temporal trends in nitrogen concentrations in mosses and comparison of these trends with temporal trends in total nitrogen deposition, as has been done in selected countries already (e.g. Poikolainen *et al.*, 2008).

To investigate species-specific differences in nitrogen concentrations in mosses under field conditions, participants are encouraged to conduct interspecies calibration exercises by sampling different moss species at the same location. Sampling of mosses near national or EMEP monitoring stations will allow us to investigate in greater detail the relationship between measured atmospheric nitrogen deposition and the nitrogen concentration in mosses (e.g. Thöni *et al.*, in press).

The spatial variation in nitrogen concentration in mosses across Europe should be analysed in greater detail to identify the main causes of this variation (Schröder *et al.*, 2008; Holy *et al.*, submitted). Such an analysis should include linking the moss data with other available environmental data, including climate and soil data. Detailed statistical analysis of the spatial trends and the quantification of the importance of confounding factors are required.

A main challenge for the future will be to establish how the results of the moss survey can be used in an integrated assessment of effects of nitrogen on ecosystems (e.g. Zechmeister *et al.*, 2007) and subsequently the identification of ecosystems at risk from nitrogen pollution. This would provide useful information for the critical load approach adopted by the LRTAP Convention.

6. References

- Al-Mufti, M.M., Sydes, C.L., Furness, S.B., Grime, J.P., Band, S.R. (1977). A quantitative analysis of shoot phenology and dominance in herbaceous vegetation. *Journal of Ecology* 65: 759-792.
- Baddeley, J.A., Thompson, D.B.A., Lee, J. A. (1994). Regional and historical variation in the nitrogen content of *Racomitrium lanuginosum* in Britain in relation to atmospheric nitrogen deposition. *Environmental Pollution* 84: 189-196.
- Bates, J.W. (1987). Nutrient retention by *Pseudoscleropodium purum* and its relation to growth. *Journal of Bryology* 14: 565-580.
- Berg, T., Hjellbrekke, A., Rühling, Å., Steinnes, E., Kubin, E., Larsen, M.M., Piispanen, J. (2003). Absolute deposition maps of heavy metals for the Nordic countries based on the moss survey. *TemaNord* 2003:505, Nordic Council of Ministers, Copenhagen, Denmark.
- Berg, T., Steinnes, E. (1997). Use of mosses (*Hylocomium splendens* and *Pleurozium schreberi*) as biomonitors of heavy metal deposition: from relative to absolute values. *Environmental Pollution* 98: 61-71.
- Bobbink, R., Ashmore, M., Braun, S. Flückiger, W., Van Den Wyngaert, I.J.J. (2003). Empirical nitrogen critical loads for natural and semi-natural ecosystems: 2002 update. In: *Empirical Critical Loads of Nitrogen*. Achermann, B., Bobbink, R. (Eds). Swiss Agency for the Environment, Forests and Landscape, Berne, pp. 43-170
- Bragazza, L., Limpens, J., Gerdol, R., Grosvernier, P., Hájek, M., Hájek, T., Hajkova, P., Hansen, I., Iacumin, P., Kutnar, L., Rydin, H., Tahvanainen, T. (2005). Nitrogen concentration and $\delta^{15}\text{N}$ signature of ombrotrophic *Sphagnum* mosses at different N deposition levels in Europe. *Global Change Biology* 11: 106-114.
- Brown, D.H. (1982). Mineral nutrition. In: *Bryophyte Ecology*. Smith, A.J.E. (Ed.). Chapman and Hall, London, pp. 383-444.
- Busby, J.R., Bliss, L.C., Hamilton, C.D. (1978). Microclimate control of growth rates and habitats of the boreal forest mosses, *Tomenthypnum nitens* and *Hylocomium splendens*. *Ecological Monographs* 48: 95-110.
- Buse, A., Norris, D., Harmens, H., Büker, P., Ashenden, T., Mills, G. (2003). Heavy metals in European mosses: 2000/2001 survey. UNECE ICP Vegetation Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK. <http://icpvegetation.ceh.ac.uk>
- Curtis, C.J., Emmett, B.A., Grant, H., Kernan, M., Reynolds, B., Shilland, E. (2005). Nitrogen saturation in UK moorlands: the critical role of bryophytes and lichens in determining retention of atmospheric N deposition. *Journal of Applied Ecology* 42: 507-517.
- During, H.J. (1990). The bryophytes of calcareous grassland. In: *Calcareous grasslands – Ecology and Management*. Hillier, S.H., Walton, D.W.H., Wells, D.A. Proceedings Joint BES/NCC Symposium, Sheffield. Bluntisham Books, Huntingdon, UK.
- Fowler, D., Cape, J.N., Leith, I.D., Choularton, T.W., Gay, M.J., Jones, A. (1988). The influence of altitude on rainfall composition at Great Dun Fell. *Atmospheric Environment* 22: 1355-1362.
- Fowler, D., Pitcairn, C.E.R., Sutton, M.A., Flechard, C., Loubet, B., Coyle, M., Munro, R.C. (1998). The mass budget of atmospheric ammonia within 1 km of livestock buildings and effects of land use. *Environmental Pollution* 102: 343-348.
- Harmens, H., Mills, G., Hayes, F., Williams, P., De Temmerman, L. and the participants of ICP Vegetation (2005). Air pollution and vegetation. ICP Vegetation Annual Report 2004/2005. UNECE ICP Vegetation Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK. <http://icpvegetation.ceh.ac.uk>

