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Accumulation of Atmospheric Metals and Nitrogen Deposition in Mosses: Temporal Development between 1990 and 2020, Comparison with Emission Data and Tree Canopy Drip Effects

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Abstract: Mosses are suitable for recording the bioaccumulation of atmospheric deposition over large areas at many sites. In Europe, such monitoring has been carried out every five years since 1990. Mosses have been collected and chemically analysed for metals (since 1990), nitrogen (since 2005), persistent organic pollutants (since 2010) and microplastics (2020). The aims of this study were the following: (1) to analyse the temporal trends of metal and nitrogen accumulation in mosses between 1990 or 2005, respectively, and 2020 in Germany; (2) to compare the accumulation trends with emission data; and (3) to determine the effect of tree canopy drip on metal and nitrogen accumulation in mosses. For the temporal trend analysis, the minimum sample number required for a reliable estimation of arithmetic mean values and statistical parameters based on it was calculated. It was only achieved for nitrogen, but not for metals. Therefore, the temporal trends of the bioaccumulation of metals and nitrogen were calculated on the basis of median values. For the analysis of tree canopy effects on element accumulation in mosses, 14 vegetation structure measures were used, which together with 80 other descriptors characterise each moss collection site and its environment. The comparison of the data obtained during the first monitoring campaign with those of the 2020 survey showed a significant decrease in metal bioaccumulation. However, in contrast to the emission data, an increase in the accumulation of some metals was observed between 2000 and 2005 and of all metals from 2015 to 2020. Trends in Germany-wide nitrogen medians over the last three campaigns (2005, 2015 and 2020) show that nitrogen medians decreased by −2% between 2005 and 2015 and increased by +8% between 2015 and 2020. These differences are not significant and do not match the emission trends. Inferential statistics confirmed significantly higher metals and nitrogen accumulation in mosses collected under tree canopies compared to adjacent open areas. Measured concentrations of metals and nitrogen were significantly higher under tree canopies than outside of them, by 18–150%.

Keywords: bioaccumulation; regression analysis; trend analysis

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Citation: Schröder, W.; Nickel, S.; Dreyer, A.; Völksen, B. Accumulation of Atmospheric Metals and Nitrogen Deposition in Mosses: Temporal Development between 1990 and 2020, Comparison with Emission Data and Tree Canopy Drip Effects. *Pollutants* **2023**, *3*, 89–101. https://doi.org/10.3390/pollutants3010008

Academic Editors: Simonetta Giordano, Valeria Spagnuolo, Fiore Capozzi and Malarvannan Govindan

Received: 9 December 2022
Revised: 27 December 2022
Accepted: 5 January 2023
Published: 1 February 2023

1. Introduction

Substances emitted into the atmosphere from natural or technical sources are deposited on soils, plants and waters after their transport through the atmosphere. The rate of atmospheric deposition is determined, among other things, by the quantity of the emitted substances, their substance-specific physical and chemical properties, atmospheric and topographical boundary conditions and horizontal and vertical vegetation structures. Atmospheric substance deposition occurs with falling precipitation (wet deposition), by interception of mist/cloud droplets (occult deposition) and/or by sedimentation and gas diffusion (dry deposition). Depending on the substances to which ecosystems are exposed, they may be affected. In order to be able to counteract the associated ecological risks through environmental policy measures, it is necessary to measure the accumulation of the atmospheric deposition of potentially harmful substances in addition to determining impact thresholds [1,2].

Exposure in the sense of pollutant accumulation in plants and animals is the beginning of ecotoxicological effects. Atmospheric substance depositions are accumulated by mosses over several years. The determination of element concentrations in mosses and their correlation with the substances accumulated and measured in technical collectors and with modelled deposition data allow estimates of atmospheric deposition [3,4]. Compared to deposition measurement networks with technical collectors, measurement networks with bioaccumulators such as mosses provide spatially much denser data fields for the validation of deposition data maps calculated with chemical transport models [5].

