### RESEARCH

**Open Access** 

## Accounting for canopy drip effects of spatiotemporal trends of the concentrations of N in mosses, atmospheric N depositions and critical load exceedances: a case study from North-Western Germany

Michaela Kluge<sup>1\*</sup>, Roland Pesch<sup>1</sup>, Winfried Schröder<sup>1</sup> and Andreas Hoffmann<sup>2</sup>

#### Abstract

**Background:** Atmospheric nitrogen (N) deposition into terrestrial ecosystems is frequently considered as a threat to phyto-diversity. In previous investigations, the atmospheric N inputs enriched in mosses were recorded in 2004 as part of a regional investigation at 54 locations in north-west Germany and in 2005 at 726 locations across the whole country. This article deals with a study conducted in 2012 comparing N concentrations in mosses sampled within 30 forest stands and in 26 adjacent open fields in north-west Germany. The N concentration in mosses were determined and, by the use of a regression model, converted to N atmospheric deposition values. These deposition estimations enabled to calculate N critical load exceedances.

**Results:** Compared to the average N concentration in mosses sampled in open fields 2012 (7.4 kg/ha\*a), the average N concentrations in mosses within adjacent forests were almost four times higher (26.6 kg/ha\*a), and the maximum within the stands accounted for approximately 56 kg/ha\*a. Compared to 2005, there was a slight decline of the average N deposition by 2.4 kg/ha\*a in open fields. However, the average N concentrations in mosses within forests stands in 2012 remained nearly the same since 2004 (29 kg/ha\*a). The atmospheric N deposition as estimated from the N concentration in mosses ranged between the minimum and maximum N critical load at 71% of the 56 sites investigated. At 14% of the sites, the N deposition was close to the maximum N critical load value which was exceeded in 11%.

**Conclusions:** The study at hand revealed statistically significant differences between N concentrations measured in mosses sampled within forests and in open fields. The presented findings should be accounted for both modelling and mapping atmospheric N deposition into terrestrial ecosystems on the one hand and related estimations of N critical load exceedances on the other hand.

Keywords: Bio-indication; Moss survey; Nitrogen; Canopy drip; Critical loads

\* Correspondence: mkluge@iuw.uni-vechta.de

<sup>1</sup>Chair of Landscape Ecology, University of Vechta, Driverstraße 22, POB 15 53, Vechta 49377, Germany

Full list of author information is available at the end of the article



© 2013 Kluge et al.; licensee Springer. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/2.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

#### Background

Substances emitted into the atmosphere, such as nitrogen (N) and metals, come down to earth by wet, occult (i.e. cloud water) and dry atmospheric deposition. Then, in terrestrial ecosystems, they can be accumulated in soils and plants. The partitioning between dry, occult and wet deposition depends on atmospheric gas and aerosol N concentrations, meteorological conditions as well as land use and vegetation characteristics, e.g. surface roughness, canopy leaf surface area and vegetation wetness. Unlike wet deposition, which is widely monitored in regional networks of wet-only or bulk precipitation collectors, measurements of dry N fluxes have largely remained experimental and limited to few research sites, lasting for a few days to a few months only. Dry deposition monitoring networks across areas of large spatial extent remain, up to now, impracticable [1]. A comparison of results calculated by four dry deposition models for 55 European sites revealed that the differences between models reached a factor of 2 to 3 and exceeded the differences between monitoring sites [2].

Next to atmospheric deposition measurements and models of atmospheric compounds, environmental analyses concentrated on biomonitoring activities. Soilinhabiting ectohydric mosses thereby turned out to be particularly suitable for the inventory of elements on different spatial scales [3-7] since they have rhizoids serving for anchorage but not for water and mineral uptake. The application of mosses as biological samplers for dry, occult and wet atmospheric deposition has several advantages: in addition to the long-term accumulation of atmospheric deposition without physiological damages, this method is cost effective and time saving. Furthermore, the moss technique enables achieving a high spatial resolution compared to technical deposition samplers. Since 1990, so-called 'moss surveys' were therefore carried out every 5 years in at least 21 European countries at about 7,000 sites [8-10]. These surveys enabled mapping the spatial and temporal trends of metal accumulation in Europe [11,12]. The moss monitoring campaigns corroborated a significant decrease of metal accumulation between 1990 and 2005 by, e.g. 52% up to 72% cadmium (Cd) and lead (Pb). For mercury (Hg), however, there was only a slight but not significant decrease (12%) since 1995 [11,13].

In the run-up to the European moss survey in 2005, a study was conducted in 2004 to analyse the regional variability of N concentrations in mosses in terrestrial ecosystems due to different land uses. For this investigation, 24 representative sampling sites within the Euro Region Nissa and 30 sampling sites within the Weser-Ems Region were selected [7,14]. Then, in 2005, within the framework of the European moss survey, N concentrations in mosses were mapped for the first time nationwide in Germany. For that purpose, data

were collected at 726 locations across the German territory and used to validate the atmospheric N deposition determined and modelled by the European-wide European Monitoring and Evaluation Programme (*EMEP*) [10]. In addition, atmospheric N deposition into Natura 2000 sites was estimated from the data collected in the moss survey in 2005 (median 16.7 kg/ha\*a) [15]. As shown by [9,14,16] and [17], the atmospheric N deposition and the enrichment of N in mosses differ considerably on a regional scale.

