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Relationship between site-specific nitrogen concentrations in mosses and measured wet bulk atmospheric nitrogen deposition across Europe

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To assess the relationship between nitrogen concentrations in mosses and wet bulk nitrogen deposition or concentrations in precipitation, moss tissue and deposition were sampled within a distance of 1 km of each other in seven European countries. Relationships for various forms of nitrogen appeared to be asymptotic, with data for different countries being positioned at different locations along the asymptotic relationship and saturation occurring at a wet bulk nitrogen deposition of ca. 20 kg N ha^{-1} yr^{-1}. The asymptotic behaviour was more pronounced for ammonium-N than nitrate-N, with high ammonium deposition at German sites being most influential in providing evidence of the asymptotic behaviour. Within countries, relationships were only significant for Finland and Switzerland and were more or less linear. The results confirm previous relationships described for modelled total deposition. Nitrogen concentration in mosses can be applied to identify areas at risk of high nitrogen deposition at European scale.

1. Introduction

For ectohydric moss species, the lack of a well-developed root system, vascular system and protective cuticle means that they receive and take up water, nutrients and contaminants mainly from atmospheric deposition (dry, wet and occult). Hence, such mosses have shown to be suitable indicators of atmospheric deposition of, for example, nitrogen (Harmens et al., 2011; Pitcairn et al., 2006; Salemaa et al., 2008; Solga et al., 2005; Zechmeister et al., 2008), heavy metals (Harmens et al., 2010, 2012; Schröder et al., 2010b) and selected persistent organic pollutants (Foan et al., 2010, 2014; Harmens et al., 2013a). The moss monitoring technique provides a complementary, time-integrated measure of element deposition from the atmosphere to terrestrial systems. As it is easier and cheaper than conventional deposition analysis, a much higher sampling density can be achieved than with conventional deposition analysis. Hence, passive biomonitoring of atmospheric nitrogen deposition using mosses would allow the determination of the variation in atmospheric nitrogen deposition at a high spatial resolution,

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including in countries or areas where nitrogen deposition monitoring networks are absent.

For nitrogen, sometimes the relationship between atmospheric deposition rates and the concentration in mosses is weak (Stevens et al., 2011) or shown to be species-specific (Arroniz-Crespo et al., 2008; Salemaa et al., 2008). One possible explanation for the weak relationship between the deposition and accumulation of nitrogen is the regulation of tissue loads in mosses because nitrogen is known to play an important role in the metabolism of organisms (e.g., Koranda et al., 2007; Arroniz-Crespo et al., 2008), in contrast to for example non-essential heavy metals such as cadmium and lead. Such regulation may distort the patterns of nitrogen deposition identified by biomonitoring with terrestrial mosses. Schröder et al. (2010a) have shown that atmospheric nitrogen deposition, as modelled by the European Monitoring and Evaluation Programme (EMEP), is the primary factor determining total nitrogen concentrations in mosses. Harmens et al. (2011) observed an asymptotic relationship between the total nitrogen concentrations in mosses and EMEP modelled total nitrogen deposition (averaged per 50 km $\times$ 50 km grid) across Europe, with saturation (i.e. no further increasing nitrogen concentration in moss tissues with increasing nitrogen deposition) occurring at a total deposition rate of ca. 15 kg N ha^{-1} yr^{-1}. Whether such as relationship also holds when both the nitrogen concentration in moss and atmospheric wet nitrogen deposition are measured at nearby sites across Europe, is unknown.

Only a few studies have examined the relationship between the nitrogen concentration in mosses and measured (as opposed to modelled) nitrogen deposition in the immediate vicinity of the moss sampling sites (Skudnik et al., 2014; Solga et al., 2005; Thöni et al., 2008; Zechmeister et al., 2008), in monitoring studies not conducted in the immediate vicinity of local sources (e.g. Pitcairn et al., 2006). These studies were all conducted at the (sub-)national scale and such data is not available at the European scale. The strength and shape of the relationship observed in these (sub-) national studies varies between countries. For example, in Switzerland, a strong, significant ($r^2 = 0.91$) linear relationship was found between the total nitrogen concentration in mosses and measured site-specific wet bulk nitrogen deposition (Harmens et al., 2011; Thöni et al., 2008). Less strong but still significant linear relationships were also reported for North Rhine-Westphalia in Germany (Solga et al., 2005) and Austria (Zechmeister et al., 2008). Skudnik et al. (2014) showed a weak but significant linear-logarithmic relationship between the nitrogen concentration in mosses and atmospheric bulk nitrogen deposition. To investigate the strength and shape of the relationship at the European scale, data on nitrogen concentrations in mosses and measured wet bulk nitrogen deposition were collected in seven European countries. Only monitoring sites where the distance between the moss sampling site and the atmospheric deposition was less than 1 km were considered.

As different moss species were used in the current study, we also investigated whether moss species differ in their nitrogen concentration when sampled at the same sites, as this might confound the relationship between atmospheric nitrogen deposition and the nitrogen concentration in mosses (Arroniz-Crespo et al., 2008; Salemaa et al., 2008). Although there are other factors potentially confounding the relationship between atmospheric nitrogen deposition and its concentration in mosses, these were not investigated here but have been discussed previously in more detail (Harmens et al., 2011; Schröder et al., 2010a) and some are further discussed in the results and discussion section.