Mosses (Bryophyta) absorb dry, wet or occultly deposited pollutants directly with the ambient moisture via their surface, accumulate them over their entire lifetime and thus enable their analysis far above the detection limit. Suitable bioindicators are widespread, such as the substance-resistant moss species *Pleurozium schreberi* (BRID.) MITT., *Hypnum cupressiforme* HEDW. s.str. and *Pseudoscleropodium purum* (HEDW.) M.FLEISCH (synonym *Scleropodium purum* HEDW. LIMPR.). Bioindication with mosses also has financial advantages over technical methods for quantifying atmospheric deposition and is therefore well suited for detecting large-scale trends in the bioaccumulation of atmospheric substance deposition in spatially dense monitoring networks.

In 1987, the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation) was established to investigate the scientific basis for quantifying the damage to plants caused by the deposition of air pollutants. In 2001, ICP Vegetation took over from the Nordic Council of Ministers the responsibility for coordinating the Europe-wide determination of heavy metals in mosses, which has been carried out every five years since 1990 and has included a maximum of about 7300 moss sampling sites, compared to about 60 deposition monitoring sites of the European Monitoring and Assessment Programme throughout Europe [6]. Since 2005, nitrogen concentrations in mosses have also been recorded. Persistent organic pollutants were included in 2010 and the first pilot studies on microplastics took place in Survey 2020 [7]. The sampling and analysis of the mosses as well as the data evaluation are carried out according to a standardised protocol [8].

The ICP Vegetation is part of the activities of the Working Group on Impacts under the Convention on Long-Range Transboundary Air Pollution, which covers the UNECE (United Nations Economic Commission for Europe) region in Europe and North America. The protocols of the Convention commit countries to reducing pollutant emissions by certain target years. The results of the ICPs and their annual task force meetings inform both the development of these protocols and the monitoring of their success in reducing the impact of air pollutants on health and the environment. Critical to this are, among other things, reliable data on pollution trends and improvements in deposition modelling. Therefore, the aims of this study, which was carried out as part of the German Moss Survey from the beginning of October 2020 to the end of 2023, were the following: (1) to analyse the temporal trend of metals (1990–2020) and nitrogen (2005–2020); (2) to compare these trends with emission trends; and (3) to quantify the influence of vegetation structure at moss sampling sites on the accumulation of metals and nitrogen. The latter information is crucial for reliable deposition modelling with high spatial resolution, which is important for ecosystem-specific risk analysis [5,9–13]. This is due to the fact that concentrations of chemical elements can change as they pass through the vegetation cover. The difference in element concentrations in plant or soil samples collected under and outside the vegetation cover, but also in technical collectors, depends on the horizontal and vertical structure of the vegetation, climatic conditions, physical and chemical properties of the elements, the amount and type of deposition (wet, occult or dry) and the following characteristics and processes: (i) higher uptake capacity of plant cover compared to uncovered areas due to greater roughness; (ii) leaching of elements from plant tissue, exudates and decomposition products, and ion exchange reactions in the vegetation cover; and (iii) ability of plants to take up elements from atmospheric deposition. As a result of the combination of all these processes, ion concentrations may differ to a greater or lesser extent from those in areas without vegetation cover. A review paper dealing with such potential influences of vegetation cover on the deposition and bioaccumulation of elements in ecosystems, among a variety of other aspects, reports only 15 studies dealing with this topic, several of which come from Germany [14]. Since this review, only a few corresponding studies have been published [15]. The results on objectives one and two in this paper originate from an ongoing research project and are published for the first time. The results on the crown effect have been published once before in a different form [13]. However, these three partial results belong together when the results of the moss surveys are compared with the results from deposition modelling in a method-critical manner.

2. Materials and Methods

As in the previous moss surveys in 1990, 1995, 2000, 2005, 2010 and 2015, the design of the sampling network, the collection and the chemical analysis of the moss samples were methodologically coordinated by a manual in the 2020 campaign [8]. The concrete implementation of the ICP manuals in the German contributions to the moss surveys was described in the respective reports on the monitoring campaigns in which Germany participated (1990 [16], 1995 [17], 2000 [18], 2005 [19] and 2015 [20]) and derived articles in scientific journals. These have been archived and are available on request.

