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Moss species-specific accumulation of atmospheric deposition?

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Abstract

Background: This article presents statistical analyses of elements concentrations in mosses collected in two monitoring programmes: 1. The German moss monitoring as part of the European Moss Survey conducted in 1990, 1995, 2000, 2005 and 2015 at 592, 1026, 1028, 726 and 400 sites across Germany, respectively, and chemically analysed according to harmonised methods throughout Europe; and 2. The moss surveys additionally performed throughout Bavaria, federal state of Germany. The evaluations of the present study are intended to examine indications whether the element accumulations are specific to moss species and whether, 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 different studies without a common methodology. Therefore, the objective of this investigation was to analyse large and long-term datasets from moss surveys for differences in element concentrations in different moss species. This analysis was based on data derived from several moss species collected across Germany and specimens of only one moss species collected in the monitoring programme performed by the environmental authority of Bavaria. So far, the presented investigation is the most comprehensive one in terms of running time, spatial density of the measurement network and method harmonisation.

Results: The present study does neither verify nor falsify the hypothesis of moss species-specific element accumulations in mosses. This, like the other studies, is not possible because of its empirical design, since that would require strictly controlled laboratory experiments. However, this investigation yielded hints, that the differences in element accumulation in several moss species across German surveys between 1990 and 2015 are in the range of the intra- and inter-specific variance reported.

Conclusion: It is, therefore, advisable to continue dispensing with conversion factors so far.

Keywords: Bavaria, Conversion factors, Germany, Heavy metals, Moss surveys

Background

Substance inputs from the atmosphere into aquatic and terrestrial ecosystems are caused by falling or deposited precipitation ("wet/occult deposition") and/or by sedimentation and gas diffusion ("dry deposition"). In terrestrial ecosystems, such atmospheric deposition can be collected by technical facilities and accumulation bioindicators (also called: accumulation biomonitors) such as mosses for subsequent chemical element determination [16, 25, 27, 39, 40, 44, 50].

Due to the lack of real root and vascular system, mosses accumulate elements only through atmospheric deposition and are, therefore, better than tree leaves or needles in monitoring atmospheric pollution [16]. Since Rühling and Tyler [33] recommended mosses as bioindicators for the accumulation of atmospheric element deposition, terrestrial mosses were widely used for biomonitoring of atmospheric pollution. Thereby, *Hylocomium splendens, Pleurozium schreberi* and *Hypnum cupressiforme* were commonly employed in Europe and North America. Due to their geographical distribution, as the case may be, other moss species have to be used to cover areas of large spatial extend. From such surveys, it was obvious that the heavy metal depositions in mosses varied greatly, even

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in the same species or biotope [45]. However, according to Chen et al. [7], only a few detailed interspecies and intra-species comparisons were carried out in mosses [32, 53, 55]. Chen et al. [7] found that most moss species selected in two regions in China had different accumulation capacity even for the same heavy metal element. The inter-species comparison of specific heavy metal content in the present study indicated that the biological characters of each species, such as living form, morpha, had a great influence on accumulative capacity of the elements in mosses, even if collected from the same biotope [28, 46]. However, because of the limitation of sampling, Chen et al. [7] concede that their results need further confirmation.

Fernandez et al. [9] reviewed 369 studies including both methodological and application studies of the passive biomonitoring of the atmospheric deposition of heavy metals with terrestrial mosses. The review regarded pre-sampling issues (number of sampling sites, sampling design, timing of surveys, moss species), field sampling (distance between sampling sites, vegetation and pollution sources, elevation, distance from the coast, representativeness of sampling sites, dimensions of the sampling sites, number of subsamples, quantity of sample collected, sampling precautions, sampling period), cleaning and storing (sample treatment, selection of material, sample cleaning, sample drying, sample homogenization and storage). From that literature review, Fernandez et al. [9] concluded that the moss species collected is one of the most important factors influencing the concentrations of elements in moss tissues. However, they concede that moss surveys covering large areas cannot only be based on one single moss species [52]. This problem can only be solved using more than one moss species within the same survey, even if it seems obvious that the concentrations of elements may vary considerably between moss species [6, 10]. This precludes comparisons of the results obtained [9]. According to the experimental protocol of the European Moss Survey [15], only pleurocarpous mosses should be sampled whereby *Hylocomium splendens* and *Pleurozium schreberi* should be favoured, followed by *Hypnum cupressiforme* and *Pseudoscleropodium purum*. The use of other species such as *Abietinella abietina* in mountainous areas or *Barbula indica* in arid regions should be preceded by a comparison and calibration of element uptake relative to that in the main preferred species. Around 50 % of the worldwide studies reviewed by Fernandez et al. [9] used just one biomonitoring species. Although the investigated studies which regarded a large number of species (9, 10, 14 or even 23) are very scarce, at least five or more species were used in 14% of the studies review. However, the number of different moss genera used increased to nearly 90. Of these,