Despite the sometimes reported linear relationship between the nitrogen concentration in mosses and measured wet bulk nitrogen deposition at the (sub-) national scale (Harmens et al., 2011; Solga et al., 2005; Thöni et al., 2008), we hypothesise that the relationship will show an asymptotic behaviour at the European scale (conform Harmens et al., 2011; using modelled nitrogen deposition) when higher deposition rates are included. However, we expect less scatter in the underlying data than for modelled deposition (Harmens et al., 2011). We also tested whether the relationship is affected by nitrogen speciation in deposition and whether the strength of the relationship differs for nitrogen deposition or nitrogen concentration in precipitation.

2. Materials and methods

2.1. Sites

Mosses were collected between 1998 and 2012 at selected sites in seven European countries (Fig. 1): Austria (AT), Switzerland (CH), the German Bundesland Niedersachsen (DE-NI), Spain (ES), Finland (FI), France (FR), and Slovenia (SI, although some of sites were in Austria and Italy close to the Slovenian border). For this study, moss data were only included from sites (97 in total) where the distance to the deposition monitoring site was less than 1 km (the maximum distance recorded was 900 m). At some sites (s) sampling was repeated in time, leading to 160 data points (p) for comparison (AT 26s, 26p; CH 18s, 33p; DE-NI 6s, 33p; FR 24s, 36p; SI 11s, 11p; FI 11s, 19p; ES 1s, 2p). At some forested sites the deposition was characterised as throughfall below the canopy of trees rather than bulk deposition only. This was the case for the majority of data points in Germany, all sites in France and the one site in Spain. Including throughfall for forested sites in Germany allowed the inclusion of high deposition data beyond the level that was included in the study described previously by Harmens et al. (2011).

2.2. Moss species and sample preparation

The main moss species sampled were *Pleurozium schreberi* (Willd. ex Brid.) Mitt. (*Ps*, at 44.4% of the sites) and *Hypnum cupressiforme* Hedw. (*Hc*, 36.3%). Where neither of these could be found, other species were collected (19.4%): *Hylocomium splendens* (Hedw.) Schimp. (*Hs*; 6.3%), *Pseudoscleropodium purum* (Hedw.) M.Fleisch. (*Pp*; 6.3%), *Thuidium tamariscinum* (Hedw.) Schimp. (*Tt*; 5.6%) or *Abietinella abietina* (Hedw.) M.Fleisch. (*Aa*; 1.3%; Fig. 1). Moss sampling and preparation were conducted according to guidelines described in the ICP Vegetation moss monitoring manual (ICP Vegetation, 2010). Moss samples were either collected below the canopy of trees but not from stems (hence, exposed to throughfall deposition), or in open areas or forest clearings at least 3 m away from tree crowns (see Table 1 for details). Litter and other debris was removed from the mosses and green and brownish parts were separated for analysis (estimated 2–3 years' growth). After drying the mosses were ground to a powder for the determination of nitrogen.

2.3. Deposition sampling

Most countries collected precipitation using bulk samplers with open funnels, although France collected precipitation in gutters beneath the canopy of trees; Finland and Slovenia also used snow collectors during winter, i.e. bulk samplers designed for winter conditions (Table 1). Often, deposition was sampled according the manuals of the ICP Forests (see Table 1 for details). Precipitation was collected in two or four week intervals. Wet bulk nitrogen deposition (open field or throughfall) was determined from nitrogen concentration in the samples and the amount of precipitation. Where possible, the averages of three years of deposition data (year of moss sampling and the previous two years) were calculated to correspond with the estimated two to three years of moss growth and to allow for the variation in deposition between years. For Germany, 10 data points have deposition data from only one year and 11 data points have only averages of two years.

2.4. Nitrogen analysis

The nitrogen concentration in mosses was determined using the Kjeldahl method (Kjeldahl, 1883), a modified micro–Kjeldahl method (Kubin and Siira, 1980), or by elemental analysis following the Dumas method (Dumas, 1831, Table 1). Various methods were applied to determine the nitrogen concentration in precipitation and throughfall (see Table 1 for details). Nitrogen deposition in precipitation or throughfall was also calculated as the sum of $N{-}NH_4^+$ and $N{-}NO_3^-$ as collected by the samplers and we will refer to this as 'bulk nitrogen' deposition. In addition, some countries (Finland and Germany) measured dissolved organic nitrogen (DON) or the total nitrogen concentration (France and Slovenia) in precipitation (96 data points for comparison). We will refer to this as 'total bulk nitrogen' deposition, either measured (France and Slovenia) or calculated from 'bulk nitrogen' plus organic nitrogen deposition (other countries). One should bear in mind that this is not total nitrogen deposition as the total dry deposition of nitrogen from aerosols and gas was not determined. In contrast to wet-only collectors, bulk samplers often contain a fraction of total dry deposition, so open bulk samplers do not only collect wet deposition (Thimonier, 1998, and reference therein).