For the statistical analysis of the temporal development over the years from 1990 to 2020, measurement data on twelve heavy metals (Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, V and Zn) and N were available from a total of 26 sites (Table 1). Of these, 19 sites came from the nationwide 2020 monitoring network and have already been sampled for trend analyses since 1990. A further seven sites came from the Lower Saxony supplementary network, where systematic studies on the influence of the tree canopy drip on the deposition and bioaccumulation of metals and nitrogen took place in 2012, 2013, 2015 and 2020 ([9,13,21,22]). At these sites, moss samples were taken from 25 subplots representing the site categories "under tree canopy" and adjacent "open land".

The selection of sampling sites, collection and chemical analysis of element concentrations in moss samples were carried out according to the ICP manual for vegetation [8] and included quality control measures [13].

As recommended by the ICP Vegetation [23], the minimum sample number required to estimate arithmetic mean values with a maximum tolerance of 20% was calculated for the data used for the time trend analysis [23,24]. Data from moss samples collected at 400 sites in Germany in 2015 were used. Since the data situation for the time series analysis of the element concentrations in the moss samples collected at 26 sites during the 2020 monitoring campaign was only sufficient for nitrogen, but not for metals, the medians of the element-specific measured value distributions of the 1990, 1995, 2000, 2005, 2015 and 2020 campaigns were used for the time trend calculation. Depending on the element, these campaigns comprised between 475 and 592 moss sampling sites in 1990, between 1026 and 1028 in 1995 and 2000, respectively, between 724 and 726 in 2005, between 397 and 400 in 2015 and 26 sampling sites in 2020. The differences between the campaign- and element-specific median values were examined using the Wilcoxon test. The same test was used to examine the statistical differences between element concentrations in mosses collected under and outside tree canopies.

The variance in measurements of element concentrations in ecosystem compartments is possibly due to the following: 1. regional characteristics surrounding the sampling sites such as atmospheric deposition, distance to emission sources or land use; and 2. characteristics of the sampling site such as vegetation structure (vertical or horizontal). Therefore, in addition to the measurement data on element concentrations in mosses, further information was collected and statistically evaluated in the form of descriptors specific to the sampling sites and region-specific descriptors. Both the measurement data on element concentrations in mosses and the information on the descriptors were integrated into the statistical analyses. This makes it possible to relate the element concentrations to site- and region-specific descriptors and to rank them by multivariate statistical ranking, so that the descriptors can be interpreted as predictors of element concentrations in moss helping to predict element concentrations collected and accumulated with moss or technical collectors [9,13,21,22,25–27]. In this investigation, data on the descriptors together with those on the element contents were statistically evaluated with correlation and regression analyses [28].

Table 1. Sampling sites in Germany 2020 for monitoring metal and nitrogen concentrations in moss.

Site Name	Longitude	Latitude	Moss Species	Surrounding Vegetation
BB119_1	13.06463	53.13782	*Plesch*	Clearing within mixed forest
BW980_1	7.911113	47.913212	*Hypcup*	Clearing within mixed forest
BY206	13.41914	48.96492	*Hypcup*	Clearing within mixed forest
BY227_1	12.9236	47.595316	*Plesch*	Clearing within mixed forest
BY228_1	11.438111	48.482	*Plesch*	Clearing within coniferous forest
HE64	9.33924	50.92591	*Hypcup*	Clearing within broad leaved forest
MV114_2	12.72328	54.4364	*Psepur*	Clearing within mixed forest
NI03_95	9.22912	53.22084	*Plesch*	Forests—coniferous (Grasslands)
NI104_88	8.56453	53.22864	*Psepur*	Heathland(Forests—coniferous. Clearing within broad leaved)
NI108_9	7.91666	52.941612	*Psepur*	Grasslands (Forests—coniferous. Forests—broad leaved)
NI116_123	8.4461	52.87257	*Plesch*	Forests—broad leaved (Forests—coniferous. Heathland)
NI117_124	8.84464	52.82716	*Psepur*	Forests—coniferous (Forests - broad leaved. Grasslands)
NI118_128	9.21101	52.81197	*Psepur*	Forests—broad leaved (Forests—coniferous. Grasslands)
NI124_139	8.998761	52.642282	*Plesch*	Heathland (Forests—broad leaved)
NI130_157	9.21033	52.50861	*Plesch*	Grasslands (Forests—coniferous. Forests—mixed)
NI86_1	10.759259	52.805983	*Plesch*	Clearing within coniferous forest
NW27	7.44047	51.02383	*Hypcup*	Clearing within mixed forest
NW39	7.84453	52.17595	*Hypcup*	Clearing within broad leaved forest
RP27	8.18045	49.95429	*Psepur*	Clearing within broad leaved forest
SH36_2	10.24728	54.10648	*Psepur*	Clearing within mixed forest
SL5	6.78962	49.22595	*Psepur*	Clearing within mixed forest
SL9_2	6.843643	49.281593	*Hypcup*	Clearing within broad leaved forest
SN240_1	12.326555	51.357992	*Hypcup*	Clearing within broad leaved forest
ST199_1	12.59049	51.67068	*Psepur*	Clearing within mixed forest
ST204_1	10.639492	51.821196	*Plesch*	Clearing within coniferous forest
TH68	10.78596	50.63235	*Hypcup*	Clearing within coniferous forest