The same holds true for the maximum estimated exposure to N deposition below which significant harmful effects on specified sensitive elements of the environment are not assumed to occur according to present knowledge [1,17-20]: such critical loads specifying that dose that can be deposited in ecosystems per area unit and period without any long-term harmful effect vary spatially, depending on receptor-specific characteristics. The area at risk due to the exceedance of critical loads of eutrophication and the average accumulated exceedance in EU27 in 2000 and 2020 under the baseline scenario relying on national reports, i.e. representing current legislation, were estimated to amount for 74% and 61%, respectively. Under the maximum feasible reduction scenario, the area at risk in EU27 could be 24% [18]. In part, ecotoxicologically critical input levels, critical loads, for N are exceeded extensively. However, long-term exceedances of the critical N input rate can lead to an imbalance of nutrients and to changes in the species composition in sensitive ecosystems [4,6,17,21,22]. Hence, 15% of the natural area within in the EU27 countries can be seen at risk of significant change of biodiversity in 2000. This area is expected to be reduced to about 6% under the Baseline scenario and to approximately 1% under the Maximum Feasible Reduction scenario, respectively [18]. Nutrient imbalances can increase the sensitivity of plants to climatic extremes and to biotic pests [4,6,17,22].

In previous studies, the N concentration in mosses were used to estimate and map deposition rates on a 5  $\times$ 5 km<sup>2</sup> raster. So far, there are only few studies on the amount and the effect of N concentrations in mosses in forest ecosystems in terms of the influence of canopy drip on forest ecosystems although such may have a significant influence on the assessment of atmosphere deposition patterns [4,6,20]. Therefore, this article deals with investigations on the influence of canopy drip to the concentration of nitrogen in mosses. To this end, mosses were collected within forest stands and in open fields in north-west Germany, analysed for N concentrations and compared to the data collected in 2004 [7,14] and 2005 [16]. Furthermore, the impact of different site-specific and regional factors potentially influencing N concentrations in mosses was investigated by decision trees.

#### **Results and discussion**

Over several years, mosses collect and accumulate dry, occult and wet atmospheric deposition. Moss surveys can reveal both differences in N concentrations across large distances and within small-scale areas (e.g. sitespecific differences due to canopy drip effects) [3,4,6,7]. The study at hand revealed significant differences between N concentrations measured in mosses sampled within forests and on open fields. Due to its large surface, its height and its roughness, the total N deposition in forests is systematically higher than in other ecosystems also confirmed by the results of this study at hand. However, the dimension of this filtering effect depends on the air concentration and the meteorological variables such as wind speed and humidity [23]. Furthermore, interactive effects are complex and different ecosystems react with varying sensitivity. The increased N input in the former years enhanced the N saturation of forest ecosystems additionally to an increased soil acidification. While N was the limiting factor for forest ecosystems in the past, it is nowadays a potential hazard to the vitality of tree populations and the total ecosystem functioning. The results of this study showed that there are, in part, exceedances of the maximum critical N input value. According to [24], short-time exceedances can be compensated by ecosystems. Biological responses to high atmospheric N deposition as for instance ecosystem stability and biodiversity are often delayed. Due to the multi-factorial relationship between the N input and the ecological reactions in forests, the dose-response relationship is very complex. High N inputs into forest ecosystems lead to an increased amount of N in leaves and needles resulting in an unbalanced nutrition. In the long term, a permanent exceedance of N inputs in combination with other factors such as pest infestations, droughts or frost periods can lead to a reduced vitality of forest ecosystems, changes in rather endemic species composition and to a limited self-regulation [4,14,17,25-28]. The reduction of atmospheric N deposition below the respective ecosystem specific critical load value can lead to a recovery of the ecosystem concerned. However, the recovery is often delayed and does not include all parts of the ecosystem [19]. Thus, atmospheric N deposition is still considered to be a serious environmental problem that must be solved, i.e. by the reduction of N emissions [9,14,17].

#### Canopy drip effects

The Wilcoxon signed-rank test carried out to compare the median values of the different sampling site categories (open field, forest stand) showed that the respective N concentrations at open fields are significantly lower than at sites directly within the forest stands (p = 0.000, Wilcoxon test) (Figure 1).

The N concentrations in mosses sampled in forest stands (2.2%) were in average twice as high as in mosses collected in open fields (1.1%). In addition, the N concentrations (given in %) were transferred into atmospheric N deposition values (in kg/ha\*a) following [10]. Accordingly, the minimum atmospheric N deposition amounted for 4.6 kg/ha\*a (open field), the maximum for 55.9 kg/ha\*a (forest stand). The average value of the open sites was 7.4 kg/ha\*a, the average of forest stands 26.6 kg/ha\*a (Figure 2).





Grid cell	2004 Forest stand		2005 Open field		2012				
					Forest stand		Open field		
	N (%)	N (kg/ha*a)	N (%)	N (kg/ha*a)	N (%)	N (kg/ha*a)	N (%)	N (kg/ha*a)	
1	-	-	1.22	8.61	2.86	39.90	1.01	6.13	
2	2.36	28.23	1.08	6.91	2.39	28.88	1.36	10.47	
3	1.79	17.16	1.05	6.57	2.48	30.87	-	-	
5	-	-	-	-	2.14	23.67	-	-	
6	-	-	1.38	10.75	2.49	31.09	1.18	8.11	
7	2.84	39.40	-	-	2.90	40.91	1.28	9.39	
8	-	-	1.30	9.65	2.90	40.91	-	-	
10	2.62	34.07	-	-	2.06	22.10	1.01	6.13	
11	-	-	1.37	10.61	1.87	18.57	1.17	7.98	
13	-	-	1.30	9.65	2.61	33.84	1.03	6.35	
14	2.89	40.65	1.41	11.17	2.35	28.02	1.11	7.26	
19	1.82	17.69	-	-	2.77	37.67	1.25	8.99	
23	-	-	1.05	6.57	2.17	24.27	-	-	
25	2.01	21.15	2.01	21.15	2.28	26.53	1.17	7.98	
27	2.47	30.64	1.41	11.17	2.47	30.64	0.99	5.91	
28	-	-	1.10	7.14	1.84	18.04	1.27	9.25	
29	-	-	1.37	10.61	1.98	20.58	0.96	5.59	
30	-	-	1.33	10.06	1.56	13.40	0.92	5.18	
Median	2.42	29.44	1.30	9.65	2.37	28.45	1.11	7.26	
Average	2.35	28.62	1.29	9.78	2.34	28.33	1.05	6.98	

Table 1 N concentrations in mosses for 2004 (forest stand), 2005 (open field) and 2012 (forest stand, open field)

Grid cells without data are not listed.