Hylocomium, Pleurozium and *Hypnum* were very common, while 90 % of the genera were used on fewer than 10 occasions. In 74 % of the studies in which a maximum of two species were used, these belonged to *Pleurozium schreberi* and/or *Hylocomium splendens* and/or *Hypnum cupressiforme.*

Some studies have compared the concentrations of elements in pairs of species collected within the same sampling site [4]. The number of species involved in pairwise comparisons is very limited relative to the total number of species used. In a total of 13 articles, only 7 different pairwise comparisons were made: *Pleurozium schreberi* vs. *Hylocomium splendens/Brachythecium rutabulum./ Hypnum cupressiforme/Pseudoscleropodium purum/ Rhytidiadelphus squarrosus, Hylocomium splendens vs. Sphagnum L. spp., and Hypnum cupressiforme vs. Pseudoscleropodium purum.* According to Halleraker et al. [11], the results of paired comparison can be directly combined if the concentrations are significantly correlated (as indicated by Pearson's or Spearman's correlation coefficients) and if the species ratio (concentrations in species 1 divided by concentrations in species 2) does not differ significantly from 1 in the sampling site in which the species were sampled. Carballeira et al. [6] suggested that when the regression line slope and elevation do not differ significantly from the line of slope 1, the species could be combined. Interspecies calibration has been recommended for situations when the concentrations are significantly different, but correlated [31]. The use of type II (calculated as standardised major axis regression) rather than type I regressions was recommended because field values are used and none of the variables are independent [6]. Conversion of element concentrations found in one species to those in another species has been carried out using the ratio of concentrations in the two species as a correction factor [11]. However, this ratio seems not to be reliable because it varies depending on where the samples have been collected. Most studies involving interspecies comparison only assess the correlations between the species, and therefore, no conclusions about their combined use can be reached [4].

According to Fernandez et al. [9], the elements for which the previous requirements are fulfilled vary from one study to another [4], even when the same species are compared. For instance, data on Pb and Zn concentrations in *Pleurozium schreberi* and *Hylocomium splendens* were combined, taking into account the former criteria, in Canada and Germany [1, 53]. However, according to Halleraker et al. [11], *Pleurozium schreberi/Hylocomium* splendens ratios of Cu, Fe and Ni are significantly different from 1 in the central Barents region. These results may be explained by differences in the accumulation capacity of bryophytes due to the range of concentrations

of the pollutants in the environment. Reimann et al. [31] reported that the ratios of concentrations of the same element between species can vary depending on the sampling site.

Fernandez et al. [9] conclude that interspecies calibration seems only valid for the range of concentrations considered and under the same environmental conditions to those in which the inter-calibration studies have been carried out. Therefore, inter-calibrations cannot be extrapolated [52]. Additionally, it should be considered that the uncertainty of the whole dataset is complemented by the uncertainty associated with the coefficients of the regression [53]. Most authors have, therefore, concluded that the interspecies calibration should not be conducted as it introduces further variability to the data [11, 47]. Carballeira et al. [6] suggest only carrying out calibrations when the values of the regression coefficients are very high. Therefore, Fernandez et al. [9] concluded that interspecies calibration of the uptake of heavy metals should not be applied. The differences in the levels of heavy metals concentrated by different moss species would prevent valid comparison of the results obtained with these studies. When the use of more than one species is mandatory, this would limit interpretation of the data to a qualitative estimate of the levels of pollutants. However, the results from studies carried out in the same region will be comparable over time, and temporal patterns from different areas will also be comparable.

So far, only a few detailed interspecies and intra-species comparisons were carried out in mosses except for the common mosses mentioned above [32, 53, 55]. According to Stankovic et al. [44], it can be assumed that different genotypes of the same species can also react differently to the accuracy and reliability of information obtained using mosses as biomonitors depend on the understanding of the mechanisms, factors and bryophyte species responses that can influence the uptake and the linearity of the relationship between dose and tissue content [2, 3]. Therefore, studies in controlled conditions of axenic cultures are urgently needed for our better understanding of the relationship between bryophytes and heavy metals [44].

