Effect of Canopy Drip on Accumulation of Nitrogen and Heavy Metals in Moss

Effet de la rosée sur l'accumulation d'azote et de métaux lourds dans les mousses

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Abstract

Research objectives: atmospheric deposition of heavy metals (HM) and nitrogen (N) can have long-term effects on species composition of ecosystems. Especially forests are particular affected due to filter effects of their canopy. The study at hand deals with the effect of canopy drip on the accumulation of N and HM in moss used as biomonitors for atmospheric deposition.

Methods: following the experimental protocol for the European Heavy Metals in Moss Survey, N and selected HM concentrations were determined in moss sampled at sites with and without canopy drip in North-Western Germany in 2012 (Kluge *et al.*, 2013) and in 2013. The N concentration was converted into atmospheric N deposition (Schröder *et al.,* 2014) to identify critical loads exceedances.

Results: compared to the atmospheric N deposition as estimated by the N concentration in moss sampled at sites without canopy drip (mean 2012: 7,3 kg ha^{-1} a^{-1}, 2013: 10,9 kg ha^{-1} a^{-1}) the average atmospheric N deposition at adjacent sites with canopy drip were approximately three times higher (2012: 26,4 kg ha^{-1} a^{-1}, 2013: 31,1 kg ha^{-1} a^{-1}). At 30 % (averages over both years) of the analysed sample sites with canopy drip the given critical load value was exceeded. Regarding the HM concentration in moss, in case of cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb) and zinc (Zn) the concentration in moss was also significantly higher at sites with canopy drip (averages over both years: Cd 0,2 mg kg^{-1}, Cu 8,5 mg kg^{-1}, Hg 0,03 mg kg-1, Pb 2,7 mg kg^{-1}, Zn 45,7 mg kg^{-1}) than at sites without canopy drip. Chromium (Cr) and nickel (Ni) showed no significant differences between both site types.

Major conclusions: the study shows significant spatial variances of the N and HM concentrations that should be taken into account when mapping and modelling atmospheric deposition and implementing measures to reduce atmospheric deposition.

Keywords

biomonitoring, small-scale variance, canopy drip.

Résumé

Objectifs de recherche : les dépôts atmosphériques de métaux lourds (ETM) et d'azote (N) peuvent avoir des effets à long terme sur la composition des espèces des écosystèmes. Les forêts sont particulièrement touchées à cause du rôle de filtre de leur canopée. L'étude traite de l'effet de la rosée issue de la canopée sur l'accumulation d'azote et d'éléments traces métalliques dans la mousse, utilisée comme bioindicateur des dépôts atmosphériques.

Méthodes : suivant le protocole expérimental européen pour les métaux lourds concernant la surveillance des mousses, l'azote et les métaux sélectionnés ont été déterminés dans les échantillons de mousse récoltés sur des sites avec et sans rosée issue de la canopée, dans le Nord-Ouest de l'Allemagne en 2012 (Kluge *et al*., 2013) et en 2013. La concentration en N a été convertie en dépôt d'azote atmosphérique (Schröder *et al.*, 2014) pour identifier les dépassements des charges critiques.

Résultats : en comparant le dépôt estimé d'azote atmosphérique à la concentration d'azote dans les échantillons de mousse sur des sites sans rosée issue de la canopée (moyenne 2012 : 7,3 kg ha^{-1} an^{-1}, 2013 : 10,9 kg ha^{-1} an^{-1}), la moyenne d'azote atmosphérique déposée sur des sites adjacents avec la présence d'une canopée était environ trois fois plus élevée (2012 : 26,4 kg ha^{-1} an^{-1}, 2013 : 31,1 kg ha^{-1} an^{-1}). Pour les 30 % des échantillons analysés avec canopée (moyenne sur les deux années), la valeur des charges critiques donnée a été dépassée. Pour la concentration en ETM dans la mousse, pour le cadmium (Cd), le cuivre (Cu) , le mercure (Hg) , le plomb (Pb) et le zinc (Zn), la concentration dans la mousse était également significativement plus élevée pour les sites avec canopée (moyennes sur plus deux ans : Cd 0,2 mg kg^{-1}, Cu 8,5 mg kg^{-1}, Hg 0,03 mg kg^{-1}, Pb 2,7 mg kg^{-1}, Zn 45,7 mg kg^{-1}) que sur les sites sans canopée. Le chrome (Cr) et le nickel (Ni) ne présentaient aucune différence significative entre les deux types de sites.

Principales conclusions : l'étude montre des variances spatiales significatives pour les concentrations d'azote et d'ETM. Celles-ci devraient être prises en compte lors de cartographie et de modélisation des dépôts atmosphériques, ainsi que lors de la mise en œuvre des mesures pour réduire les dépôts atmosphériques.

Mots-clés

biosurveillance, variance à petite échelle, rosée issue de la canopée.

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1. Background

Atmospheric deposition of heavy metals (HM) and nitrogen (N) can have long-term effects on species composition of ecosystems and human health. Monitoring is therefore important to evaluate potential air pollution and associated effects on ecosystems and humans (Harmens *et al.*, 2013; Nagajyoti *et al.*, 2010; Stankovic *et al.*, 2014). In addition to measurements and modelling of atmospheric deposition, environmental analyses focus attention on biological monitoring activities on different spatial scales. Moss, in particular, can be used for element inventories (Frahm, 1998; Mohr, 1999; Mohr, 2007; Schröder *et al.,* 2008; Zechmeister *et al*., 2006) due to specific characteristics: In addition to a lack of real root systems and poorly developed cuticle, they particularly show only minor changes in their morphology during their lifetime and are further able to accumulate relatively large amounts of atmospheric deposition without getting physiological damages. Thus, dry, wet and occult atmospheric deposition, especially of HM, is fairly well mirrored by measured element concentration in moss. Compared to technical deposition samplers, this method enables a high spatial resolution and is additionally cost-efficient and time-saving (Blagnyté *et al.,* 2010; Frahm, 1998; Steinnes *et al.*, 1997; Tyler, 1990).

In at least 21 European countries, moss surveys are carried out every 5 years since 1990, especially focusing on mapping spatial and temporal trends of HM accumulation until 2005 and extended by N and persistent organic pollutants (POP) since then (Harmens *et al.,* 2013; Mohr *et al.,* 2009; Pesch *et al*., 2008; Schröder *et al.,* 2004; Schröder *et al.,* 2005). Adopted in 1998, the Protocol on Heavy Metals of the Convention on Long-range Transboundary Air Pollution (UNECE, 1998) mainly focused on the gradual reduction of HM emissions from different pollutant sources (e.g. industry, combustion processes, agriculture). Between 1990 and 2010, there have been reductions in HM, especially of Pb (74 %), Cd (51 %) and Hg (36 %), but nevertheless there still remains a risk for the environment and human health (Harmens *et al.,* 2013).

The European moss survey focuses on measuring background levels of N and HM at open areas. So far, there is very little comparative research on the influence of canopy drip in forest ecosystems on the amount of N and HM concentration in moss that may have significant influence on the evaluation of atmospheric deposition patterns (Mohr, 1999; Mohr, 2007; Mohr *et al*., 2011). Forest ecosystems are particularly affected by high long-term N inputs due to the filter effect of their canopy. Thus, mainly the N concentration in forests is systematically higher than at sites without canopy drip depending on various factors (Builtjes *et al.,* 2011). Therefore, the study at hand deals with the first systematic investigation of canopy drip effects on element concentration in moss species in North-Western Germany, with emphasis on N concentration by contrast with HM concentration.

2. Material and methods

2.1. Study area

To analyse potential canopy drip effects on the accumulation of N and HM in moss, moss was sampled at sites with (n = 30) and adjacent sites without (n = 26) canopy drip in North-Western Germany in 2012 and resampled at the same sites in 2013 (Figure 1).