- Harmens, H., Norris, D. and the participants of the moss survey (2008). Spatial and temporal trends in heavy metal accumulation in mosses in Europe (1990-2005). Programme Coordination Centre for the ICP Vegetation, Centre for Ecology and Hydrology, Bangor, UK. ISBN 978-1-85531-239-5. <http://icpvegetation.ceh.ac.uk>
- Hicks, K., Harmens, H., Ashmore, M., Hall, J., Cinderby, S., Frey, S., Cooper, D., Rowe, E., Emmett, B. (2008). Impacts of nitrogen on vegetation. Report to Defra. Stockholm Environment Institute, York and Centre for Ecology and Hydrology, Bangor, UK.
- Holy, M., Pesch, R., Schröder, W., Leblond, S., Harmens, H. (submitted). Assessment of factors influencing the copper and nitrogen concentration in French mosses. Atmospheric Environment.
- LRTAP Convention (2004). Manual on methodologies and criteria for modelling and mapping Critical Loads and Levels and air pollution effects, risks and trends. <http://www.icpmapping.org>.
- ICP Vegetation (2005). Heavy metals in European mosses: 2005/2006 survey. Monitoring manual. UNECE ICP Vegetation Coordination Centre, CEH Bangor, UK. <http://icpvegetation.ceh.ac.uk>
- Jovan S., Carlberg T. (2007). Nitrogen content of *Letharia vulpina* tissue from forests of the Sierra Nevada, California: Geographic patterns and relationships to ammonia estimates and climate. Environmental Monitoring and Assessment 129: 243–251.
- Mills, G., Harmens, H., Hayes, F., Jones, L., Norris, D., Hall, J., Cooper, D. and the participants of the ICP Vegetation. Air pollution and vegetation. ICP Vegetation Annual Report 2007/2008. UNECE ICP Vegetation Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK. <http://icpvegetation.ceh.ac.uk>
- Nordin, A., Strengbom, J., Ericson, L. (2006). Responses to ammonium and nitrate additions by boreal plants and their natural enemies. Environmental Pollution 141: 167-174.
- Pesch, R., Schröder, W., Mohr, K., Matter, Y., Kleppin, L., Holy M., Goeritz, A., Genßler L. (2007). Moos-Monitoring 2005 / 2006: Schwermetalle IV und Gesamtstickstoff. R&D Project 205 64 200, Final Report, on behalf of the Federal Environment Agency, Dessau.
- Pitcairn, C.E.R., Fowler, D., Grace, J. (1995). Deposition of fixed atmospheric nitrogen and foliar nitrogen content of bryophytes and *Calluna vulgaris* (L.) Hull. Environmental Pollution 99: 193-205.
- Pitcairn, C., Fowler, D., Leith, I., Sheppard, L., Tang, S., Sutton, M., Famulari, D. (2006). Diagnostic indicators of elevated nitrogen deposition. Environmental Pollution 144: 941-950.
- Poikolainen, J., Piispanen, J., Karhu, J., Kubin, E. (2008). Nitrogen deposition in Finland 1990 – 2006 by using mosses as bioindicators. In: Abstracts of 21st Task Force Meeting of the ICP Vegetation, 26th-29th February 2008, Oulu, Finland. http://icpvegetation.ceh.ac.uk/Reports/abstract_book_210208.pdf
- Rühling, Å. (1994). Atmospheric heavy metal deposition in Europe – estimation based on moss analysis. NORD 1994:9. Nordic Council of Ministers, Copenhagen, Denmark.
- Rühling, Å., Steinnes, E. (1998). Atmospheric heavy metal deposition in Europe 1995-1996. NORD 1998:15. Nordic Council of Ministers, Copenhagen.
- Salemaa, M., Mäkipää, R., Oksanen, J. (2008). Differences in the growth response of three bryophyte species to nitrogen. Environmental Pollution 152: 82-91.
- Skyre, O., Oechel, W.C. (1979). Moss production in a black spruce *Picea mariana* forest with permafrost near Fairbanks, Alaska, as compared with two permafrost-free stands. Holarctic Ecology 2: 249-254.