#### Temporal analyses of N concentrations in mosses

For the illustration of the N deposition accumulated by mosses over time, the N concentrations in mosses collected from open fields (survey in 2012) were compared to the values of 2005. In addition, the N concentration values of forest stands (survey in 2012) were compared to the values of a regional investigation carried out in 2004 [7,14]. To this end, only those sites with a distance smaller than 5 km were statistically analysed. As can be seen from Table 1 and Figure 3, the N concentrations measured in mosses sampled in open fields in 2012 significantly differ from those in 2005 (p = 0.001, Wilcoxon test). There was a slight decline of the median N concentrations (1 kg/ha\*a) in open fields since 2005. The N concentrations in mosses were lower in 81% of cases. The comparison between the average N concentrations in mosses within forest stands in 2012 and the average N concentrations in mosses in 2004 also showed a significant difference (p = 0.018, Wilcoxon test). The median N concentration decreased by 2.4 to 7.3 kg/ha\*a.

#### **CART** analysis

N is emitted into the atmosphere by agriculture and by combustion processes (industry, traffic) and is deposited at some distances to these sources. This source-sink relation can be seen from the CART dendrogram (Figure 4). The following predictors were identified to have the most powerful influence on the N concentration in mosses: sampling point (within forests/outside of forests) (level 1), distance to interstate roads and moss species (level 2) and distance to animal housings and distance to highways (level 3). This CART model explains 81% of the variance in the data set comprising 56 measurements. Node 0 describes the distribution of the N measurements of the 56 sampling points with an average value of approximately 1.7%. With regards to the entire data set, the location of the sampling point in open fields and in forest stands is identified to be the factor the most associated to the N concentrations in mosses. The average N concentration of sites not influenced by canopy drip is about 1.1%, the average value of sampling sites directly within the forest stand, however, is roughly 2.4%. Node 1 (open area) is split into nodes 3 and 4 by the distance to the interstate roads. Sampling sites at a distance of up to 8,169.5 m have lower N concentrations (approximately 1.1%) than sites in a distance higher than this value (approximately 1.3%). This could be explained by the fact that sampling sites that are further away from interstate roads are located nearer to dense agricultural areas. Node 2 (forest stands) is split into nodes 5 and 6 by the moss



species. Moss samples consisting of *S. purum* have a higher N concentration (approximately 2.5%) than those of *P. schreberi* (approximately 2.0%). Node 3, in turn, is split into nodes 7 and 8 by the distance to animal housings. Sampling sites that are far away from animal housings up to roughly 925 m show a slightly higher average N concentration (approximately 1.2%) than sites above this distance value (1.037%). Node 5 is split by the distance of the sets to highways. The N concentration in mosses sampled at sites up to approximately 12,050 m away from highways have a higher average N concentration (approximately 2.2%) than on sites with a greater distance to highways (approximately 1.8%).

# Estimating atmospheric N deposition from N concentrations in mosses and calculation of critical load exceedances

The comparison of N atmospheric depositions estimated from N concentration in mosses sampled in 2012 with the critical load values taken from [26,29] show that the N atmospheric deposition was at most sites investigated between the minimum and maximum critical load value (Tables 2 and 3): the atmospheric N deposition as estimated from the N concentration in mosses ranged between the minimum and maximum critical load at 48 out of 54 sampling sites in total (89%); at 8 of these 48 sites (approximately 17%), the corresponding N deposition was close to the maximum critical load value. The maximum critical load was exceeded at 6 of 54 sites investigated (11%).

Comparing deposition data estimated from measured N concentrations in mosses and such modelled by [23] reveals higher similarities for forest stands than for open fields (median N deposition estimated from moss concentrations for forest stands, 25.7 kg/ha\*a; median N deposition estimated from moss concentrations for open fields, 7 kg/ha\*a; median modelled deposition for forests without



