Moss-specific accumulation of atmospheric element deposition?

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Abstract
This article presents statistical analyses of elements concentrations in mosses which were collected in 1990, 1995, 2000, 2005 and 2015 throughout Germany at 592, 1026, 1028, 726 and 400 sites, respectively, and chemically analysed according to harmonised methods throughout Europe. The evaluations intended to examine whether the element concentrations are specific to moss species and whether conversion factors should be used. Such observations and recommendations have so far been limited to spatially confined areas with relatively few moss samples and were derived from studies without methodological harmonisation.
The data collected 1990-2015 across Germany was analysed by percentile statistics. The samplings from 2015 were additionally evaluated by bivariate correlation analyses and multivariate techniques to identify and rank the statistical relevance of site-specific and regional characteristics for the concentrations of 12 heavy metals and nitrogen in mosses. The strongest predictor for Cd, Cu, Ni, Pb, Zn and N concentrations was the sampled moss species. In 2015, the atmospheric deposition showed a lower predictive power compared to earlier campaigns. However, the present study does not refute the hypothesis of moss species-specific element concentrations which are in the range of local and metrological variance. It is therefore advisable to continue dispensing with conversion factors.
Keywords. Conversion factors; heavy metals; Random Forest Regression; Multiple Linear Regression; Commonality Analysis.

1. Introduction

This article presents statistical analyses of elements concentrations in mosses collected in 1990, 1995, 2000, 2005 and 2015 throughout Germany at 592, 1026, 1028, 726 and 400 sites, respectively, and chemically analysed according to harmonised methods throughout Europe. The statistical analyses are intended to examine indications that the element accumulations are specific to moss species and that therefore conversion factors should be used. Such observations and recommendations have so far been limited to spatially confined areas and relatively few moss samples and were derived from studies without methodological harmonisation.

2. Methods

To examine the element accumulation of moss species used in moss surveys, comparative studies between *Pleurozium schreberi* (*P.s.*), *Scleropodium purum* (*S.p.*; synonym: *Pseudoscleropodium purum*) and *Hypnum cupressiforme* (*H.c.*) were carried out at the same moss sampling sites across Germany. The elements considered were, amongst others: Cd, Cu, Cr, Fe, Ni, Ti, Pb, V and Zn in 1990 as well as As, Cd, Cu, Cr, Fe, Ni, Ti, Pb, V, Zn, Sb and Hg in 1995, 2000, 2005 and 2015. N concentrations were measured in 2005 and 2015.

The data analyses applied encompassed median statistics, regression analysis and Commonality Analysis. The latter one allows for identifying and ranking factors associated with the element concentrations in mosses. In the multivariate analyses measured concentrations of 12 heavy metals and N in the mosses were set as target variables and the following potential predictors: Atmospheric deposition, meteorology, geology, soil, topography, sampling, vegetation structure, land use density, population density and potential emission sources. In addition to a correlation analysis of the relationships between the predictors and the target variables, a regression analysis was performed using two different methods: Random Forest Regression (RF, Breiman 2001) and Multiple Linear Regression (MLR, Sachs & Hedderich 2009) combined with Commonality Analysis (CA, Pedhazur 1997, Thompson 2006).

3. Results

The strongest predictor for Cd, Cu, Ni, Pb, Zn and N in moss was the sampled moss species. In 2015, the atmospheric deposition showed a lower predictive power compared to earlier campaigns. The mean precipitation (2013-2015) is a significant factor influencing Cd, Pb and Zn. Among the topographical parameters, altitude (Cu, Hg, and Ni) and slope (Cd) are the strongest predictors. With regard to 14 vegetation structure measures studied, the distance to adjacent tree stands is the strongest predictor (Cd, Cu, Hg, Zn and N), followed by the tree layer height (Cd, Hg, Pb and N), the leaf area index (Cd, N, Zn), and finally the coverage of the tree layer (Ni, Cd and Hg). For forests, the spatial density in radii 100-300 km predominate as significant predictors for Cu, Hg, Ni and N. For the urban areas, there are element-specific different radii between 25 and 300 km (Cd, Cu, Ni, Pb and N) and for agricultural areas usually radii between 50 and 300 km, which are important. The population density in the 50 and 100 km radius is a variable with high explanatory power for all elements except Hg and N.

4. Conclusions

In order to derive statistically verified accumulation trends from *P.s.*, *S.p.* and *H.c.*, it is actually necessary to compare the elements concentrations of moss samples taken in parallel at the same site. In the median comparisons carried out here, however, central tendencies of measured value distributions from different spatial samples from different ecosystems were compared, since larger samples can be compared. Due to different site conditions, neither an even nor a constant distribution of *P.s.*, *S.p.* and *H.c.* across the federal territory over the years was given in the moss surveys. Rather, in some federal states of Germany one of the selected moss species often dominates while in others it was not sampled at all (e.g. in 2000 in Baden-Württemberg almost exclusively *H.c.* was sampled). The share of H.c. in Germany also doubled from 13 % in 1990 to 26 % in 2000. If one compares countries on the basis of medians, one must take into account how many measurement results the respective median was calculated from.

Therefore, it should be noted that the samples compared in the analyses described above are never spatially identical. Samples of the same moss species collected at the same site may have different elements concentrations due to predictors such as atmospheric deposition and vegetation structure (site variability) and different adsorption and accumulation properties of mosses (moss species variability).

From the results the recommendation was derived not to use correction and conversion factors. On the one hand, this is justified by the fact that neither the comparison at country level (medians) nor the cartographic implementation showed any significant influence. On the other hand, especially because of the large scatter of the measured values at the same site (site variability), no correction should be made even for each individual moss species in the element-dependent order of 12 to 28 % (Siewers et al. 2000: 12). Moreover, these conversions could only be carried out correctly if sufficient moss species were collected in parallel at identical locations and the averaged factors are calculated taking into account the scatter of element concentrations. studies of neighbouring European participating states (Netherlands, Austria, and Switzerland) on species comparison also came to the conclusion that no conversion coefficients should be used, as the statistically reliable amount of data did not justify this. In this context, Zechmeister (1997) points out that the derivation of correction factors must also take into account the different annual biomass formation of the individual moss species.

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