The extent to which element concentrations of atmospheric deposition, which have been technically and biologically collected, are similar and to what extent the substance concentrations determined in different moss species coincide [9, 13] often relies solely on literature research but not on statistical analyses of data collected according a harmonised methodology or even systematic laboratory experiments. Therefore, the investigations presented in this article compared the results of the Germany-wide moss monitoring (MMD), which is a contribution to the European moss monitoring (MME)

carried out every 5 years since 1990, with the Bavarian moss monitoring (MMB). While in the MMD and in the European Moss Survey (MME), several moss species can be collected according to a priority list due to the larger study areas compared to the German federal state Bavaria and the associated higher number of occurring moss species, the MMB is limited to one moss species ("Comparison of the Germany-wide and Bavarian moss surveys (2005–2016)" section). Against this background, one aim of this work is to present previous findings on the question of whether different moss species enrich elements from atmospheric deposition to a similar extent, on the basis of methodologically harmonised MMD data and median statistics ("MMD 1990 and 1995" section: MMD 1990, 1995; "MMMD surveys 1990, 1995 and 2000" section: MMD 1990, 1995 and 2000) and multivariate statistics ("Mmd 2015" section: MMD 2015). The second objective is to determine to what extent the MMD data correspond to those of the MMB ("Comparison of the Germany-wide and Bavarian moss surveys (2005–2016)" section) and what conclusions can be drawn from this for future MMD and MME campaigns ("Conclusions" section).

Materials and methods
MMD 1990 and 1995
To examine the element accumulation of moss species used in moss surveys, comparative studies between *Pleurozium schreberi (Ps), Scleropodium purum (Sp; synonym: Pseudoscleropodium purum)* and *Hypnum cupressiforme (Hc) were* carried out at the same moss sampling sites in the MMD 1990 and 1995 [14, 41]. The elements considered were:

- Cd, Cu, Cr, Fe, Ni, Ti, Pb, V and Zn in the MMD 1990, and
- As, Cd, Cu, Cr, Fe, Ni, Ti, Pb, V, Zn, Sb and Hg in the MMD 1995.

The statistical evaluation of the resulting measurements was carried out in both MMD campaigns by correlation and regression analyses, with *Ps* as the reference value and *Sp* and *Hc* as the dependent value. Siewers and Herpin [41] summarised the findings from these calculations. They are outlined below, supplemented by a comparison of the accumulation behaviour of the moss species taken during moss monitoring in 1990, 1995 and 2000.

MMD surveys 1990, 1995 and 2000
The results on moss species variability in the MMD 1990 and MMD 1995 ("MMD 1990 and 1995" section) were supplemented for the moss species *Ps, Sp* and *Hc* by

additional inclusion of data from the MMD 2000 [37, 38]. The concentrations of the standard elements As, Cd, Cu, Cr, Fe, Ni, Pb, Ti, V, Zn, Hg and Sb as well as the additional elements Al, Ba, Ca, K, Mg, Mn, Na and Sr were shown for the three moss species mentioned above, focussing on three questions:

1. To what extent do the three moss species investigated show different element accumulation?
2. To what extent does the moss species-specific consideration of the elements concentrations in MMD 2000 differ from the moss species-independent evaluation?
3. To what extent does the moss species-specific analysis of the temporal development of the elements concentrations in the MMD 1990, 1995 and 2000 differ from a moss species-independent presentation?

The moss species-specific description of the results of the surveys in 1990, 1995 and 2000 is based on comparing the median element concentrations specified for the German federal states. For each element, each moss species and each federal state, the central tendency of the measurement data is represented by medians and bar charts. This happens regardless of whether certain moss species only occur at certain sites with specific air pollution and whether sites have been investigated with different moss species throughout the surveys. On this basis, the following evaluations are performed for each element:

- The results of the MMD 1990, 1995 and 2000 are compared for *Ps, Sp* and *Hc* using the median values calculated for the German federal states and nationwide.
- The moss species-specific medians of the elements concentrations in the MMD 2000 are compared for *Ps, Sp* and *Hc* with those of the moss species-unspecific medians.
- The development of the elements concentrations since the MMD 1990 in the moss species *Ps, Sp* and *Hc* is compared with the development independent of the moss species on the basis of the medians calculated for the German federal states and nationwide.
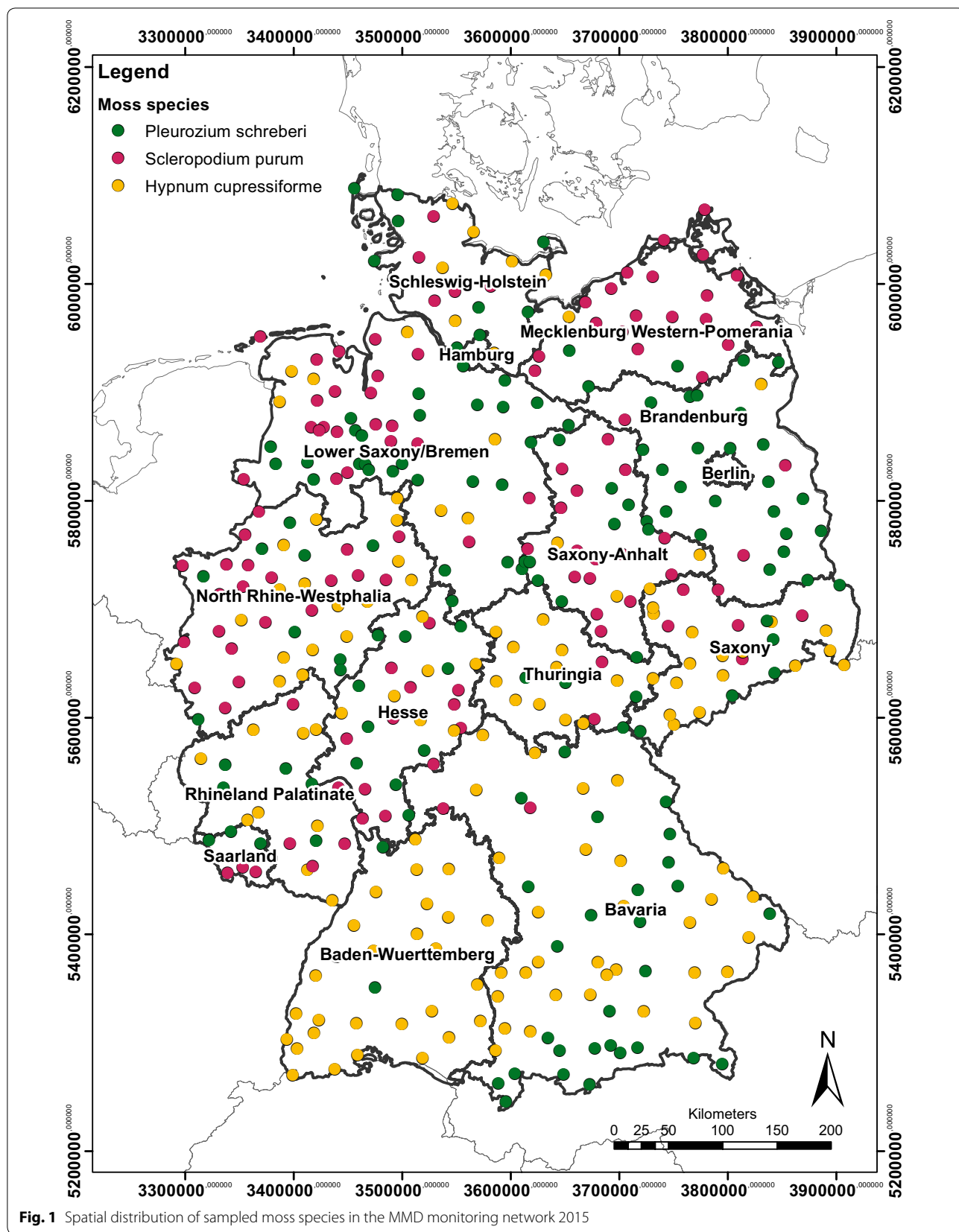
MMD 2015

The methodology and measurement networks of the MMD campaigns 2005 and 2015 are described by Nickel and Schröder [25, 27], Schröder and Nickel [39] and Schröder et al. [40]. The MMD 2015 monitoring network is shown in Fig. 1. The following summary of the multivariate statistical determination of the significance

of the moss species and other predictors for element concentrations in mosses based on the MMD 2015 [40] was detailed by [40]. The aim of this part of the study presented is the multivariate statistical evaluation of the significance of a set of potentially explanatory variables for the estimation of substance concentrations in mosses. The basis was formed by the concentrations of 12 heavy metals and N in the mosses as target variables measured on the 400 standard sample areas 2015 in Germany and an updated or extended set of descriptors compared to the MMD 2005 [30]: 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 descriptors and the target variables, a regression analysis was performed using two different methods: Random Forest Regression (RF, [5] and Multiple Linear Regression (MLR, [34] combined with Commonality Analysis (CA, [29, 48].

Comparison of the Germany-wide and Bavarian moss surveys (2005–2016)

In addition to the investigations presented in the previous sections, an additional aim of this study is to compare the findings of the German Moss Monitoring (MMD) with available data from the additional monitoring carried out in Bavaria with the epiphytic moss *Hypnum cupressiforme* (MMB; [18, 19, 21]. The questions to be investigated are whether the element-specific data distributions of both monitoring programmes of moss samples collected in Bavaria in the same year are significantly the same, whether the variance of the measured values in the MMD is higher than in the MMB due to the heterogeneity of the collected moss species, and whether the spatial patterns and temporal trends of the metal bioaccumulation of the MMD coincide with those of the MMB in the region under consideration.