- Slootweg, J., Posch, M., Hetteling, J.-P. (2007). Critical loads of nitrogen and dynamic modelling. CCE Progress Report 2007. ICP Modelling and Mapping, Coordination Centre for Effect, Netherlands Environmental Assessment Agency, Bilthoven, The Netherlands.
- Smith, R.I., Fowler, D., Sutton, M.A., Flechard, C., Coyle, M. (2000). Regional estimation of pollutant gas deposition in the UK: model description, sensitivity analysis and outputs. *Atmospheric Environment* 34: 3757-3777.
- Solga, A., Burkhardt, J., Zechmeister, H.G., Frahm, J.-P. (2005). Nitrogen content, ^{15}N natural abundance and biomass of the two pleurocarpous mosses *Pleurozium schreberi* (Brid.) Mitt., and *Scleropodium purum* (Hedw.) Limpr. in relation to atmospheric nitrogen deposition. *Environmental Pollution* 134: 465-473.
- Steinnes, E., Rühling, Å., Lippo, H., Mäkinen, A. (1997). Reference material for large-scale metal deposition surveys. *Accreditation and Quality Assurance* 2: 243-249.
- Streeter, D.T. (1965). Seasonal variations in the nutrient content of carpets of *Acrocladium cuspidatum* (Hedw.) Lindb. *Journal of Bryology* 4: 818-827.
- Sutton, M.A., Tang, Y.S., Miners, B.P., Coyle, M., Smith, R.I., Fowler, D. (1998). Results of UK National Ammonia Monitoring Network. Final Report to Defra. Institute of Terrestrial Ecology, Edinburgh, UK.
- Thöni, L., Matthaei, D., Seidler, E., Bergamini, A. (in press). Deposition von Luftschadstoffen in der Schweiz. Moosanalysen 1990 - 2005. Bundesamt für Umwelt, Bern, Switzerland.
- Tyler, G. (1970). Moss analysis – a method for surveying heavy metal deposition. In: Englund, H.H. and Berry, W.T. (Eds). *Proceedings of the Second International Clean Air Congress*. Academic Press, New York.
- Working Group on Effects (2004). Review and assessment of air pollution effects and their recorded trends. Working Group on Effects, Convention on Long-range Transboundary Air Pollution. Natural Environment Research Council, UK.
- Working Group on Strategies and Review (2007). Report on the workshop on atmospheric ammonia: detecting emission changes and environmental impacts. ECE/EB.AIR/WG.5/2007/3. <http://www.unece.org/env/documents/2007/eb/wg5/ece.eb.air.wg.5.2007.3.e.pdf>
- Zechmeister, H.G., Dirnböck, T., Hülber, K., Mirtl, M. (2007). Assessing airborne pollution effects on bryophytes – lessons learned through long-term integrated monitoring in Austria. *Environmental Pollution* 147: 696-705.