Site name = Sampling sites for monitoring temporal trends; SH Schleswig-Holstein, MV Mecklenburg-Western Pomerania, HH Hamburg, NI Lower Saxony, BE Berlin; ST Saxony-Anhalt, BB Brandenburg, NW North Rhine-Westphalia, SN Saxony, TH Thuringia, HE Hesse, RP Rhineland Palatinate, SL Saarland, BY Bavaria, BW Baden-Wuerttemberg; Plesch = Pleurozium schreberi, Psepur = Pseudoscleropodium purum, Hypcup = Hypnum cupressiforme; Surrounding vegetation (in brackets) = Surrounding vegetation at additional sampling sites in north-western Germany for investigating the effects of vegetations structure on element concentrations in moss

For the correlation analysis and the subsequent regression analysis, conspicuously high values were eliminated from the entire data collective 1. All relations between the substance concentrations in the mosses and the leaf area index with the highest corre-lations were quantified by linear regression based on the aureate-refined data (data collective 2). The residuals were analysed for symmetry using a quantile-quantile plot (QQ plot) and for variance using a residual standard error (RSE). The quality of the model resulting from the regression analysis was assessed using the coefficient of de-termination (B or R^2) as the square of the Pearson correlation coefficient and the adjusted coefficient of determination (Adjusted R^2). Both parameters describe the pro-portion of the variance that can be explained by linear regression. Since both quality measures generally represent rather optimistic estimates of the explanatory power when using the same data set for model building and validation, a pseudo-determinism measure (pseudo R^2) was determined as a supplement.

Pseudo R^2 was calculated as the square of Pearson's correlation between modelled and observed values. To minimise commonly known limitations of using such pseu-do-determinism measures for assessing model performance, the total data set was di-vided into three equally sized, randomly selected subsets. Three times, 2/3 of the total dataset was used to build the statistical model, 1/3 for model validation and then the three Pseudo R^2 were averaged. The coefficients of determination (R^2, Adjusted R^2, Pseudo R^2) were finally used to select the predictors with the best fit of the models to the data used.

Table 2 contains a grouped overview of the data on the descriptors of the moss collection sites and their surroundings, which were collected in addition to the measurement data of the element contents. Of the total of 94 descriptors, 14 are related to vegetation structure.

Table 2. Site- and region-specific descriptors of element concentrations in mosses.

Descriptors	Number of Variables
Atmospheric deposition	9
Meteorology	5
Geology, soil and relief	7
Moss type and density and vegetation	4
Vegetation structure	14
Potential emission sources	51
Distance to North Sea and Baltic Sea	1
Potential risk of wind erosion on arable land	3
	94

3. Results and Discussion

For nitrogen only, the minimum sample number calculated with data from 400 moss collection sites in 2015 is sufficient to estimate an arithmetic mean with a tolerance of 20%. For metals, the opposite was the case. For example, in the case of cadmium, moss samples would have to be taken at 117 sites instead of the 26 sampled (Table 3).

Table 3. Minimum Sample Number (* MSN) and actual sample size (*n* **) in MM2020 (* calculated with data from 400 sample points in 2015).