Since 1982, the MMB has been used to map spatial distributions and temporal developments of metal loads in Bavaria, federal state of Germany [18, 19, 21]. The samples consist exclusively of epiphytic moss of the species *Hypnum cupressiforme* growing on deciduous trees. In one- or 2-year intervals—every 3 years since 2007—moss samples were taken each autumn within a survey network consisting of 298 locations (16 km × 16 km grid), whereby the complete network was not examined in every campaign. For comparisons with the time trends of MMD campaigns, data from the MMB campaigns 2007 ($n = 287$), 2010 ($n = 281$), 2013 ($n = 49$) and 2016 ($n = 46$) were used. The chemical analysis for these samples included 26 elements. Ten of these elements (As, Cd, Cr, Cu, Hg, Ni, Pb, Sb, V and Zn) were also analysed in the MMD 2005 [30] and MMD 2015, with no data available

Fig. 1 Spatial distribution of sampled moss species in the MMD monitoring network 2015

for Sb in MMB 2016. The distances between the locations of the MMD 2015 and the MMB 2016 range between 600 m and 40 km (on average approx. 18 km). Six locations are less than 5 km apart from each other, 4 locations less than 2 km.

The empirical methodology of the MMD 2005 and 2015 follows the guideline of the MME [15] and enables quality-controlled element determinations. Their detailed description and the design of the sampling network can be found in Nickel and Schröder [25, 27], Schröder and Nickel [39], Schröder et al. [40].

In MMD 2015, all analysed samples belong to the moss species *Pleurozium schreberi (Ps)*, *Hypnum cupressiforme (Hc)* and *Scleropodium purum (Sp)* and thus correspond to the priority list of the manual. One-third of the moss samples each can be assigned to one of the three moss species, with *Ps* (37 %) compared to *Hc* (32 %) and *Sp* (31 %) takes a slightly higher proportion of samples collected nationwide. Figure 1 shows the geographical distribution at the 400 locations of the MMD monitoring network in the 2015 campaign.

Despite a roughly equal share of the sample, the three moss species show considerable differences in spatial distribution (Fig. 1). The sample volume of *Ps* shows a clear focus in the North German lowlands and in the heights of Bavaria. In the federal state Berlin/Brandenburg, 90 % of the samples belong to this moss species, in Lower Saxony and Bavaria about 45 % and 40 %, respectively. *Hc accounts for* a particularly high proportion of the sample volume in southern and central Germany; in Baden-Württemberg about 90 %, in Thuringia and Saxony about 60 %, in Rhineland-Palatinate 50 % and in Bavaria and North Rhine-Westphalia 40 %. In contrast, *Sp* dominates the sample volume in Mecklenburg-Western Pomerania (75 %) and Saxony-Anhalt (60 %) and is also represented in North Rhine-Westphalia (45 %) with a high proportion of samples.

For quality control purposes, the moss samples were also checked for correct determination of the moss species. For this purpose, the moss species of a random sample ($n = 39$), was determined. The quality control showed that 97 % of the samples tested were correctly determined. 4 samples (10 %) showed a low and 1 sample (2.5 %) a strong admixture of another moss species. A sample (2.5 %) was determined incorrectly (*Ps* instead of *Sp*).

For the MMB data descriptive-statistical parameters (minimum, maximum, median value, mean value, standard deviation, relative coefficient of variation as well as 20th, 50th, 90th, 98th percentile) were determined. The statistical data distributions of the nine elements mentioned were analysed by the use of box plots by comparing those of the German Moss Monitoring 2015 (MMD

2015, sampling year 2016, sites covering Bavaria only) with those of the MMB 2016.

This was followed by a comparison of percentile and inferential statistical parameters (min., max., 20th percentile, median, 90th Percentile, Mann–Whitney *U*-Test) for MMD 2015/MMB 2016. The Mann–Whitney *U*-Test was used to test whether both samples originate from the same population (null hypothesis) or not (alternative hypothesis), i.e., whether both distributions and thus also the median value are the same or significantly different [34]. The null hypothesis is assumed if the significance value (*p* value) is > 0.05. The hypothesis tested was that the measurement distributions of the *Hc* samples of the MMB did not differ significantly from those of the *Hc*, *Sp* or *Ps* samples of the MMD.

To compare the spatial patterns of heavy metals concentrations in the Bavarian mosses, the point information from the MMB campaign 2016 was examined by use of variogram analysis[1,2] and Moran's I statistics[3] for spatial autocorrelation and, if necessary, generalised spatially by means of Kriging interpolation[4] [40]. The results were then compared with the corresponding geostatistical estimates of the MMD 2015 in Bavaria and the similarity of the spatial patterns quantified by means of correlation analysis (Spearman, Pearson as comparative value). Due to the small number of sites located close to each other (< 5 km), the correlation-analytical comparison based on the point-related measurement data was not necessary.

The element-specific median values from the data of the MMD (1990–2015: five campaigns) and the MMB (2007–2016: four campaigns, Table 1) were compiled

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[1] *Variogram analysis:* Statistical method for checking the spatial autocorrelation of spatially located measured values. This is realised, if pairs of measured values from locations close to each other are more similar than pairs of measured values from locations further apart [17].