Annex 1. Participants in the 2005/6 nitrogen in mosses survey

Note: many others have contributed to sampling and analysis, but only main contributors are listed below.

Zechmeister	Harald G.	University of Vienna	Austria
Riss	Alarich	Federal Environment Agency, Vienna	Austria
De Temmerman	Ludwig	Veterinary and Agrochemical Research Centre, Tervuren	Belgium
Yurukova	Lilyana	Institute of Botany, Bulgarian Academy of Sciences, Sofia	Bulgaria
Suchara	Ivan	Silva Tarouca Research Institute for Landscape and Ornamental Gardening	Czech Republic
Sucharová	Julie	Silva Tarouca Research Institute for Landscape and Ornamental Gardening	Czech Republic
Liiv	Siiri	Tallinn Botanic Garden	Estonia
Kubin	Eero	Finnish Forest Research Institute, Muhos Research Station	Finland
Karhu	Jouni	Finnish Forest Research Institute, Muhos Research Station	Finland
Poikolainen	Jarmo	Finnish Forest Research Institute, Muhos Research Station	Finland
Piispanen	Juha	Finnish Forest Research Institute, Muhos Research Station	Finland
Leblond	Sébastien	National Museum of Natural History, Paris	France
Rausch – de Traubenberg	Catherine	National Museum of Natural History, Paris	France
Galsomiès	Laurence	French Agency for the Environment and Energy Management, Paris	France
Schröder	Winfried	University of Vechta	Germany
Pesch	Roland	University of Vechta	Germany
Dieffenbach-Fries	Helga	Federal Environment Agency, Langen	Germany
Alber	Renate	Environmental Agency of Bolzano, Laives	Italy
Frolova	Marina	Latvian Environment, Geology and Meteorology Agency, Riga	Latvia
Nikodemus	Oļģerts	University of Latvia, Riga	Latvia
Tabors	Guntis	University of Latvia, Riga	Latvia
Maňková	Blanka	Institute of Landscape Ecology, Slovak Academy of Science, Bratislava	Slovakia
Oszlanyi	Július	Institute of Landscape Ecology, Slovak Academy of Science, Bratislava	Slovakia
Jeran	Zvonka	Jožef Stefan Institute, Ljubljana	Slovenia

Fernández Escribano	José Angel	University of Santiago de Compostela	Spain (Galicia)
Carballeira Ocaña	Alejo	University of Santiago de Compostela	Spain (Galicia)
Aboal Viñas	Jesús	University of Santiago de Compostela	Spain (Galicia)
Santamaría	Jesús Miguel	University of Navarra, Pamplona	Spain (Navarra)
González-Miqueo	Laura	University of Navarra, Pamplona	Spain (Navarra)
Elustondo	David	University of Navarra, Pamplona	Spain (Navarra)
Lasheras	Esther	University of Navarra, Pamplona	Spain (Navarra)
Bermejo	Raúl	University of Navarra, Pamplona	Spain (Navarra)
Thöni	Lotti	FUB - Research Group for Environmental Monitoring, Rapperswil	Switzerland
Coşkun	Mahmut	Canakkale Onsekiz Mart University	Turkey
Coşkun	Münevver	Canakkale Onsekiz Mart University	Turkey
Çayır	Akın	Canakkale Onsekiz Mart University	Turkey
Harmens	Harry	Centre for Ecology and Hydrology, Bangor	United Kingdom
Lloyd	Andrew	Centre for Ecology and Hydrology, Bangor	United Kingdom
Jarvis	Kim	Kingston University, Kingston upon Thames	United Kingdom
Ashmore	Mike	University of York	United Kingdom
Jordan	Crawford	Agri-Food and Biosciences Institute, Belfast	United Kingdom (Northern Ireland)