Table 2 Critical loads and deposition data

Grid cell	Forest stands					Open field				
	EUNIS-code	CL (kg/ha*a)		N-Dep (l	kg/ha*a)	EUNIS-code	CL (k	g/ha*a)	N-Dep (kg/ha*a)	
		Min	Max	Mosses	Model		Min	Max	Mosses	Model
1	G1.51	3.8	155.1	39.9	41.0	G1.51	3.8	155.1	6.1	38.0
2	G1.87	3.9	174.4	28.9	37.0	G1.87	5.3	61.2	10.5	34.0
3	G4.71	4.3	52.2	30.9	34.0					
4	G4.4	3.2	29.3	11.5	37.0	G1.91	4.2	30.0	5.1	29.0
5	G4.71	4.0	34.6	23.7	31.0					
6	G1.51	4.0	130.6	31.1	35.0	G1.51	4.0	130.6	8.1	35.0
7	G1.91	4.1	33.2	40.9	46.0	G1.91	4.1	33.0	9.4	35.0
8	G1.91	4.1	33.3	40.9	43.0	G1.91	4.1	33.3	9.3	43.0
9	G1.91	4.2	30.2	24.9	38.0	G1.91	4.2	30.5	11.2	38.0
10	G1.91	4.2	27.6	22.1	36.0	G1.91	4.2	27.6	6.1	34.0
11	G1.91	4.8	28.4	18.6	29.0	G1.91	4.8	28.4	8.0	29.0
12	E1.72	7.6	24.4	18.9	29.0	E1.72	7.6	24.4	4.6	29.0
13	G1.91	4.2	33.8	33.8	43.0	G1.51	4.2	33.8	6.3	46.0
14	G1.91	4.2	31.5	28.0	42.0	G1.91	4.2	31.5	7.3	42.0
15	G1.91	4.2	28.6	23.9	45.0	G1.91	4.2	28.6	6.0	45.0
16	G1.91	3.4	28.4	29.1	37.0	G1.91	3.4	28.4	10.9	37.0
17	G4.71	5.5	40.8	55.9	31.0	G4.71	5.5	40.8	9.0	31.0
18	G3.42	9.1	47.1	14.8	28.0	G1.221	9.1	47.1	5.0	28.0
19	G1.51	3.8	143.7	37.7	48.0	G1.91	3.8	143.7	9.0	48.0
20	G1.221	5.7	34.5	21.3	42.0					
21				17.2	38.0				6.1	38.0
22	G1.91	4.1	22.8	15.1	37.0	G1.91	4.1	22.9	6.8	37.0
23	G1A.16	4.9	26.3	24.3	33.0					
24	D5.3	10.8	24.5	28.9	25.0	D5.3	10.8	24.5	5.4	25.0
25	G1A.16	5.4	48.7	26.5	45.0	G1A.16	5.4	48.7	8.0	41.0
26	G1.91	4.8	28.4	45.3	59.0	G4.4	3.8	28.4	8.4	44.0
27	G1.91	4.1	25.9	30.6	48.0	G1.91	4.1	25.9	5.9	48.0
28	G1.91	4.1	22.8	18.0	37.0	G1.91	4.1	22.8	9.3	37.0
29	G1.51	3.8	120.6	20.6	25.0	G1.51	3.8	120.6	5.6	25.0
30	G1.91	4.0	26.0	13.4	29.0	G1.91	4.1	26.0	5.2	30.0
Median				25.7	37.0				7.0	37.0

regards to adjacent open fields, 37 kg/ha\*a) (Table 2). This was corroborated by the results of the correlation analysis, yielding a higher significant association between deposition data derived from moss concentrations within forest stands and modelled deposition data (Spearman rank correlation, 0.47; p < 0.05) compared to open fields. Here, the correlation between N deposition estimated from N concentrations in mosses was lower and not significant (Spearman rank correlation, 0.37; p > 0.05). The shown differences could be explained by the fact that the critical loads were calculated with regard to forests as receptors but not for open fields [18,26].

#### Conclusions

The presented findings should be accounted for future monitoring activities dealing with atmospheric deposition of N in terrestrial ecosystems. Due to the results of this study, it seems important to differentiate more precisely and strictly between open fields and forest stands to ensure the comparability of the N concentration measurements over time, to avoid an over- and an underestimation of N concentrations and, thus, to yield data for validating the modelling and mapping of atmospheric N deposition and related critical loads [30]. Thus, it should be mandatory to describe the sampling sites exactly,

Table 3 Habitat of EUNIS codes

EUNIS code	Habitat
D5.3	Swamps and marshes dominated by <i>Juncus effusus</i> or other large <i>Juncus</i> spp.
E1.72	(Agrostis-Festuca) grassland
G1.221	Great medio-European fluvial forests
G1.51	Sphagnum ( <i>Betula</i> ) woods
G1.87	Medio-European acidophilous (Quercus) forests
G1.91	(Betula) woodland not on marshy terrain
G1A.16	Sub-continental (Quercus-Carpinus betulus) forests
G3.42	Middle European (Pinus sylvestris) forests
G4.4	Mixed (Pinus sylvestris-Betula) woodland
G4.71	Subcontinental nemoral (Pinus-Quercus) forests

especially with regard to the distance of the moss sampling or the deposition collectors to trees and canopies. Accordingly, future moss surveys in Europe will be undertaken using a digital questionnaire comprising information and aspects regarding, among other things, vegetation, land use and soil observed at the monitoring sites [9,13,31,32]. The questionnaire was developed within the German moss surveys and adopted to the moss sampling and requirements of other European countries.

#### Methods

#### Study area and sampling points

In accordance with the investigation purposes, a study area with an overall size of 110 km  $\times$  92 km was chosen in north-west Germany (Figure 5). As calculated from the 2006 Corine Land cover map [33], the study area is primarily dominated by 'non-irrigated arable land' (approximately 82%) followed by 'pastures' (approximately 12%), by 'complex cultivation' (approximately 2%), by 'coniferous forest' (approximately 1%) and by 'discontinuous urban fabric' (approximately 1%) (Table 4). Along with very high densities of animal farming, high atmospheric N deposition can be expected [25].

According to the ecological land classification of Germany [34], the study area is mainly covered by ecoregions 42 (Niedersächsische Geest) (approximately 78%), 43 (Niedersächsische Geest und Lüneburger Heide) (approximately 10%) and 47 (Niedersächsische Börden) (approximately 8%). In Table 5, ecological characteristics of these ecoregions of Lower Saxony and percentages of ecological land classes in Germany and in the study area are compiled.

Following [3], the total study area was divided into 30 grids, each covering  $18 \text{ km} \times 18 \text{ km}$  (Figure 6). Within each of the 30 grid cells covering the study area, one sampling point was chosen, consisting of one site within forest stands and one adjacent sampling site in open

areas where mosses without canopy drip influence were sampled. In order to enhance the comparability to the values determined in the European moss monitoring in 2005 [16] and in a regional study conducted in 2004 [7,14], former sites were re-sampled wherever possible.