	As	Cd	Cu	Ni	Pb	Sb	N
MPZ	110	117	55	73	75	36	10
n	26	26	26	26	26	26	**26**

MPZ = Minimum Sample Number calculated according to the SSAD method [23,24]; n = number of sample elements in MM2020; **bold** = MPZ reached or exceeded. ** = $p \leq 0.05$ (Significant); * = $p \leq 0.1$ (Weakly significant).

Table 4 shows the mean concentrations of metals in moss samples collected between 1990 and 2020. The calculation results corroborate a significant reduction in element concentrations from 1990 to 2020; increasing concentrations of Cu, Ni and Sb, as well as Cr and Zn (not shown here) between 2000 and 2005; and increasing concentrations of all measured metals between 2015 and 2020.

Table 4. Median values of metal concentrations in mosses collected between 1990 and 2020.

Element	Unit	1990 (*n* = 475 to 592)	1995 (*n* = 1026 to 1028)	2000 (*n* = 1026 to 1028)	2005 (*n* = 724 to 726)	2015 (*n* = 397 to 400)	2020 (*n* = 26)
As	µg/g	0.338	0.249	0.160	0.160	0.108 (0.101–0.114)	0.119 (0.082–0.135)
Cd	µg/g	0.287	0.293	0.210	0.210	0.136 (0.130–0.148)	0.210 (0.158–0.244)
Cu	µg/g	8.79	9.45	7.14	7.27	4.65 (4.44–4.84)	5.87 (5.08–6.11)
Ni	µg/g	2.353	1.630	1.130	1.160	0.681 (0.653–0.722)	1.800 (1.291–2.095)
Pb	µg/g	12.94	7.78	4.62	3.69	1.83 (1.69–1.97)	1.88 (1.29–3.02)
Sb	µg/g	n.a.	0.173	0.150	0.160	0.090 (0.085–0.097)	0.148 (0.130–0.165)

n = Sample size; n.a. = Not specified; In brackets: 95% confidence interval for the median value.

Table 5 compiles the percentage changes in the median element concentrations of all measurement campaigns in relation to their respective precursor campaign. Accordingly, the following can be determined:

- Statistically significant increase in Pb and Sb concentrations between 2015 and 2020;
- Statistically significant reduction in concentrations of all metals between 1990 and 2020;
- Statistically significant increase in concentrations of all metals between 2015 and 2020.

Table 5. Changes in median metal concentrations compared to the respective previous moss survey(s) (in %).

Element	1995/1990	2000/1995	2005/2000	2015/2005	2020/2015	1995/B. Year	2000/B. Year	2005/B. Year	2015/B. Year	2020/B. Year
As	−26 ***	−36 ***	0	−32 ***	+10	−26 **	−53 ***	−53 ***	−68 ***	−65 ***
Cd	+2	−28 ***	0	−35 ***	+55 ***	2	−27 ***	−27 ***	−53 ***	−27 ***
Cu	+8 ***	−24 ***	+2 **	−36 ***	+26 ***	8 **	−19 ***	−17 ***	−47 ***	−33 ***
Ni	−31 ***	−31 ***	+3	−41 ***	+165 ***	−31 **	−52 ***	−51 ***	−71 ***	−23 ***
Pb	−40 ***	−41 ***	−20 ***	−50 ***	+2	−40 **	−64 ***	−71 ***	−86 ***	−86 ***
Sb	n.a.	−13 ***	7 **	−44 ***	+64 ***	n.a.	−13 ***	−8 ***	−48 ***	−14 **

B. year = Base year (Year of first sampling); n.a. = Not specified; −/+ = Decrease/Increase in median; *** = $p \leq 0.01$ (Very significant); ** = $p \leq 0.05$ (Significant).

Relating the increases in metal concentrations between 2015 and 2020 and the decreases between 1990 and 2020 to the emission inventory data (Table 6), the following become clear:

- The decreases between 1990 and 2020 are in line with the emissions register.
- The increase between 2015 and 2020 is not in line with the emissions register.

Table 6. Median values of metal concentrations in mosses compared to metal emissions in Germany [29].