Following the 2006 Corine Land cover map (Keril *et al.,* 2010), the study area is mainly dominated by 'non-irrigated arable land' (82 %) associated with a high density of animal farming resulting in potentially higher atmospheric N deposition (Mohr *et al.,* 2005). According to Schröder *et al.* (2001), the study area is primarily dominated by an annual total precipitation of 760,2 mm, an annual total evaporation of 557,5 mm and an annual average temperature of 9 °C. Further information on the study area is provided by Kluge *et al.,* 2013.

2.2. Moss sampling and chemical analyses

Moss sampling and chemical analyses followed the experimental protocol of the European Moss Survey (Schröder *et al.*, 2009; UNECE, 2010) that was derived from Scandinavian recommendations (Rühling *et al.,* 2001) and constantly improved (Harmens *et al.,* 2008; Schröder *et al.,* 2002; UNECE, 2010;). Sampling and chemical analyses of HM and N are described in detail in Kluge *et al.* (2013) and in Schröder *et al.* (2009), respectively. Chemical analyses were performed by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for Cd, Cr, Pb and Ni and by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for Cu and Zn, while Hg was analysed by Cold-Vapour Atomic Absorption Spectrometry (CV-AAS). All analyses were done in the laboratory of the Institute for Fertilizers and Seeds (LUFA Nord-West, Hameln, Germany). For quality control (QC), several reference materials specifically adapted to the whole range of HM and N concentrations in moss was used. These reference materials continuously are proved in the framework of inter-laboratory tests. Several QC features such as working range, correlation between reference materials and analytes, detection and determination limits as well as repeatability of measurements were determined. The respective results are given in Table I.

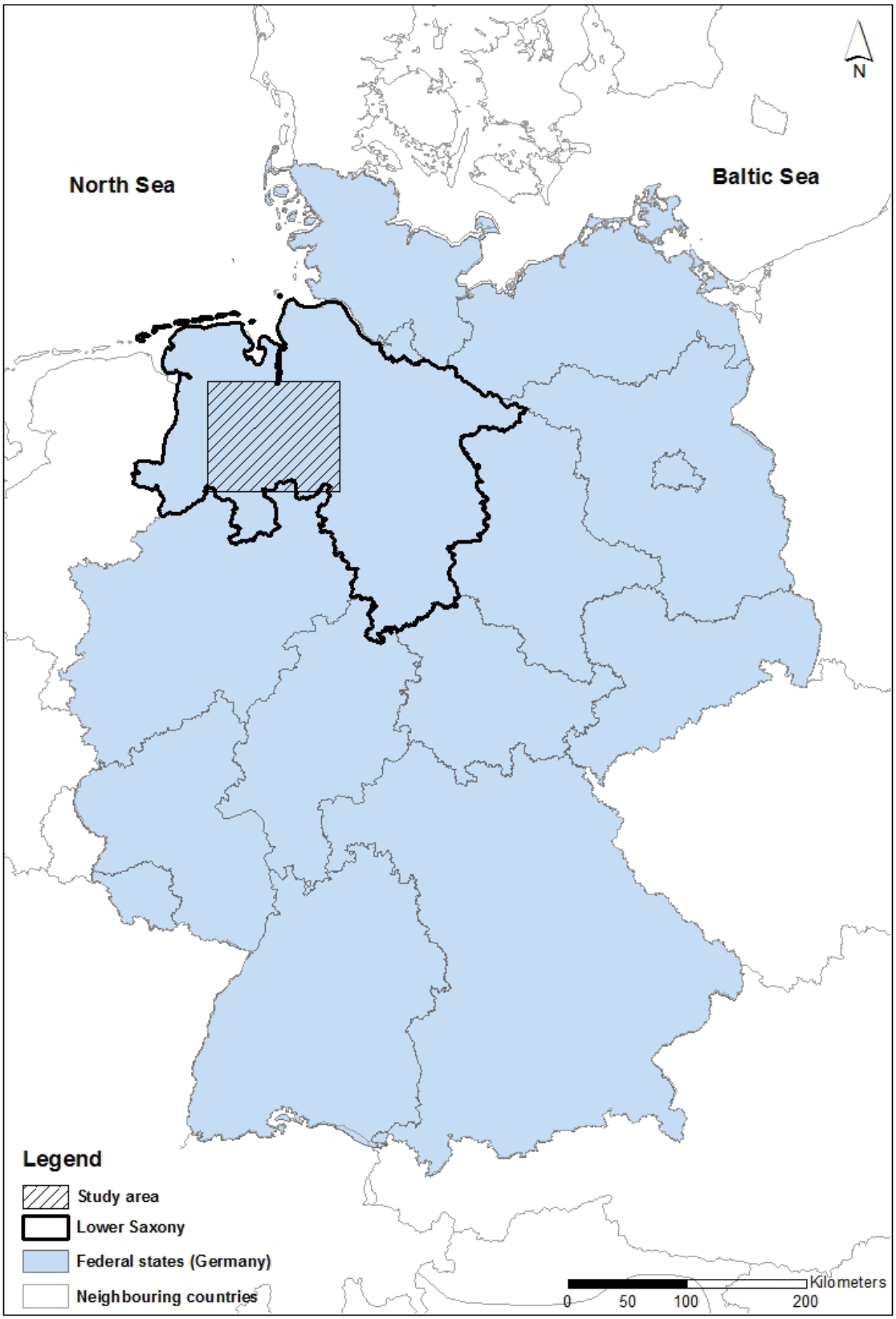


Figure 1. Study area within Lower Saxony, Germany.

Aire d'étude au sein de la Basse-Saxe, Allemagne.

As extensively described in Kluge *et al.* (2013), in addition to the moss samples taken at sites with and without canopy drip, metadata was obtained in order to describe each sampling site as detailed as possible and to uncover possible relations to N and HM concentrations in moss, respectively.

2.3. Statistical analyses

2.3.1. Descriptive statistics

Basic descriptive statistical measures (number of sites, minimum, maximum, mean, median) for N, Cd, Cr, Cu, Hg, Ni, Pb and Zn concentrations in moss were calculated from the moss data collected in 2012 and 2013 in North-Western Germany, differentiated in sites with and without canopy drip (Table II). Wilcoxon signed-rank tests were carried out to identify significant differences both between the particular sampling site categories (sites with and without canopy drip) and between the different sampling years (within the respective sampling site category) (Tables III, IV).

2.3.2. Multivariate analyses with emphasis on N concentration

With emphasis on N concentration in moss, *Classification and Regression Trees* (CART) (Breiman *et al.,* 1984; SPSS, 2001) were conducted by use of IBM SPSS Statistics Version 22 in order to uncover relationships between N concentrations and site-specific factors. Thus, in addition to the respective sampling site category (site with resp. without canopy drip), moss species (*Pleurozium schreberi*, *Scleropodium purum*), sampling year (2012, 2013), tree height and distances to emission sources (traffic, industry, agriculture) recorded at the particular moss sampling sites (Kluge *et al.,* 2013), percentages of urban, agricultural and forest areas around 1, 5, 10 and 25 km around the sampling sites derived from Keil *et al.* (2010), population density, precipitation and distance to sea were integrated into the multivariate analyses. Regarding N concentration in moss as target variable, the heterogeneous initial data set was repetitively divided into more homogeneous subsets by CART using the most powerful predictors.