[2] *Semi-Variogram:* Diagram for the representation of relationships between spatially located pairs of measured values using distance steps (lags) and the semi-variance as a measure for the similarity of the pairs of measured values, which results from the bisected square of the measured value differences (Johnston et al. 2001). The Range is the maximum distance below which a dependency between distance and semi-variance is recognizable. The nugget effect provides information about distorting factors such as measurement errors or high small-scale variabilities. The semi-variance assigned to the range is called a sill. The higher is the nugget/sill ratio in %, the lower is the spatial autocorrelation. Prerequisite for Kriging interpolations are generally nugget/sill ratios < 75 %.

[3] *Moran's I-Statistics:* Statistical method for checking whether the spatial pattern formed by a group of objects (e.g. moss sampling sites) is randomly distributed or spatially clustered [24]; [51]. Positive Moran I index values indicate a tendency towards cluster formation and negative values indicate a tendency towards dispersion. Error probabilities of $p < 0.05$ mean that the measured values are not randomly distributed, i.e., the spatial autocorrelation found is significant.

[4] *Kriging:* Geostatistical method for the interpolation of point data using the spatial autocorrelation structure modelled by variogram analysis for spatially weighted interpolation of measurement data [23].

Table 1 Overview of the data used for statistical analyses

Survey	Measurand	Elements	Unit	1990	1995	2000	2006	2007	2010	2013	2016	2017
MMD	Conc. in moss	As, Cd, Cr, Cu, Hg, Ni, Pb, V, Zn	mg/kg	O	O	O	O				O	
MMD	Conc. in moss, geostatistical area estimation Germany	As, Cd, Cr, Cu, Hg, Ni, Pb, V, Zn	mg/kg	O	O	O	O				O	
MMB	Conc. in moss	As, Cd, Cr, Cu, Hg, Ni, Pb, V, Zn	mg/kg					O	O	O	O	

MMD German moss monitoring (only sites covering Bavaria), *MMB* Bavarian moss monitoring

in a line diagram for the graphical analysis of the temporal trends of heavy metal accumulation in Bavaria. For the statistical substantiation of the trend statements, based on the hypothesis that the declines of element concentrations in the MMD prove to be just as significant for most heavy metals in the MMB, the median value differences were examined by inference statistics using the combinations of the data collectives MMD 2005/MMD 2015 and MMB 2007/MMB 2016 and tested for significance ($\alpha = 0.05$).

Results and discussion
MMD 1990 and 1995
Comparison Pleurozium schreberi–Scleropodium purum
The number of sample pairs *Ps* and *Sp* compared was 49 in the MMD 1990, 72 (Ni, Pb, V) and 73 (Cd, Cr, Cu, Fe, Ti, Zn) in the MMD 1995. For this species combination, significant correlations were found for all elements considered. The results of the regression analyses revealed the following conspicuous features:

- For Cd, Cu, Fe, Pb, V and Zn, the results of the regression analyses in both moss monitoring programmes are similar.
- The regression analyses of the two moss monitoring campaigns showed slight deviations for Cr and strong deviations for Ni and Ti.
- For all elements compared, there were considerable scatters around the regression line.

In the MMD 1990, *Hylocomium splendens (H.s.)* was also included in the comparative studies. However, since *H.s.* was only sampled at three sites nationwide in the MMD 2000, this species is not regarded in the following.

- For the elements Cd, Cr, Cu, Ni, Hg and Ti, the regression calculations in the MMD 1995 suggested the same behaviour of the moss species considered. For the elements Cd, Cr, Cu, Ni, Hg and Ti, it was not considered meaningful to convert the values from *Sp* according to the regression line to *Ps*, since the deviations are less than 10 %. These deviations were considered negligible in view of the site-specific variations of element concentrations.
- The results of the regression analyses from the MMD 1995 show that *Ps* seems to enrich Pb, V, Sb and As more than *Sp* in particular.
- For Pb and Zn, the values were converted exemplarily and compared cartographically. There were no significant differences nationwide.

Comparison Pleurozium schreberi–Hypnum cupressiforme
The number of compared sample pairs *Ps* and *Hc* was 25 in the MMD 1990 and 24 in the MMD 1995. In general, similar conditions could be found for this species combination as in the comparison *Ps/Sp*:

- For the elements Cd, Cr, Cu, Fe and V the results of the regression analysis are comparable in both moss monitoring campaigns.
- Ni, Pb and Zn showed strikingly large differences in the results of the regression calculations of both moss surveys.
- As in the *Ps/Sp* comparison, all elements compared showed considerable scatter around the regression line.
- Only for Ti (moss monitoring 1995), similar accumulation behaviour between *Ps* and *Hc* could be determined.
- Fe showed on average higher elements concentrations in *Ps*, Cd predominantly higher concentrations in *Hc*.
- Cr, Cu, V, Ni, Zn, Hg, Sb and As (moss monitoring 1995) showed higher concentrations in *Ps* in higher concentration ranges.