	As	Cd	Cu	Ni	Pb	Sb
Change in median HM content in moss in 2020 compared to 2015 in % (in brackets: emission trend, Germany, 2015–2020)	+10 (−19)	+55 (−13)	+26 (−9)	+165 (−3)	+2 (−14)	+64 n.a.
Change in median HM content in the moss in 2015 compared to 1990 in % (in brackets: emission trend, Germany 1990–2020)	−65 (−94)	−27 (−63)	−33 (−15)	−23 (−61)	−86 (−92)	−14 n.a.

These results underline the need to control emission data with exposure data from deposition and/or bioaccumulation data.

In contrast to the metals, nitrogen bioaccumulation in Germany has remained more or less the same between 2005 and 2020. The changes in nitrogen concentrations in mosses between 2005 and 2015 (−2%) and between 2015 and 2020 (+8%) as well as the long-term trend (2005–2020) prove not to be significant and only partially agree with the data of the nitrogen emission register [29].

Table 7 shows that the moss samples collected outside of tree canopies have significantly lower element contents than the moss samples collected under tree canopies: element concentrations in mosses collected under tree canopies are higher than those of moss samples collected outside of tree canopies. The median ratio between mosses collected outside and under tree canopies is 1.46 for nitrogen based on the 2020 survey data, and the corresponding median ratio is 1.68 in moss specimens sampled in 2015 [20] and 1.95 in moss samples collected in 2012 and 2013 [22,27]. The median ratios of metal concentrations in mosses collected inside and outside treetops rank between 2.5 (mercury) and 1.18 (antimony). These and the other values compiled in Table 6 are essential for mapping atmospheric deposition using chemical transport models such as LOTOS-EUROS [30–32] and EMEP MSC East [12,33].

Table 7. Median ratios of elemental concentrations in moss samples collected below and beyond tree canopies based on the Moss Survey 2020 (data collectives 1 and 2), moss samplings in 2012 and 2013 (data collective 3) [27] and on the Moss Survey 2015 (data collective 4) [20].

Element	Data Collective 1 (n = 20)	Data Collective 2 (n = 17 to 20)	Data Collective 3 (n = 52)	Data Collective 4 (n = 25)
Al	1.26	1.43 **	—	1.41
As	1.44	1.50	—	1.57
Cd	1.35 *	1.69 ***	1.60 ***	1.75 ***
Cr	1.42	1.40 *	1.01	1.22
Cu	1.44 ***	1.46 ***	1.71 ***	1.80 ***
Fe	1.31	1.31	—	1.32 ***
Hg	1.50 ***	1.33 ***	1.68 ***	2.50 ***
Ni	1.46	1.63 ***	1.15 ***	1.24 ***
Pb	1.26	1.38 (*)	1.32 ***	1.72 ***
Sb	1.18 *	1.18 ***	—	1.62 ***
V	1.21	1.26	—	1.60 ***
Zn	1.21 ***	1.20 ***	1.33 ***	1.43 ***
N	1.46 ***	1.46 ***	1.95 ***	1.68 ***

Data collective 1: Measured values of the Moss Survey 2020; Data collective 2: Measured values of the Moss Survey 2020 after removal of outliers; n = Sample size; *** = $p \leq 0.01$ (Very significant); ** = $p \leq 0.05$ (Significant); * = $p \leq 0.1$ (Weakly significant); (*) = p just above 0.1.

Of the vegetation structure measures (Table 2), the leaf area index shows a very pronounced and statistically significant correlation (Spearman) with the element contents in mosses (Table 8).

The results of the regression analysis and the statistical modelling for the relationships between the 12 heavy metals or nitrogen and the leaf area index were as follows: For the analysis and modelling, 28 to 40 pairs of values were available for each of the 13 elements. A linear, monotonic, progressively increasing relationship was assumed between the target variables and the predictors. The quotient of the simple tree species-specific LAI without weighting of the tree layer cover (sLAI.spec) was chosen as predictor. For Al, Cu, Hg, Sb, Ni and N, regression models with quality measures of > 0.5 (pseudo R^2) were obtained. For Cr and Pb the coefficient of determination is between 0.4 and 0.5, for Cd, Fe and Zn between 0.3 and 0.4 and for As and V below 0.3 (Table 9). Linear models with $R^2 > 0.5$ could be calculated for aluminium, copper, mercury, antimony, nickel and nitrogen. Their validity ranges from 0.3 < sLAI.spec quotient < 2.5 and apply to site combinations of grassland, heath, deciduous, mixed and coniferous forest sites. Following estimates were made possible with the regression models (Table 9):