2.3.3. Kriging estimations for mapping critical load exceedances of N

In order to identify critical load exceedances, N concentrations in moss given in (%) were converted to atmospheric N deposition rates (kg ha^{-1} a^{-1}) for each sampling site by means of a regression model given by Schröder *et al.* (2014), averaged over both sampling years. The regression model was derived both from modelled atmospheric N deposition data from the European Monitoring and Evaluation Programme and from geostatistically assessed N concentration in moss provided by the participants of the European moss survey. Following Gauger *et al.* (2000), critical load values being available as point data and given in ionic equivalents (eq ha^{-1} a^{-1}) (Bobbink *et al*., 2011; Gauger *et al.,* 2008) were transferred into kg ha^{-1} a^{-1}. The given point values cover primarily forest ecosystems (96 %) and further (semi)natural areas in Germany (Gauger *et al*., 2008). Minimum and maximum critical load values were classified in accordance with the European Nature Information System (Bund/Länder-Arbeitsgemeinschaft für Immissionsschutz, 2012; Davies *et al.*, 2004; Moss *et al*., 2002) depending on specific ecosystem characteristics. For statistical analyses, only those sampling points with a spatial distance of 2 km at maximum to sites with given critical load values were chosen. With regard to critical load exceedances, for each sampling site atmospheric N deposition values estimated by N concentration in moss were divided by the associated maximum critical load value multiplied by 100. The result can be interpreted as probability of maximum critical load exceedances.

In order to produce surface maps based on atmospheric N deposition rates as estimated by the measured N concentration in moss that are also valid for areas beyond the respective sampling sites, kriging procedures were applied by use of the ArcGIS 10.2 extension *Geostatistical Analyst.* Weighted averages of the given point values are computed considering the neighbourhood of the particular point. In this study, indicator kriging was applied transforming the data to (0,1) in accordance with the threshold value before calculating the semivariogram. Based on the threshold values calculated for each sampling site averaged for both sampling years, kriging estimations were applied in this study. In order to perform the surface estimations, within a four-sector window the 20 sites closest to each measurement point were used. Based on the results of cross-validation being used for the verification of the interpolation method, the Mean Error (ME) was calculated to assess the estimation quality.

3. Results and discussion

QC results are compiled in Table I. Detailed explanations and complementary information on QC are given in Kluge *et al.* (2013) and Schröder *et al*. (2009).

Table II shows the main descriptive statistical values for the afore-mentioned N and HM in moss samples for 2012 and 2013, differentiated in sites with and without canopy drip. Figures 2-8 shows the averaged HM concentration in moss in [mg kg^{-1}] in 2012 and 2013, respectively. Due to the wide range of HM concentration, both Cu and Zn, Pb, Cr and Ni and Cd and Hg were presented individually. The average N concentration in moss in [%] in both sampling years is displayed in Figure 9.

Table I. Quality control (QC) results for Cd, Cr, Cu, Hg, Ni, Pb and Zn (2012 and 2013) and for N 2012 ("N12") and N 2013 ("N13"). The correlation coefficient indicates the relationship between the reference material and the analyte. ICP-MS: Coupled Plasma Mass Spectrometry, ICP-OES: Inductively Coupled Plasma Optical Emission Spectrometry, CV-AAS: Cold-Vapour Atomic Absorption Spectrometry.

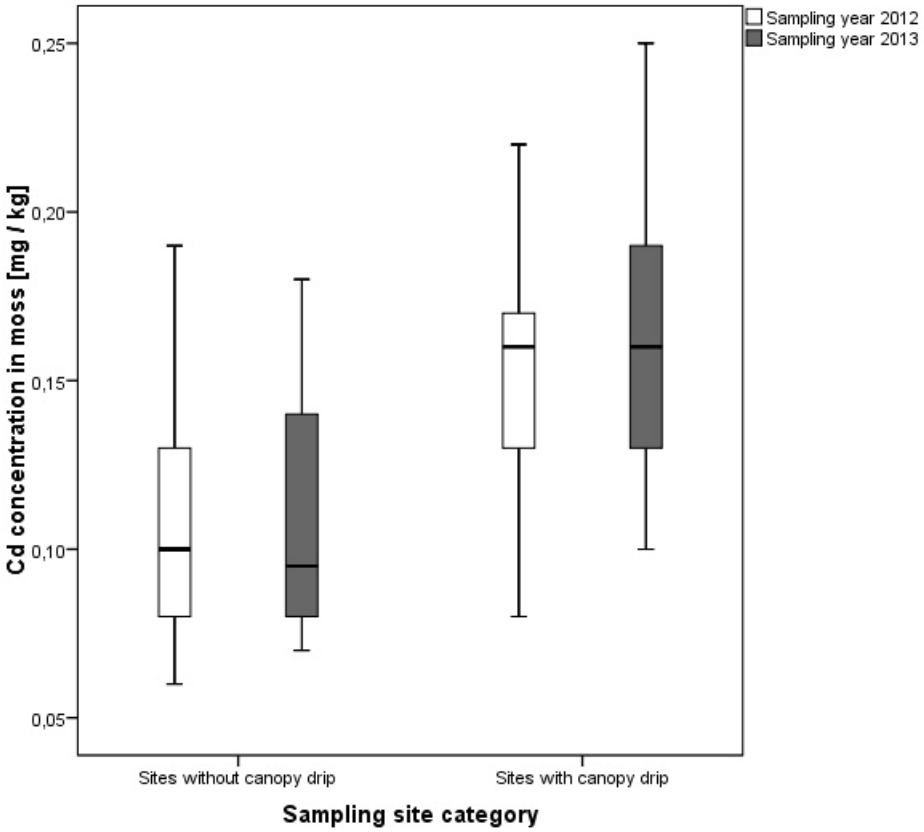
Les résultats du contrôle qualité pour Cd, Cr, Cu, Hg, Ni, Pb et Zn (2012 et 2013) et de N 2012 («N12») et N 2013 («N13»). Le coefficient de corrélation indique la relation entre le matériau de référence et l'analyte. ICP-MS : spectrométrie de masse couplée à un plasma, ICP-OES : spectrométrie d'émission optique, CV-AAS : spectrométrie d'absorption atomique à vapeur froide.

	Cd	Cr	Cu	Hg	Ni	Pb	Zn	N12	N13
Measuring Instrument	**ICP-MS**	**ICP-MS**	**ICP-OES**	**CV-AAS**	**ICP-MS**	**ICP-MS**	**ICP-OES**	**C/N-Analyser**	**C/N-Analyser**
Working range	0,005-5,0 mg kg^{-1}	0,1-5,0 mg kg^{-1}	0,5-500 mg kg^{-1}	0,005-0,25 mg kg^{-1}	0,1-5,0 mg kg^{-1}	0,01-5,0 mg kg^{-1}	0,5-500 mg kg^{-1}	0,1 - 1%	0,1 - 1%
Corr. Coeff. (Pearson)	0,9995	0,9995	0,9995	0,9995	0,9995	0,9995	0,9995	0,9998	0,9998
Detection limit	0,003 mg kg^{-1}	0,03 mg kg^{-1}	0,17 mg kg^{-1}	0,002 mg kg^{-1}	0,03 mg kg^{-1}	0,003 mg kg^{-1}	0,17 mg kg^{-1}	0.02 %	0,02 %
Determination limit	0,005 mg kg^{-1}	0,1 mg kg^{-1}	0,5 mg kg^{-1}	0,005 mg kg^{-1}	0,1 mg kg^{-1}	0,01 mg kg^{-1}	0,5 mg kg^{-1}	0,08 %	0,06 %
Repeatability (%)	12,10	16,30	2,43	13,75	11,20	9,26	4,07	6,03	6,51

Table II. Overview table of the main descriptive statistical values for N, Cd, Cr, Cu, Hg, Ni, Pb and Zn concentration measured in moss at sites with and without canopy drip in 2012 and 2013.

Tableau récapitulatif des principales valeurs statistiques descriptives pour les concentrations en N, Cd, Cr, Cu, Hg, Ni, Pb et Zn mesurées dans de la mousse sur les sites avec et sans canopée (rosée) en 2012 et 2013.