Due to the small number of samples used in the regression analyses and the strong scatter around the regression line, it was not considered sensible in the MMD 1995 to convert the elements concentrations from *Hc* to *Ps*.

For the MMD 1990 and MMD 1995, it was examined whether the different moss species enrich the elements differently (species variability) and to what extent these differences between the moss species *Pleurozium schreberi, Scleropodium purum* and *Hypnum cupressiforme* are to be dealt with when analysing and presenting the measurements [14, 41]. The investigations lead to the recommendation 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 % [42]. Moreover, these conversions can only be carried out correctly if sufficient moss species are extracted in parallel at identical locations and the averaged factors are calculated taking into account the scatter of the elements concentrations. In MMD 1995, moss species pairs were available for *Ps* and *Sp* from 72 sites. Furthermore, the 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 [54] points out that the derivation of correction factors must also take into account the different annual biomass formation of the individual moss species.

MMD 1990, 1995, and 2000

The standard and additional element concentrations analysed in the MMD campaigns of 1990, 1995 and 2000 are given in Table 2 and summarised below. The presentation is independent of the federal states and refers to the entire territory of Germany.

Species comparison

The comparison of the standard elements concentrations determined in *Ps, Sp* and *Hc* in the MMD campaigns 1990, 1995 and 2000 shows that:

- *Hc* has the highest medians for As, Cd, Cu, Ni and Pb (1990) and in 1995 and 2000 for all standard elements except Cu and Zn;

- *Sp* shows highest medians in 1990 for Cr, Fe and Zn and 1995 and 2000 for Cu and Zn;
- *Ps* has the lowest medians in 1990, 1995 and 2000 for Cd and Fe, in 1990 and 1995 for As and Hg, in 1990 and 2000 for Zn, in 1990 for Ni, in 1995 for Cr and Ti, and in 2000 for Cu.
- In all three MMD campaigns, *Hc* often shows higher values than *Ps* and *Sp* as well as *Ps* often the lower medians. Furthermore, the tendency towards agreement between the moss species-specific median comparisons from 1995 is noticeable.

Standard elements in Ps, Sp, Hc

If one compares the species-unspecific medians of the standard elements with the medians determined for *Ps, Sp* and *Hc,* it can be stated that:

- *Hc* has higher medians for As, Cd, chromium, Ni and Pb (1990, 1995 and 2000), 1995 and 2000 for V, Hg and Sb, 1990 and 2000 for Cu;

Table 2 Ratios of element accumulations between *Ps, Sp* and *Hc*

	MMD 1990			MMD 1995			MMD 2000			Averages		
	Ps/Sp	Ps/Hc	Sp/Hc	Ps/Sp	Ps/Hc	Sp/Hc	Ps/Sp	Ps/Hc	Sp/Hc	Ps/Sp	Ps/Hc	Sp/Hc
Standard elements												
As	0.89	0.76	0.85	0.87	0.65	0.74	1.07	0.65	0.61	0.94	0.69	0.73
Cd	0.81	0.70	0.86	0.88	0.81	0.93	0.86	0.75	0.86	0.85	0.75	0.88
Cr	0.98	1.14	1.17	0.95	0.75	0.79	1.01	0.79	0.78	0.98	0.90	0.91
Cu	1.03	0.93	0.90	0.84	1.05	1.25	0.90	0.91	1.01	0.92	0.96	1.05
Fe	0.75	1.07	1.43	0.87	0.71	0.82	0.96	0.68	0.71	0.86	0.82	0.98
Ni	0.91	0.75	0.82	1.01	0.61	0.60	1.02	0.55	0.54	0.98	0.63	0.65
Pb	1.15	0.89	0.78	1.19	0.68	0.57	1.21	0.65	0.53	1.19	0.74	0.63
Ti	1.00	1.33	1.33	0.86	0.72	0.84	1.05	0.65	0.62	0.97	0.90	0.93
V	1.04	1.04	1.00	1.11	0.74	0.67	1.12	0.69	0.62	1.09	0.82	0.76
Zn	0.80	0.97	1.22	0.75	1.10	1.47	0.77	0.98	1.28	0.77	1.02	1.32
Hg				0.89	0.80	0.90	0.95	0.67	0.70	0.92	0.73	0.80
Sb				1.30	0.99	0.76	1.55	1.00	0.65	1.42	0.99	0.70
Additional elements												
Al				0.89	0.65	0.72	1.06	0.65	0.61	0.98	0.65	0.67
Ba				0.85	0.52	0.61	0.75	0.42	0.56	0.80	0.47	0.58
Ca				0.77	0.66	0.85	0.79	0.62	0.78	0.78	0.64	0.82
K				0.71	1.37	1.92	0.72	1.16	1.61	0.71	1.26	1.77
Mg				0.75	0.96	1.28	0.76	0.82	1.08	0.75	0.89	1.18
Mn				0.98	1.27	1.30	1.06	1.21	1.14	1.02	1.24	1.22
Well				0.56	1.58	2.81	0.47	1.29	2.73	0.52	1.43	2.77
Sr				0.72	0.63	0.88	0.76	0.61	0.80	0.74	0.62	0.84