- Element content in moss for an outdoor area in the immediate vicinity of a moss collection site under tree canopies;
- Element content in moss for a site under tree canopies in the immediate vicinity of a moss collection site outside of tree canopies;
- Element content in moss using an estimated or measured leaf area index for any site, enabling nationwide maps of element distribution across Germany.

Table 8. Correlation coefficients (Pearson and Spearman) between quotients of element contents in mosses and quotients of leaf area indices based on the Moss Survey 2020 data (data collective 2, cf. Table 6) with respective results based on the Moss Survey 2015 [20] (data collective 4).

Element	Data Collective 2 r_p (n = 28 to 40) [(1)]	Data Collective 2 r_s (n = 28 to 40) [(1)]	Data Collective 4 r_p (n = 67) [(2)]	Data Collective 4 r_s (n = 67) [(2)]
Al	0.84 ***	0.76 ***	0.43 ***	0.41 ***
As	0.32 *	0.24	0.44 ***	0.50 ***
Cd	0.48 ***	0.67 ***	0.64 ***	0.57 ***
Cr	0.57 ***	0.60 ***	0.48 ***	0.47 ***
Cu	0.90 ***	0.92 ***	0.73 ***	0.75 ***
Fe	0.52 ***	0.50 ***	0.51 ***	0.52 ***
Hg	0.66 ***	0.78 ***	0.71 ***	0.72 ***
Ni	0.75 ***	0.71 ***	0.64 ***	0.60 ***
Pb	0.61 ***	0.52 ***	0.72 ***	0.65 ***
Sb	0.80 ***	0.84 ***	0.77 ***	0.68 ***
V	0.41 **	0.36 **	0.57 ***	0.59 ***
Zn	0.46 ***	0.59 ***	0.59 ***	0.60 ***
N	0.87 ***	0.87 ***	0.84 ***	0.81 ***

[(1)] Determined using the tree species-specific simple leaf area index (sLAI.spec); [(2)] Determined using the land-use-specific and cover-weighted leaf area index (wLAI.lu); n = Sample size; r_p = Correlation coefficient (Pearson); r_s = Correlation coefficient (Spearman); *** = $p \leq 0.01$ (Very significant); ** = $p \leq 0.05$ (Significant); * = $p \leq 0.1$ (Weakly significant).

Table 9. Characteristics and goodness-of-fit measures of the regression models for the relationship between the quotients of the element contents in the mosses and the quotients of the simple tree species-specific leaf area index.

Element	n	Vegetation Structure Measure	a	b	RSE	R^2	Adj. R^2	Pseudo R^2
Al	32	sLAI.spec ***	1.2432	−0.1776	0.39	0.71	0.70	**0.69**
As_	30	sLAI.spec *	0.9851	0.4071	1.42	0.10	0.07	0.10
Cd	36	sLAI.spec ***	0.6895	0.4138	0.62	0.23	0.21	0.31
Cr	28	sLAI.spec ***	0.6111	0.4423	0.43	0.32	0.29	0.47
Cu	34	sLAI.spec ***	0.9164	0.1012	0.25	0.82	0.81	**0.88**
Fe	36	sLAI.spec ***	1.1376	0.0737	0.92	0.27	0.24	0.36
Hg	34	sLAI.spec ***	0.9259	0.1594	0.54	0.43	0.41	**0.59**
Ni	32	sLAI.spec ***	1.1084	−0.0177	0.48	0.57	0.55	**0.60**
Pb	34	sLAI.spec ***	0.8505	0.2287	0.55	0.37	0.35	0.44
Sb	34	sLAI.spec ***	0.3245	0.6565	0.15	0.64	0.63	**0.70**
V	32	sLAI.spec **	0.6692	0.4851	0.72	0.16	0.14	0.16
Zn	36	sLAI.spec ***	0.2910	0.7279	0.31	0.21	0.19	0.31
N	40	sLAI.spec ***	0.8532	0.1572	0.28	0.75	0.75	**0.75**