2012								
Site without canopy drip								
	N	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Unit	**(%)**	**(mg kg^{-1})**						
Number	26	26	26	26	26	26	26	26
Minimum	0,86	0,06	0,29	2,56	0,0060	0,15	0,60	19,80
Maximum	1,41	0,19	9,05	6,03	0,0280	0,90	4,14	48,80
Mean	1,11	0,11	1,36	4,01	0,0192	0,47	1,93	30,91
Median	1,09	0,10	1,08	3,81	0,0190	0,45	1,94	30,95
Site with canopy drip								
	N	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Unit	**(%)**	**(mg kg^{-1})**						
Number	30	30	30	30	30	30	30	30
Minimum	1,43	0,08	0,40	4,92	0,0150	0,27	1,07	23,90
Maximum	3,45	0,22	2,58	26,60	0,0550	1,01	12,90	76,90
Mean	2,27	0,15	0,95	8,18	0,0354	0,56	2,72	42,49
Median	2,24	0,16	0,83	7,25	0,0320	0,55	2,46	43,10
2013								
Site without canopy drip								
	N	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Unit	**(%)**	**(mg kg^{-1})**						
Number	26	26	26	26	26	26	26	26
Minimum	1,07	0,07	0,28	3,60	0,0130	0,16	0,66	21,60
Maximum	1,88	0,18	2,23	7,85	0,0320	0,80	3,10	49,50
Mean	1,39	0,11	0,81	5,29	0,0191	0,47	1,76	33,97
Median	1,37	0,10	0,70	5,12	0,0190	0,49	1,72	33,45
Site with canopy drip								
	N	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Unit	**(%)**	**(mg kg^{-1})**						
Number	30	30	30	30	30	30	30	30
Minimum	1,64	0,10	0,33	4,50	0,0130	0,23	0,80	29,30
Maximum	2,99	0,25	1,56	13,30	0,0500	0,89	7,99	69,10
Mean	2,50	0,16	0,78	8,96	0,0339	0,54	2,73	49,12
Median	2,48	0,16	0,77	8,72	0,0330	0,54	2,48	50,65



Figures 2. Cd concentration in moss in [mg kg^{-1}] in 2012 (white plots) and 2013 (grey plots) at sites with (n: 30) and without (n: 26) canopy drip. Outliers are not depicted.

Concentration en Cd dans la mousse en [mg/kg] en 2012 (en blanc) et en 2013 (en gris) sur les sites avec (n : 30) et sans (n : 26) canopée. Les valeurs aberrantes ne sont pas représentées.

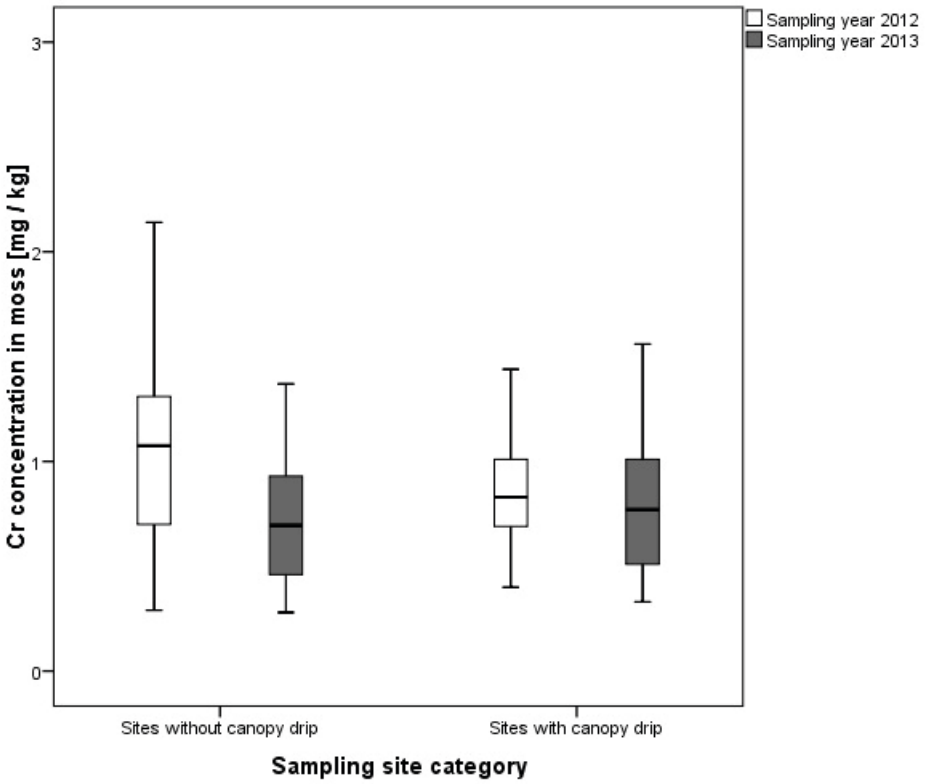


Figure 3. Cr concentration in moss in [mg kg^{-1}] in 2012 (white plots) and 2013 (grey plots) at sites with (n: 30) and without (n: 26) canopy drip. Outliers are not depicted.

Concentration en Cr dans la mousse en [mg/kg] en 2012 (en blanc) et en 2013 (en gris) sur les sites avec (n : 30) et sans (n : 26) canopée. Les valeurs aberrantes ne sont pas représentées.

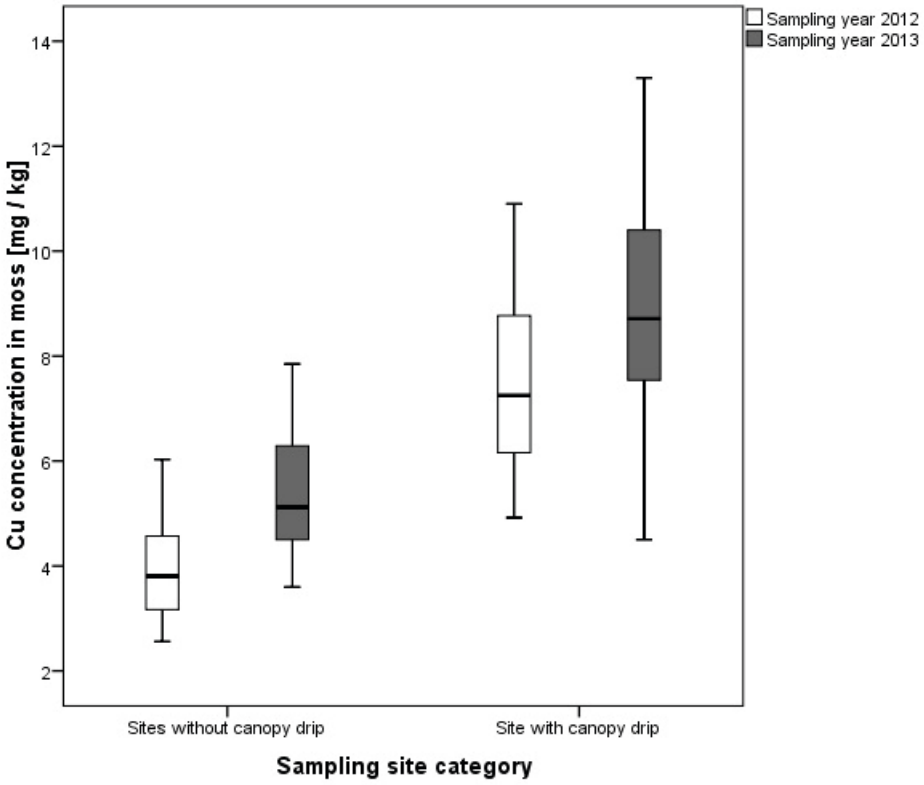


Figure 4. Cu concentration in moss in [mg kg^{-1}] in 2012 (white plots) and 2013 (grey plots) at sites with (n: 30) and without (n: 26) canopy drip. Outliers are not depicted.