According to [34], 37 out of 56 sampling points (66%) located within the study area are assigned to be coniferous forests, followed by non-irrigated arable lands (21%), by mixed forests (7%), transitional woodland-shrubs (4%) and by lands principally occupied by agriculture, with significant areas of natural vegetation (2%). Forty-six sampling points out of 56 in total (82%) are assigned to ecoregion 42 followed by ecoregion 43 (11%) and ecoregion 47 (7%) (Additional file 1: Table S1).

#### Moss sampling and chemical analyses

Sampling, conducted from September to October in 2012, and chemical analyses followed the European experimental protocol [35,36] derived from the Scandinavian recommendations [37] and continuously improved since then [31,32,35]. Within the study area, both sites affected by canopy drip effects within forests with at most 2 m distance to the tree trunk and from nearby sites without any influence of canopy drip with a distance of at least 10 m from the tree trunk were chosen. The sampling locations were at least 100 m far away from streets and single houses, 300 m from settlements and 1,000 m from industrial installations. According to the guidelines, Pleurozium schreberi was sampled in first priority. Where Pleurozium schreberi was absent, Scleropodium purum was collected (Additional file 2: Table S2). In total, there were 30 sampling sites classified as being affected by canopy drip. Twenty-six moss samplings could be carried out at sites without any influence of canopy drip.

According to [35], each moss sample was prepared and then dried at 40°C until a constant weight followed by a homogenization of every single sample. By means of a C/N-analyzer, the mass concentration of the total N accumulated in the sampled mosses was measured following the VDLUFA methodological manual II, 3.5.2.7. For quality control purposes, standard reference material was included into the chemical analyses yielding good results (Additional file 3: Table S3).

Like in the monitoring campaigns 2004 [7,14] and 2005 [16,31] in 2012, each sampling site was described in detail to document potential influences on the concentration of N in mosses. To this end, the data was integrated into a moss meta-database and linked to the measurement data on N concentration in mosses. Amongst others, the following sampling point describing meta-data were recorded (Additional file 2: Table S2): sampling in open field/forest stand, geographic coordinates, moss species (*P. schreberi, S. purum*) sampled, elevation above sea level (m), distance to tree trunk (m),

tree height (m), vegetation at sampling point, percentage proportion of agrarian and urban land use in a grid of 5  $\text{km}^2$  around sampling sites both derived from the 2006 Corine land cover map [33].

#### Statistical analyses of canopy drip effects

In order to check for significant differences between open fields and forest stands, as a first step, the N concentration in mosses given in (%) was logarithmised due to a rightskewed distribution. For comparing N deposition calculated from the N concentration in mosses with modelled total deposition calculated by [23] and critical load values for N given by [26,29], the N concentration in mosses was additionally transferred into atmospheric N deposition rates (kg/ha\*a). This was achieved by applying the following regression model which was derived from data on modelled atmospheric N deposition (EMEP) and geostatistically estimated N concentrations in mosses (European moss survey)



Level 1	Level 2	Level 3	Total area (ha)	Proportion (%)	
Artificial surfaces	Urban fabrics	Discontinuous urban fabric	63,501	1.30	
Agricultural areas	Arable land	Non-irrigated arable land	4,002,828	82.02	
	Pastures	Pastures	554,884	11.37	
	Heterogeneous agricultural areas	Complex cultivation	76,928	1.58	
Forests and semi-natural areas	Forests	Coniferous forest	66,033	1.35	

Table 4 Proportion and kind of land use within the study area

Values below 1% are not presented.

[10]: Y =  $1.8 \times +6.4$  (Additional file 4: Table S4). Subsequently, a Wilcoxon signed-rank test was carried out to compare the median values of the different sampling site categories (open field, forest stand).

#### Temporal analyses of N concentrations in mosses

The temporal analyses of N concentrations in mosses sampled in 2012 (this investigation), 2005 [16] and 2004 [7,14] rely on the comparison of respective sites with a distance smaller than 5 km from another. In 2012, the sampling took place, both, at sites affected by canopy drip effects within forests and at nearby sites without any influence of canopy drip, thus two N concentration values per site were available for most sites. In the regional investigation conducted in 2004, moss samplings took place within forest stands [7,14]. In the moss sampling campaign 2005, however, sampling took place on open fields [16]. In this study, the N concentration values of the study conducted in 2004 [7,14] were compared to the N concentration in mosses within forest stands determined in 2012 whereas the N concentration values of mosses on open fields sampled in 2012 were compared to the N concentrations determined in the moss campaign 2005. Subsequently, a Wilcoxon signedrank test was carried out to compare both the median values of the N concentrations at open fields 2005 and 2012 and the median values of the N concentrations in forest stands in 2004 and 2012.

#### Classification and regression trees analysis

Correlations between N concentrations in mosses (%) and site-specific and regional conditions potentially influencing factors were investigated by the Classification and Regression Trees (CART) [38,39]. In this study, the following describing variables taken from Additional file 2: Table S2 (Supplement) were integrated as potential predictors for N concentrations (target variable) into the CART model: sampling point (open field, forest stand); moss species (P. schreberi, S. purum); tree height; distances to roads, interstate roads, highways, settlements, industry, animal housings and agriculturally used areas; percentage proportion of the agrarian density in a radius of 5 km<sup>2</sup> around the sampling sites derived from the Corine database [33]; percentage proportion of urban land uses around 5 km of the sampling sites also derived from Corine [33]. CART divides iteratively heterogeneous data sets into more homogeneous classes regarding the target value, which is the N concentration in mosses. In this way,

Table 5 Ecological characteristics of ecoregions dominantly covering Lower Saxony