sLAI.spec = Tree species-specific simple leaf area index; n = Sample size; a = Slope of the regression line; b = Intercept of the regression line; RSE = Residual standard error; R^2 = Coefficient of determination; Adj. R^2 = Corrected coefficient of determination; Pseudo R^2 = Pseudo coefficient of determination; **Bold** = Regression models with Pseudo $R^2 > 0.5$; *** = $p \leq 0.01$ (Very significant); ** = $p \leq 0.05$ (Significant); * = $p \leq 0.1$ (Weakly significant).

4. Conclusions

The statistical analyses of the development of metal and nitrogen deposition accumulation in mosses, summarised in Table 10, confirmed the discrepancies between emission inventory data derived by inventory-based calculations and empirical exposure monitoring.

Table 10. Trends in the accumulation of metal and nitrogen deposition in moss samples collected from 1990 to 2020 across Germany.

Substances	Time	Trend?
N	2005–2020	No statistically significant time trend
	2015–2020	Increase, not significant
HM	1990–2020	Significant decline
As, Cd *, Cu *, Ni *, Pb, Sb *	2015–2020	(* Significant) increase
Pb, Fe	1990–2020	Continuous significant reduction
Cr, Sb, Zn	2000–2005	Significant increase
Al, As, Cd, Cu, Hg, Ni, V	2000–2005	Standstill

The presented studies on the effect of tree canopies on element contents in mosses prove that the filtering effect of vegetation can increase bioaccumulation by 18 to 150%. These empirical findings should be integrated into atmospheric deposition modelling with models such as LOTOS-EUROS and MSC East EMEP.

In addition to the investigations presented as examples, further investigations compared the element contents in mosses with data on element contents in leaves, needles and soils using data from the ICP Forests Level II and the environmental sample bank of Germany, and with atmospheric deposition data calculated with the chemical transport models LOTOS-EUROS [30–32] and MSC East EMEP [12,33]. There is an urgent need to calculate the atmospheric deposition of metals and nitrogen with these two models, using empirically based factors that quantify the relationships between element concentrations under and outside the canopy, and the *same* emission and meteorological data. This is not yet the case, although it is a prerequisite for a well-founded evaluation of the informative value of the modelling after comparing the modelling results thus obtained with the empirically determined element contents in mosses.

Author Contributions: Conceptualization, S.N. and W.S.; Methodology, A.D., S.N. and W.S.; Validation, A.D., S.N. and W.S.; Investigation, A.D. and B.V.; Resources, W.S.; Data Curation, S.N.; Writing—Original Draft Preparation, W.S.; Writing—Review and Editing, A.D., S.N. and W.S.; Visualization, S.N.; Supervision, W.S.; Project Administration, A.D., S.N. and W.S.; Funding Acquisition, A.D., S.N. and W.S. All authors have read and agreed to the published version of the manuscript.

Funding: This study was financed from our own funds and complements the German contribution to the ICP Vegetation Moss Survey 2020, which was funded by the Federal Environment Agency.

Data Availability Statement: There are no data publications yet on the evaluations of the Moss Survey 2020. However, data publications in publicly accessible repositories do exist for the moss surveys up to 2015 and are listed below. Wosniok W, Nickel S, Schröder W 2019. R Software Tool for Calculating Minimum Sample Sizes for Arbitrary Distributions (SSAD), Link to scientific software (Version v1). ZENODO, https://doi.org/10.5281/zenodo.2583010. Nickel S, Schröder W, Drehwald U, Dreyer A, Preußing M, Stapper NJ, Struve S, Teuber D, Völksen B 2018. Entwicklung stofflicher Konzentrationen in Moosen (Stickstoff, Schwermetalle) von 1990 bis 2015 in Deutschland, Link zu Forschungsdaten (Version v1) [Data set] [Development of substance concentrations in mosses (nitrogen, heavy metals) from 1990 to 2015 in Germany, Link to research data Version v1 [Data set]]. 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Conflicts of Interest: The authors declare no conflict of interest.

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