Concentration en Cu dans la mousse en [mg/kg] en 2012 (en blanc) et en 2013 (en gris) sur les sites avec (n : 30) et sans (n : 26) canopée. Les valeurs aberrantes ne sont pas représentées.

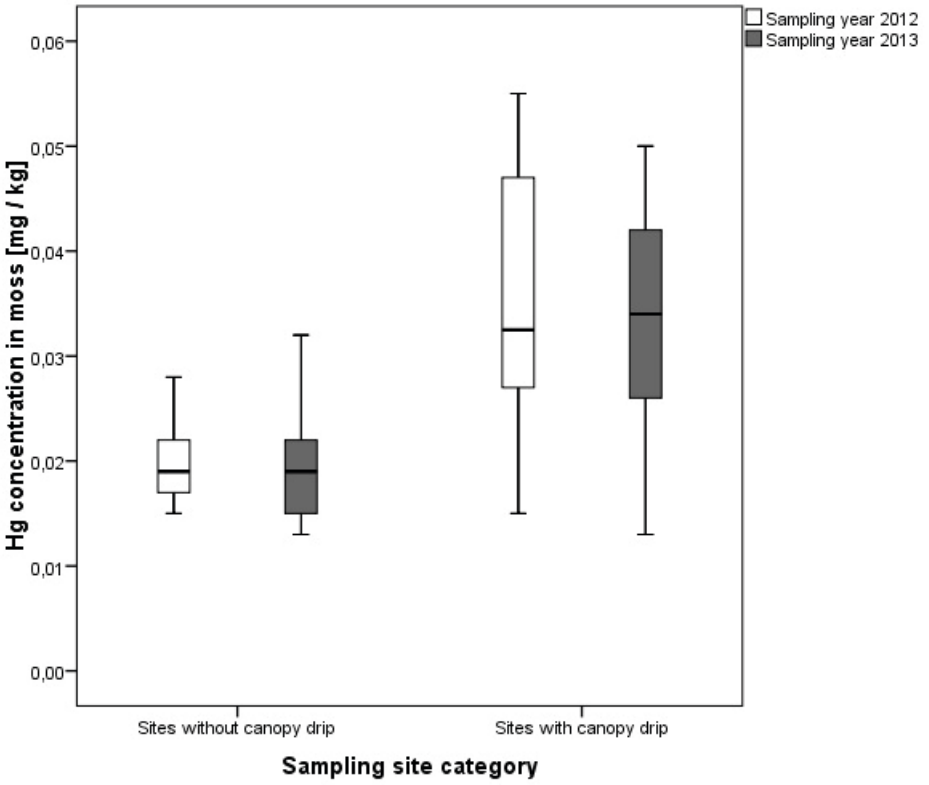


Figure 5. Hg concentration in moss in [mg kg^{-1}] in 2012 (white plots) and 2013 (grey plots) at sites with (n: 30) and without (n: 26) canopy drip. Outliers are not depicted.

Concentration en Hg dans la mousse en [mg/kg] en 2012 (en blanc) et en 2013 (en gris) sur les sites avec (n : 30) et sans (n : 26) canopée. Les valeurs aberrantes ne sont pas représentées.

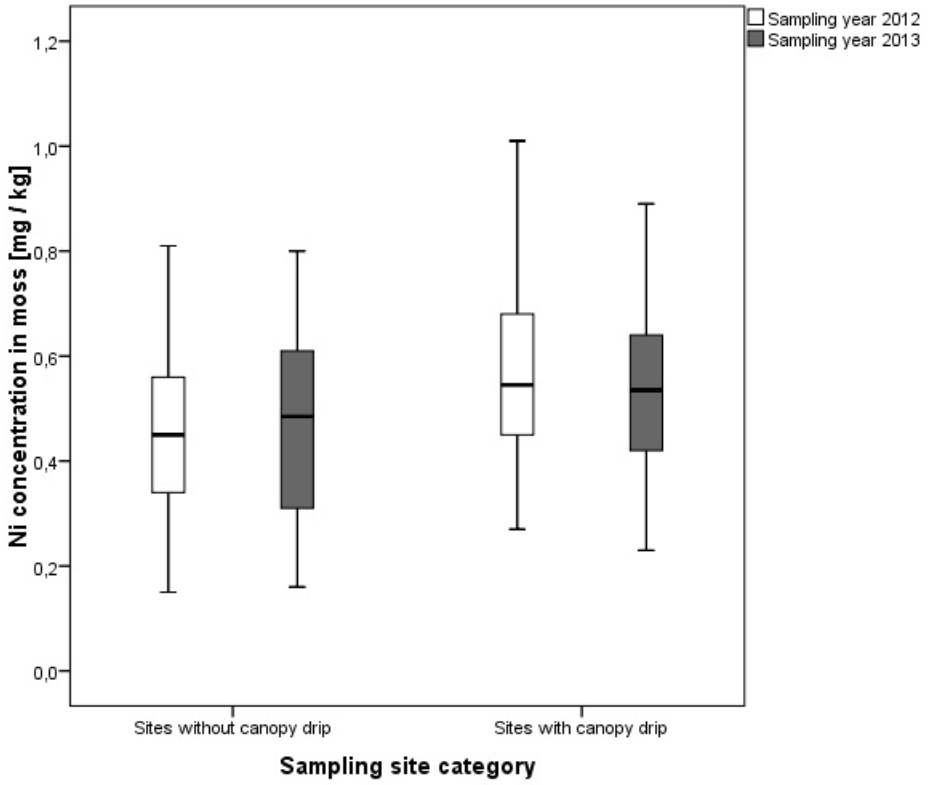


Figure 6. Ni concentration in moss in [mg kg^{-1}] in 2012 (white plots) and 2013 (grey plots) at sites with (n: 30) and without (n: 26) canopy drip. Outliers are not depicted.

Concentration en Ni dans la mousse en [mg/kg] en 2012 (en blanc) et en 2013 (en gris) sur les sites avec (n : 30) et sans (n : 26) canopée. Les valeurs aberrantes ne sont pas représentées.

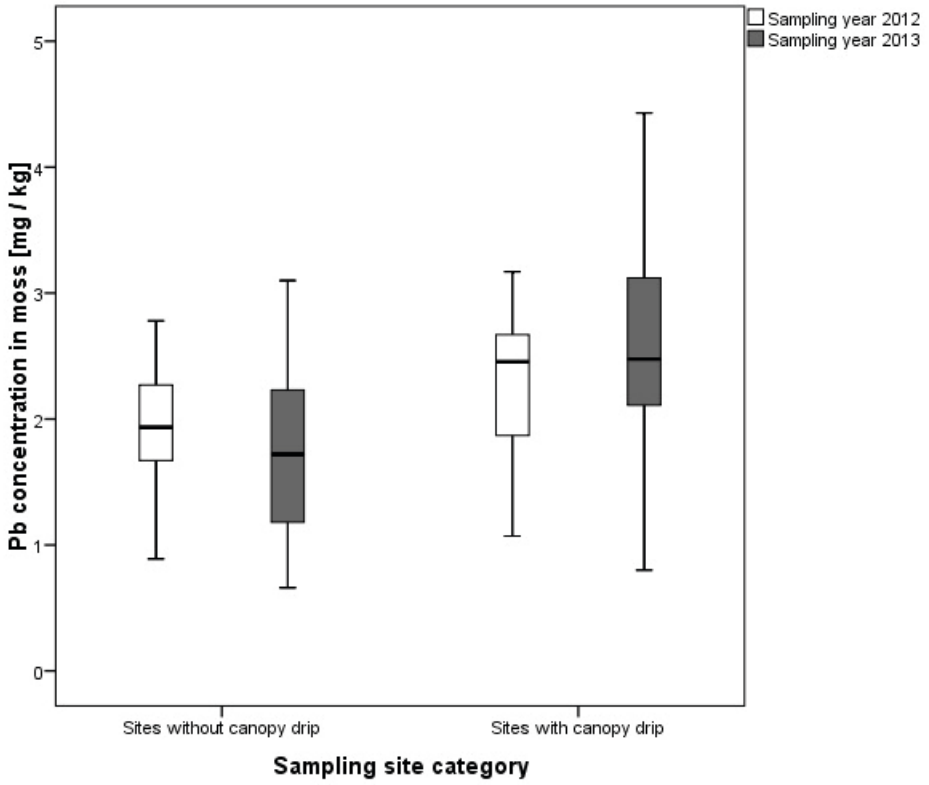


Figure 7. Pb concentration in moss in [mg kg^{-1}] in 2012 (white plots) and 2013 (grey plots) at sites with (n: 30) and without (n: 26) canopy drip. Outliers are not depicted