Ecoregion	Texture	PNV	Temperature (°C)	Evaporation (mm)	Precipitation (mm)	Radiation (Wh/qm)	Germany (%)	Study area (%)
42	Coastal and riverine sediments and sand	Atlantic/subatlantic hygrophilous birch-common oak forest with Betula pubescens, Frangula alnus and Molinia caerulea	9.0	46.5	63.4	3,273.4	7.3	78.3
43	Glacifluvial sediments and sand	lacifluvial sediments and sand ( <i>Fagus sylvatica, Quercus robur,</i> <i>Q. petraea</i> ) with <i>Lonicera</i> <i>periclymenum, Maianthemum</i> <i>bifolium, Vaccinium myrtillus,</i> partly <i>Ilex aquifolium</i>		46.7	59.0	3,286.8	7.2	9.6
47	Loess and loessial derivates	Southern subatlantic/Central European high montane spruce- pine-oak forests (F. sylvatica, Abies alba, Picea abies) with Luzula sylvatica and in the East with Calamagrostis villosa	9.3	48.0	60.9	3,303.9	8.1	8.1

Prevailing soil texture (Texture), potential natural vegetation (PNV), annual average value of temperature (Temperature), annual average value of evaporation (Evaporation), annual average value of precipitation (Precipitation), annual average value of global radiation (Radiation), percentages of ecological land classes in Germany (Germany) and in the study area (Study area).



Figure 6 Geographical distribution of sampling points within study area. For geographical coordinates, land use, ecoregion and further details, see Additional file 1: Table S1 and Additional file 2: Table S2.

classes (subgroups or nodes) are produced by a series of 'if-then' splits in order to maximise the homogeneity of the target variable step by step. Provided the target variable is metrically scaled (as holds true in this investigation), the least squared deviation is used as a measure of impurity. Such corresponds to the difference of the within-node variance between a respective node and the two resulting sub-nodes. The latter is adjusted for the different number of cases within each sub-node. Possible splits are tested for all variables until the best possible homogeneity is reached to choose the respective split variable as a predictor [38,39]. Using CART, both the target variable and the predictor values may be of categorical, ordinal or metric scale, i.e. interval or ratio, according to [40].

# Estimating atmospheric N deposition from N concentrations in mosses and calculation of critical load exceedances

In order to assess whether the atmospheric N depositions as estimated from N concentration values in mosses potentially exceed ecotoxicologically critical effect levels, critical load values given by [26,29] were incorporated into the statistical analyses. To this end, the N critical load values given in ionic equivalents (eq/ha\*a) were converted into kg/ha\*a according to [19]. Critical loads are given as value ranges (minimum and maximum critical value) due to ecosystem-specific responses to N inputs [1], classified according to European Nature Information System with a spatial resolution of 1 km<sup>2</sup> × 1 km<sup>2</sup> [1,41,42]. The corresponding critical load map was made available in terms of point geometries covering mainly forests (96%) and other pristine areas in Germany [29]. In this study, only those moss sampling sites within a distance of 2 km to the closest point with critical loads information were chosen for the analyses, hence one site (grid cell 21, see Figure 6) was not considered.

#### **Additional files**

Additional file 1: Table S1. Characterisation of the respective sampling points. These are labelled by numbers (Grid cell) based on the land use [33] and the ecological land classes [34]. Included are the sampling point (open field, forest stand), latitude and longitude (Gauß-Krüger coordinate system) and administrative district where the respective sampling point is located. Additional file 2: Table S2. Metadata used in statistical analyses. Labels of grid cells (see Figure 6), sampling points (sampling), coordinates according to the Gauß-Krüger coordinate system (latitude, longitude), administrative district, date of sampling, sampled moss species (moss species), feet above sea level (m), distance to tree trunk (m), tree height (m), position of sampling point: within forest/outside of forest (clearing), distance to roads (m) (Dist\_Road) (m), Distance to interstates (m) (Dist\_Int), distance to highways (m) (Dist\_High), distance to settlements (m) (Dist\_Set), distance to agricultural land (m) (Dist\_Agri) (m), distance to animal housings (m) (Dist\_Ani), distance to industry (m) (Dist\_Ind), agrarian density around sampling point (%) and density of urban areas (%) around sampling points.

Additional file 3: Table S3. Quality control data.

**Additional file 4: Table S4.** N concentrations in mosses 2012 (N (%) and N (%) log) and total atmospheric N depositions (N<sub>atm</sub>). Additionally included are grid cell number (see Figure 6), sampling point (open field, forest stand), latitude and longitude (Gauß-Krüger coordinate system) and administrative district where the respective sampling point is located.

#### **Competing interests**

The authors declare that they have no competing interests.

#### Authors' contributions

MK, RP and WS participated in the writing of the article. MK sampled the mosses, RP supervised the computations and WS headed both, the investigation and the writing. AH was responsible for the implementation and the monitoring of the laboratory tests. All authors read and approved the final manuscript.

#### Author details

<sup>1</sup>Chair of Landscape Ecology, University of Vechta, Driverstraße 22, POB 15 53, Vechta 49377, Germany. <sup>2</sup>LUFA Nord-West, Institute for fertilizers and seeds, Hameln 31787, Germany.