Concentration en Pb dans la mousse en [mg/kg] en 2012 (en blanc) et en 2013 (en gris) sur les sites avec (n : 30) et sans (n : 26) canopée. Les valeurs aberrantes ne sont pas représentées

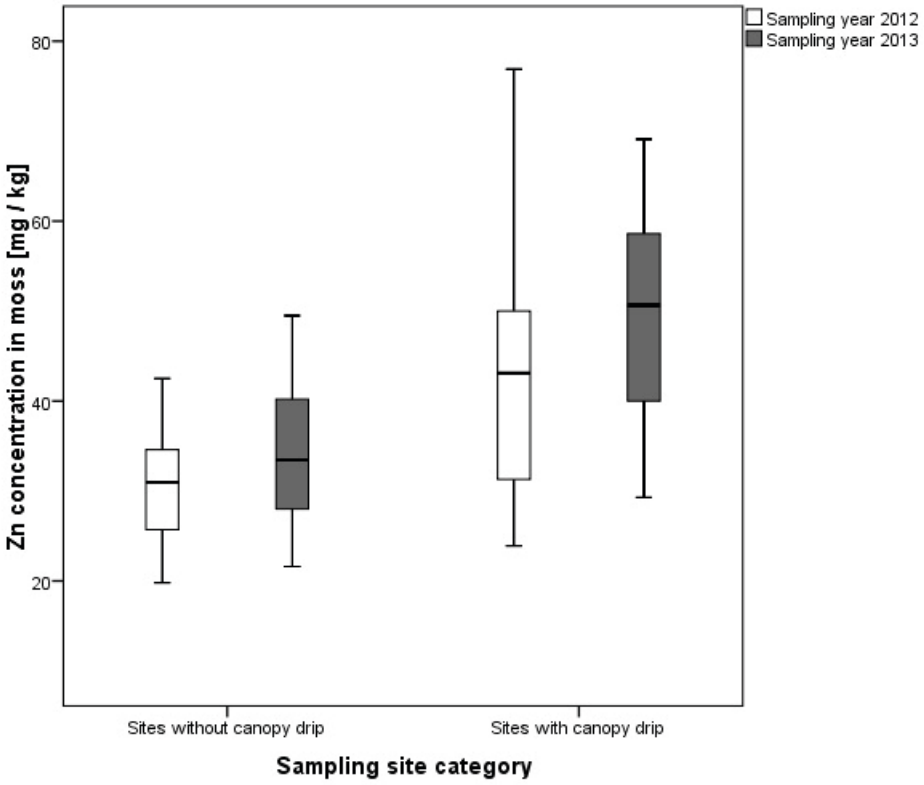


Figure 8. Zn concentration in moss in [mg kg^{-1}] in 2012 (white plots) and 2013 (grey plots) at sites with (n: 30) and without (n: 26) canopy drip. Outliers are not depicted.

Concentration en Zn dans la mousse en [mg/kg] en 2012 (en blanc) et en 2013 (en gris) sur les sites avec (n : 30) et sans (n : 26) canopée. Les valeurs aberrantes ne sont pas représentées.

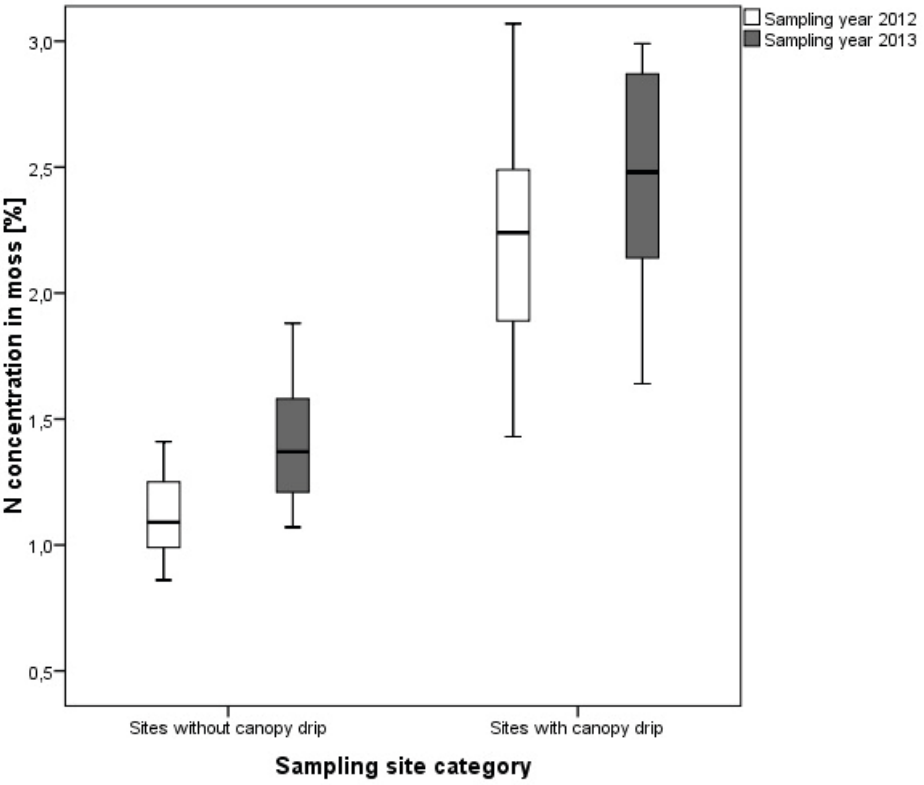


Figure 9. N concentration in moss in [%] in 2012 (white plots) and 2013 (grey plots) at sites with (n: 30) and without (n: 26) canopy drip. Outliers are not depicted.

Concentration en N dans la mousse en [mg/kg] en 2012 (en blanc) et en 2013 (en gris) sur les sites avec (n: 30) et sans (n: 26) canopée. Les valeurs aberrantes ne sont pas représentées.

Table III. p-Values from Wilcoxon signed-rank test for comparison of N, Cd, Cr, Cu, Hg, Ni, Pb and Zn concentrations in moss for the particular sampling site categories ("Cat_1": Site with canopy drip, "Cat_2": Site without canopy drip) both in 2012 and in 2013 (in bold: p < 0,01).

Test de Wilcoxon, p-values pour la comparaison des concentrations de N, Cd, Cr, Cu, Hg, Ni, Pb et Zn dans la mousse pour les sites d'échantillonnages répartis en 2 catégories («Cat_1»: site avec canopée (rosée), «Cat_2»: site sans canopée), à la fois en 2012 et en 2013 (en gras : p <0,01).

2012								
	N	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Cat_1 vs. Cat_2	0,00	0,00	0,10	0,00	0,00	0,10	0,01	0,01
2013								
	N	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Cat_1 vs. Cat_2	0,00	0,00	0,37	0,00	0,00	0,03	0,00	0,00

Table IV. p-Values from Wilcoxon signed-rank test for comparison of N, Cd, Cr, Cu, Hg, Ni, Pb and Zn concentrations in moss between the years, differentiated in site with and without canopy drip (in bold: p < 0,01).

Test de Wilcoxon, p-Values pour la comparaison des concentrations de N, Cd, Cr, Cu, Hg, Ni, Pb et Zn dans la mousse en fonction des années, et selon les sites avec ou sans canopée (en gras : p <0,01).

Site without canopy drip								
	N	Cd	Cr	Cu	Hg	Ni	Pb	Zn
2012 vs. 2013	**0,00**	0,94	**0,01**	**0,00**	0,98	0,70	0,83	0,02
Site with canopy drip								
	N	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
2012 vs. 2013	**0,00**	0,17	0,10	**0,01**	0,27	0,70	0,44	**0,00**

Tables III and IV show the results of the Wilcoxon signed-rank test in terms of calculated p-values for moss samples, both for the particular sampling site categories (Table III) and for the different sampling years (Table IV).

Considering the N concentration in moss (% in dry weight), the average concentration at sites with canopy drip was both significantly higher in 2013 (mean: 2,50 %, correspond to 31,3 kg ha^{-1} a^{-1}) compared to 2012 (2,27 %, 26,4 kg ha^{-1} a^{-1}) (Tables II, IV) and significantly higher compared to the N concentration in moss sampled at adjacent sites without canopy drip (mean 2012: 1,11 %, 7,3 kg ha^{-1} a^{-1}, 2013 : 1,39 %, 10,9 kg ha^{-1} a^{-1}) (Tables II, III). Considering the atmospheric N deposition as estimated by the N concentration in moss sampled at sites without canopy drip, the average atmospheric N deposition at adjacent sites with canopy drip were approximately three times higher.

An oversupply of reactive N can cause adverse effects on ecosystems and their services to humans. Furthermore, it may accelerate climate change and, both threaten biodiversity and human health (Rockström *et al.,* 2009). Forest ecosystems are mainly affected by long-term increased inputs of N from the atmosphere, particularly promoted by their large surface, their height and roughness leading to filtering effects (Builtjes *et al.*, 2011). The amount of N that trees are able to withstand without damages, however, largely depends on the relationship to other essential elements being available at the same time. In contrast to long-term exceedances, forest ecosystems can compensate short-term occurring high inputs of N due to delayed biological responses (Nagel *et al.,* 2004). However, due to complex dose-response relationships, the effects on forest ecosystems are difficult to assess. In addition, forest soils are already damaged resulting from acidification in the past. Compared to other important nutrients, a long-term oversupply of N can lead to an increased susceptibility to drought, frost and diseases due to softer needles and leaves, thus finally leading to reduced ecosystem vitality, species composition changes and limited self-regulation (Bobbink *et al.*, 2010; Bobbink *et al.*, 2011; Builtjes *et al.*, 2011; Mohr, 1999; Mohr *et al.*, 2005; Schröder *et al.*, 2007; WGE, 2004).

This study shows significant spatial variances of N concentration in moss (Tables II, III, Figures 2-9), also confirmed by the CART analysis identifying the sampling site category (level 1) to be the factor most associated to the N concentration in moss integrating all site-specific factors as mentioned in section 2.3.2 (Figure 10). The CART model presented explains 82 % of the variance in the data set comprising 112 measurements.

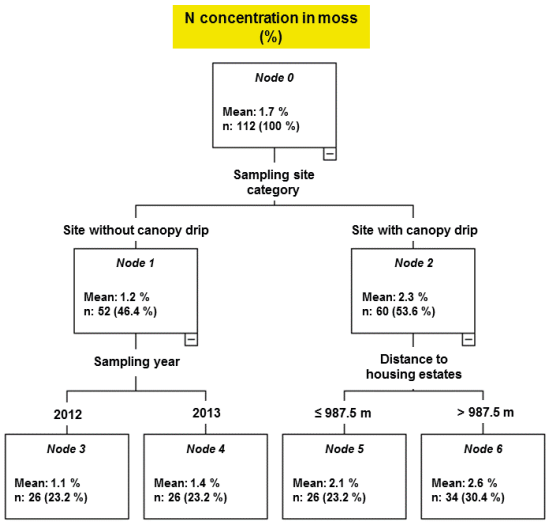
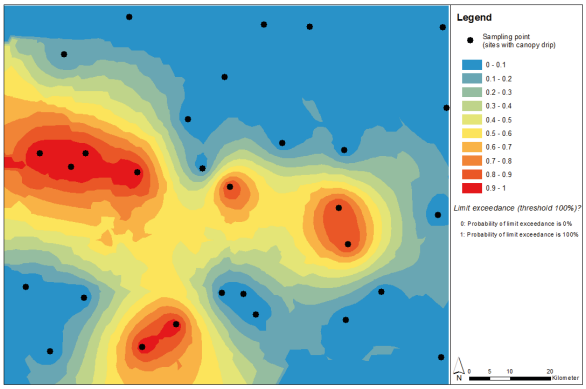


Figure 10. Ranking and interaction of factors associated with N concentration in moss sampled in 2012 and 2013 (first two levels).

Classement et interaction des facteurs associés à la concentration de N dans la mousse échantillonnée en 2012 et 2013 (les deux premiers niveaux).

At sites without canopy drip, the average N concentration is about 1,2 %, the average N concentration in moss sampled at sites with canopy drip, however, is about 2,3 %. The N concentration in moss at sites without canopy drip is, in turn, explained by the sampling year (level 2), with lower N average concentration in 2012 (1,1 %). N concentrations in moss sampled at sites with canopy drip are explained by the distance to housing estates. The further away from housing estates, the higher N concentration, which is related to the fact that those sampling sites are further away from housing estates are closer to dense agricultural areas with comparatively high N emissions. Following UBA (2013), in Germany reactive N is emitted to the atmosphere mainly by agriculture (57 %), while other economic sectors (e.g. industry, transport) together contribute 43 %. Whereas in the past, sulphur was the main source of acidification, it is nowadays ammonia (NH_4^+) and ammonium (NH_3^+) emitted from agricultural activities. In Germany, critical loads for acidity are exceeded in more than 80 % of (semi)natural ecosystems including forests. Depending on specific ecosystem characteristics, critical loads represent a measure for the intake capacity of elements of an ecosystem without getting damaged (Bobbink *et al.*, 2011; Bund/Länder-Arbeitsgemeinschaft für Immissionsschutz, 2012; Davies *et al.*, 2004; Gauger *et al.,* 2000; Gauger *et al.,* 2008; Moss *et al.*, 2002). In order to identify critical load exceedances, atmospheric N deposition as estimated by the measured N concentration in moss was related to site-specific critical load values. As presented in Figure 11 (top), the atmospheric N deposition at sites with canopy drip averaged over both years compared to the given critical load value showed that the atmospheric N deposition as derived by the N concentration in moss ranged between the minimum and maximum critical load value at 21 of 30 sites (70 %), but exceeded the given maximum critical load value at 9 of 30 sites (30 %). Considering the surface estimations (Figure 11, bottom), the produced surface map shows the probability of limit exceedance, red-coloured areas revealing a limit exceedance with a probability of 100 %. The mean error (ME) of the surface map was close to zero (-0,02) indicating an unbiasedness of the semi-variogram models and the following kriging estimation. In this study, there were no exceedances at sites without canopy drip, but ranged between the minimum and maximum given critical load values. The variance of the input dataset was too small to be calculated.