#### Received: 31 July 2013 Accepted: 30 August 2013 Published: 3 September 2013

#### References

- Bund/Länder-Arbeitsgemeinschaft für Immissionsschutz: Leitfaden zur Ermittlung und Bewertung von Stickstoffeinträgen; 2012 [http://www. umweltbundesamt.de/luft/downloads/lai-n-leitfaden.pdf.]
- Flechard CR, Nemitz E, Smith RI, Fowler D, Vermeulen AT, Bleeker A, Erisman JW, Simpson D, Zhang L, Tang YS, Sutton MA: Dry deposition of reactive nitrogen to European ecosystems: a comparison of inferential models across the NitroEurope network. ACP 2011, 11:2703–2728.
- Frahm JP: Moose als Bioindikatoren. Wiesbaden: Quelle & Meyer GmbH & Co; 1998.
- Mohr K: Passives Monitoring von Stickstoffeinträgen in Kiefernforsten mit dem Rotstengelmoos (*Pleurozium schreberi* (Brid.) Mitt). Environ Sci Pollut Res 1999, 11(5):267–274.
- Zechmeister HG, Dullinger S, Hohenwallner D, Riss A, Hanus-Illnar A, Scharf S: Pilot study on road traffic emissions (PAHs, heavy metals) measured by using mosses in a tunnel experiment in Vienna Austria. *Environ Sci Pollut Res* 2006, 13(6):398–405.
- Mohr K: Biomonitoring von Stickstoffimmissionen. Möglichkeiten und Grenzen von Bioindikationsverfahren. UWSF – Z Umweltchem Ökotox 2007, 19(4):255–264.
- Schröder W, Pesch R, Schmidt G, Fränzle S, Wünschmann S, Heidenreich H, Markert B: Moosmonitoring als Spiegel der Landnutzung? Stickstoff- und Metallakkumulation in Moosen zweier Regionen Mitteleuropas. UWSF – Z Umweltchem Ökotox 2008, 20(1):62–74.
- Pesch R, Schröder W, Dieffenbach-Fries H, Genßler L: Optimierung des Moosmonitoring-Messnetzes in Deutschland. UWSF – Z Umweltchem Ökotox 2008, 20(1):49–61.
- Mohr K, Holy M, Pesch R, Schröder W: Bioakkumulation von Metallen und Stickstoff zwischen 1990 und 2005 in Niedersachsen. Umweltwiss Schadst Forsch 2009, 21:454–469.
- Schröder W, Holy M, Pesch R, Harmens H, Fagerli H: Mapping background values of atmospheric nitrogen total depositions in Germany based on EMEP deposition modelling and the European Moss Survey 2005. Environ Sci Eur 2011, 23:18.

- Schröder W, Pesch R: Integrative monitoring analysis aiming at the detection of spatial and temporal trends of metal accumulation in mosses. J Atmos Chem 2004, 49:23–38.
- Schröder W, Pesch R: Time series of metals in mosses and their correlation with selected sampling site-specific and ecoregional characteristics in Germany. Environ Sci Pollut Res 2005, 12(3):159–167.
- 13. Harmens H, Norris DA, Steinnes E, Kubin E, Piispanen J, Alber R, Aleksiayenak Y, Blum O, Coskun M, Dam M, De Temmerman L, Fernández JA, Frolova M, Frontasyeva M, González-Miqueo L, Grodzinska K, Jeran Z, Korzekwa S, Krmar M, Kvietkus K, Leblond S, Liiv S, Magnússon SH, Mankovská B, Pesch R, Rühling Å, Santamaria JM, Schröder W, Spiric Z, Suchara I, et al: Mosses as biomonitors of atmospheric heavy metal deposition: spatial patterns and temporal trends in Europe. Environ Pollut 2010, 158:3144–3156.
- Schröder W, Hornsmann I, Pesch R, Schmidt G, Markert B, Fränzle S, Wünschmann S, Heidenreich H: Nitrogen and metals in two regions in Central Europe: significant differences in accumulation in mosses due to land use? Environ Monit Assess 2007, 133:495–505.
- Schröder W, Pesch R, Zechmeister HG, Kratz W, Holy M, Harmens H, Fagerli H, Ilyin I: Atmosphärische Deposition und Anreicherung von Schwermetallen und Stickstoff in Natura-2000-Gebiete Deutschlands. Umweltwiss Schadst Forsch 2010, 22:711–720.
- Harmens H, Norris DA, Cooper DM, Mills G, Steinnes E, Kubin E, Thöni L, Aboal JR, Alber R, Carballeira A, Coskun M, De Temmerman L, Frolova M, González-Miqueo L, Jeran Z, Leblond S, Liiv S, Mankovská B, Pesch R, Poikolainen J, Rühling Å, Santamaria JM, Simonèiè P, Schröder W, Suchara I, Yurukova L, Zechmeister HG: Nitrogen concentrations in mosses indicate the spatial distribution of atmospheric nitrogen deposition in Europe. Environ Pollut 2011, 159:2852–2860.
- UBA (Umweltbundesamt): Erfassung, Prognose und Bewertung von Stoffeinträgen und ihren Wirkungen in Deutschland. Deutschland: Final Report; 2011.
- Hettelingh JP, Posch M, Slootweg J, Le Gall AC: Analysis of environmental impacts caused by the Baseline and the Maximum Feasible Reduction scenarios. CCE Status Report 2010:13–26.
- Gauger T, Köble R, Anshelm F: Kritische Luftschadstoff-Konzentration und Eintragsraten sowieihre Überschreitung für Wald und Agrarökosysteme sowie naturnahe waldfreie Ökosysteme. Teil 1: Deposition Loads 1987–1989 und 1993–1995. Stuttgart: Final Report; 2000.
- Mohr K, Suda J, Kiehne S, Ahrens F, Landscheidt S, Pünjer LS: Untersuchungen zur Bewertung der Auswirkungen von Ammoniak- und Stickstoff-Depositionen auf Pflanzen und Ökosysteme im Nahbereich von Stallanlagen (BESTAND). Final Report: Oldenburg; 2011.
- Russow RWB, Böhme F, Neue HU: A new approach to determine the total airborne N input into the soil/plant system using <sup>15</sup>N isotope dilution (ITNI): results for agricultural areas in Central Germany. *TheScientificWorld* 2001, 1(Suppl 2):255–260.
- 22. Jenssen M, Hofmann G, Nickel S, Pesch R, Riediger J, Schröder W: Bewertungskonzept für die Gefährdung der Ökosystemintegrität durch die Wirkungen des Klimawandels in Kombination mit Stoffeinträgen unter Beachtung von Ökosystemfunktionen und -dienstleistungen. Eberswalde, Vechta: Final Report; 2013.
- 23. Gauger T: Erfassung, Prognose und Bewertung von Stoffeinträgen und ihren Wirkungen in Deutschland. MAPESI-Projekt (Modelling of Air Pollutants and EcoSystem Impact). Stuttgart: Final Report; 2010.
- Nagel HD, Becker R, Eitner H, Hübener P, Kunze F, Schlutow A, Schütze G, Weigelt-Kirchner R: Critical Loads für Säure und eutrophierenden Stickstoff. Bonn: Final Report; 2004.
- Mohr K, Meesenburg H, Horváth B, Meiwes KJ, Schaaf S, Dämmgen U: Bestimmung von Ammoniak-Einträgen aus der Luft und deren Wirkungen auf Waldökosysteme (ANSWER-Projekt). Oldenburg, Göttingen, Braunschweig: Final Report; 2005.
- Bobbink R, Hettelingh JP: Review and revision of empirical critical loads and dose-response relationships. In *Proceedings of an Expert Workshop, Noordwijkerhout, 23–25 June 2010.* the Netherlands: Coordination Centre for Effects, RIVM, NL; 2011.
- 27. WGE (Working Group on Effects): *Review and assessment of air pollution effects and their recorded trends. Working group on effects, convention on long-range transboundary air pollution.* United Kingdom: National Environment Council; 2004.

- Bobbink R, Hicks K, Galloway J, Spranger T, Alkemade R, Ashmore M, Bustamante M, Cinderby S, Davidson E, Dentener F, Emmett B, Erisman JW, Fenn M, Gilliam F, Nordin A, Pardo L, De Vries W: Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. *Ecol Appl* 2010, 20(1):30–59.
- Gauger T, Haenel HD, Rösemann C, Nagel HD, Becker R, Kraft P, Schlutow A, Schütze G, Weigelt-Kirchner R, Anshelm F: Nationale Umsetzung UNECE-Luftreinhaltekonvention (Wirkung). Teil 2: Wirkungen und Risikoabschätzungen Critical Load, Biodiversität, Dynamische Modellierung, Critical Levels Überschreitungen, Materialkorrision. Research Report: Dessau-Roßlau; 2008.
- Kratz W, Schröder W: Wider die Vernunft zum Ende eines Programms effektiver Umweltdatenerhebung in Bund-Länder-Kooperation. Umweltwiss Schadst Forsch 2010, 22:80–83.
- Harmens H, Norris D, Cooper D: Hall J and the participants of the moss survey: Spatial trends in nitrogen concentrations in mosses across Europe in 2005/2006. Bangor: NERC/Centre for Ecology & Hydrology; 2008.
- Schröder W, Bau H, Matter Y, Mohr K, Peichl L, Peiter A, Peronne T, Pesch R, Pöhlker J, Roostai H, Roostai Z, Schmidt G, Siewers U: Untersuchungen von Schadstoffeinträgen anhand von Bioindikatoren: Aus- und Bewertung der Ergebnisse aus dem Moos-Monitoring 1990/91, 1995/96 und 2000/01. Berlin: Final report; 2002.
- Keil M, Bock M, Esch T, Metz A, Nieland S, Pfitzner A: CORINE Land Cover Aktualisierung 2006 für Deutschland. Oberpfaffenhofen: Final Report; 2010.
- 34. Schröder W, Schmidt G: Defining ecoregions as framework for the assessment of ecological monitoring networks in Germany by means of GIS and classification and regression trees (*CART*). *Gate Environ Health Sci* 2001, **3**:1–9.
- UNECE: ICP vegetation experimental for the 2010 season, ICP vegetation coordination centre. Bangor, UK: CEH; 2010. http://icpvegetation.ceh.ac.uk/.
- Schröder W, Pesch R, Matter Y, Göritz A, Genßler L, Dieffenbach-Fries H: Trend der Schwermetall-Bioakkumulation 1990 bis 2005: Qualitätssicherung bei Probenahme, Analytik, geostatistischer Auswertung. Umweltwiss Schadst Forsch 2009, 21:549–574.
- 37. Rühling Å, Tyler G: Changes in atmospheric deposition rates of heavy metals in Sweden. *Water Air Soil Pollut* 2001, 1:311–323.
- Breiman L, Friedman J, Olshen R, Stone C: Classification and regression trees (CART). Pacific Grove: Wadsworth; 1984.
- 39. SPSS, Inc: Answer Tree 3.0 Users Guide. Chicago; 2001.
- Stevens S: On the theory of scales of measurement. Science 1946, 103(2684):677–680.
- Moss D, Davies CE: Cross-references between the EUNIS habitat classification and the nomenclature of CORINE Land Cover. Report: Huntingdon, Cambs, UK; 2002.
- 42. Davies CE, Moss D, Hill MO: *EUNIS habitat classification revised 2004*. Paris: European Topic Centre on Nature Protection and Biodiversity; 2004.

#### doi:10.1186/2190-4715-25-26

Cite this article as: Kluge *et al.*: Accounting for canopy drip effects of spatiotemporal trends of the concentrations of N in mosses, atmospheric N depositions and critical load exceedances: a case study from North-Western Germany. *Environmental Sciences Europe* 2013 25:26.

### Submit your manuscript to a SpringerOpen<sup>™</sup> journal and benefit from:

- Convenient online submission
- ► Rigorous peer review
- Immediate publication on acceptance
- ► Open access: articles freely available online
- ► High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at > springeropen.com