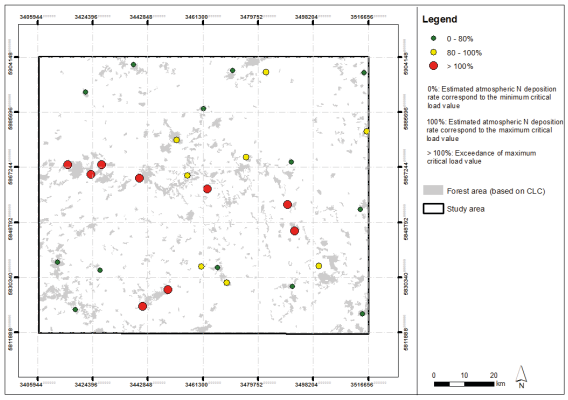


Figure 11. Critical load exceedances at sites *with* canopy drip shown as point data (top) and as area-based predictions (bottom).

Dépassements de la charge critique pour les sites avec canopée (rosée) en tant que données ponctuelles (haut) et comme prévisions par zone (bas).

Regarding the heavy metal concentration in moss, in case of Cd, Cu, Hg, Pb and Zn the concentration in moss (mg kg^{-1} in dry weight) was also significantly higher at sites with canopy drip than at sites without canopy drip (Tables II and III). Cr and Ni showed no significant differences between both site types. Considering the element concentration within each sampling site category between the years, the Cr and Cu concentration in moss sampled at sites without canopy drip was significantly different in 2012 compared to 2013. At sites with canopy drip, there were significant differences in Cu and Zn concentration in moss between 2012 and 2013 (Table IV).

Like N, an appropriate amount of HM is essential for plant nutrition. Both, an insufficient supply as well as extremely high amounts of HM particularly in soils and minerals can lead to physiological damages (Stankovic *et al.*, 2014). Both, low input rates accumulated over long periods and large amounts of HM can have toxic effects. As in case of N, the effects of increased HM inputs are largely species-specific. Tree species can vary in their tolerance towards increased HM concentrations mainly depending on substrate properties like e.g. pH value (Rehfuess, 1967; Zöttl, 1985). Following Nebe (1967), spruce and silver fir are able to accumulate a great amount of manganese in their needles resulting in an increased growth provided they develop on moist and acid soil showing a high manganese mobility. Forest ecosystems are especially exposed to dry deposition of heavy metal aerosols due to their large filtering capacity. Heavy metal aerosols are introduced via medium- or long-range transport and subsequently filtered out of the air stream that leads to an increased absorption and accumulation of HM in the biomass. Understory vegetation such as epiphytic lichens and some moss species are, thus, increasingly subjected to HM inputs as well (De Schrijver *et al.*, 2007; Zöttl, 1985).

As can be seen from Tables II and III, the measured Cd concentration in moss was higher at sites with canopy drip (mean 2012: 0,15 mg kg^{-1}, 2013: 0,16 mg kg^{-1}) than at sites without canopy drip (mean 2012: 0,11 mg kg^{-1}, 2013: 0,11 mg kg^{-1}). Due to leaching in the tree crowns, the Cd concentration increases threefold. The sink function especially for dry deposition is of great importance: Compared to open-land deposition that mainly covers wet and occult deposition, forest ecosystems show higher HM concentrations in throughfall due to filtering of dry deposition within the crowns (Zöttl, 1985). This also applies to Pb mainly distributed via long-range transboundary transport (Steinnes *et al.,* 2011). Occurring in large concentrations, Pb can have negative impact on ecosystems and human health (Harmens *et al.,* 2013; Blagnyté *et al.,* 2010; Zöttl, 1985; Hettelingh *et al.,* 2006). In this study, at sites with canopy drip the Pb concentration was also significantly higher (mean 2012: 2,72 mg kg^{-1}, 2013: 2,73 mg kg^{-1}) than at sites without canopy drip (mean 2012: 1,93 mg kg^{-1}, 2013: 1,76 mg kg^{-1}). Like Cd, the higher accumulation of Pb at sites with canopy drip is due to filtering effects.

The emission of Cu is mainly caused by local sources. In this study, the concentration of Cu is even twice as high at sites with canopy drip (mean 2012: 8,18 mg kg^{-1}, 2013: 8,96 mg kg^{-1}) compared to sites without (mean 2012: 4,01 mg kg^{-1}, 2013: 5,29 mg kg^{-1}) also shown in Schröder *et al.* (2012). Moss species that are taken in close proximity to trees showed higher Cu concentration values resulting from filtering effects. Cu is an essential nutrient for moss, thus, a basal concentration level of 2,5 mg kg^{-1} within the sampled moss may be evidenced (Berg *et al.,* 1997a; Berg *et al.,* 1997b). Therefore, the recalculated mean concentrations at sites with canopy drip are 5,68 mg kg^{-1} in 2012 and 6,45 mg kg^{-1} in 2013. Considering Iverfeldt, (1991), a moderate increased input of Cu is considered to be beneficial due to a balanced Cu cycling.

Zn is mainly emitted by road transportation and metal production (Harmens *et al.,* 2007). However, it is also an essential nutrient with being apparent in moss as a baseline level of 25 mg kg^{-1} (Berg *et al.,* 1997a; Berg *et al.,* 1997b; Steinnes *et al.,* 2011). In this study, the concentration of Zn was also significantly higher at sites with canopy drip with recalculated concentrations of 17.49 mg kg^{-1} in 2012 and of 24,12 mg kg^{-1} in 2013. This was also shown by Ceburnis *et al.* (2000). The increased concentration at sites with canopy drip could be explained by the fact that there are leaching processes by the needle tissue (Wyttenbach *et al.*, 1990).

The Hg concentration in moss sampled at sites with canopy drip was significantly higher than at sites without (see Tables II, III, Figures 5) (Iverfeldt, 1991) could also show that there was an increased Hg concentration at sites with canopy drip compared to sites that remains unaffected by canopy drip. The sink function especially for dry deposition is, again, of great importance even so it is difficult to assess. Hg primarily comes from manufacturing industries and can occur in various forms in the atmosphere (Harmens et al., 2007). With regard to forest ecosystems, Hg is incorporated in the canopy to a large extent after being dry deposited. However, further fluxes of Hg that are additionally incorporated into understory vegetation and the soil must also be considered (Iverfeldt, 1991). The greatest amount of Hg is washed from the outer surface of the needles and end up in throughfall while a minor portion is

transferred to the ground via litter fall. These mutually reinforced processes probably result in higher Hg contents in moss sampled at sites with canopy drip compared to sites without canopy drip.

Contrary to the other HM elements accumulated in moss, Cr and Ni showed no significant differences between both sampling site categories in this study (Tables II, III). Ni which mainly comes from petrol refining, public electricity and heat production showed a similar trend with higher values at sites with canopy drip while Cr that is primarily emitted by metal industry showed even higher values at sites without canopy drip. So far, there are few scientific studies both on canopy drip effects on the accumulation of N and HM in moss and with regard to HM elements other than Cd, Hg and Pb that is considered to be a priority risk for ecosystems and human health (Hettelingh *et al*., 2006).

4. Conclusions and outlook

The study shows significant spatial variances for N, Cd, Cu, Hg, Pb and Zn. With regard to N, this was also confirmed by CART analyses with sampling site category being the factor most associated to the N concentration in moss integrating all recorded site-specific factors. Considering critical loads with emphasis on N concentration, measured N concentrations were converted into atmospheric N deposition in order to identify critical load exceedances. The atmospheric N deposition at sites with canopy drip averaged over both years compared to the given critical load value showed exceedances of given maximum critical load values even at 9 of 30 sites (30 %). So far, there are only few scientific studies analysing canopy drip effects on the accumulation of N and HM in moss. This study aims at investigating such effects. Spatial differences that were uncovered by this study should be taken into account in the designing schemes for monitoring and modelling as well as for reducing atmospheric deposition.

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