This table shows the ratios of the nationwide medians of *Ps, Sp* and *Hc* from all three monitoring campaigns. The quotients marked in red are not based on any significant differences between the moss species at the 5 % level. The Mann–Whitney *U*-test was used for significance testing

- *Sp* shows higher medians in 1990, 1995 and 2000 for Cd and Zn and in 1990 and 1995 for Cr, Fe and Ti shows higher medians; and
- *Ps* has lower medians except for Pb (1990) and Sb (1995 and 2000).

The comparison of the moss-species-unspecific medians with the species-specific analysis shows large similarities with regard to the development of the elements concentrations since 1990. Apart from Cd in *Hc* and *Sp*, Cu in *Sp*, Ti in Hc and Hg in *Hc,* identical decline tendencies can be identified.

Additional elements

Species comparison   The comparison of the additional element concentrations in *Ps, Sp* and *Hc* determined in the 1995 and 2000 campaigns shows the following conspicuous features:

- In 1995 and 2000 Al, Ba, Ca and Sr show the highest, K, Mn and Na the lowest medians in *Hc*.
- In 1995 and 2000 K, Mg and Na have the highest medians in *Sp*.
- In 1995 and 2000, Ba, Ca, Mg and Sr have the lowest medians in *Ps*.
- Mn shows the highest median in *Sp in* 1995. 2000 in *Ps.*

As already observed with the standard elements, there are striking similarities between the results of the MMD 1995 and 2000 with regard to species comparison. Only Mn and Al show differences.

Additional elements in Ps, Sp, Hc   Comparing the species-unspecific medians of the additional elements with those medians determined for *Ps, Sp,* and *Hc* reveals:

- *Hc* 1995 and 2000 for Al, Ba, Ca and Sr has higher medians;
- *Sp* 1995 and 2000 for Ca, K, Mg, Mn, Na and Sr shows higher medians; and
- *Ps* 1995 and 2000, except for Mn, has consistently lower medians for the additional elements.

Furthermore, it can be stated that both the species-unspecific median comparison and the species-specific median comparisons of 1995 and 2000 show decreasing tendencies in all cases.

Schröder et al. [37, 38] investigated moss species-specific element accumulation based on extensive data from the MMD campaigns 1990, 1995 and 2000 for the moss species *Pleurozium schreberi*, *Scleropodium purum* and *Hypnum cupressiforme* based on the median indicating the centrality of the statistical measurement distribution. A comparison of the moss species-specific nationwide medians showed that As, Cd, Ni, Pb, Hg, Al, Ba, and Ca in particular accumulate most strongly in *Hypnum cupressiforme*. However, it should be noted that the samples compared are never spatially identical. Finally, it is pointed out for the interpretation of the data that samples of the same moss species taken at the same site may have different elements concentrations (*site variability*) and that the moss species taken are comparable with regard to their adsorption and accumulation properties (*moss species variability*).

The significance of the results from the accumulation monitoring with mosses presented above and below should be evaluated against the background of the statistical and spatial uncertainties.

Spatial restrictions   To derive statistically verified accumulation trends from *Ps, Sp* and *Hc,* 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 are compared, since larger samples can be compared, making a median comparison statistically more plausible.

Statistical limitations

Due to different site conditions, neither an even nor a constant distribution of *Ps, Sp* and *Hc* across the federal territory over the years was given in the MMD campaigns. Rather, in some countries, one of the selected moss species often dominates; while in other countries, it was not sampled at all (e.g. in 2000 in Baden-Württemberg almost exclusively *Hc* was sampled). The share of *Hc* 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. The textual description of the median comparisons refers to the spatial and statistical uncertainties described in particularly problematic cases.

Results MMD 2015

RF and MLR models explaining more than 20 % of the statistical variance of measurements could be calculated for Cd, Cu, Hg, Ni, Pb, Zn and N. The following predictors had the highest relative significance for estimating element concentrations in the mosses: The predictor with the strongest variable significance was the sampled *moss species* (Cd, Cu, Ni, Pb, Zn and N). The atmospheric deposition calculated with the chemical transport models LOTOS-EUROS (LE; [22, 35, 36], EMEP/MSC-E [49] and

EMEP/MSC-W [43] (year 2015, mean of the years 2013–2015), the MMD 2015 shows a lower predictive force for the respective element concentrations in the mosses than in previous campaigns. For N (LE; 2013–2015) and Hg (EMEP; 2013–2015) the calculated deposition in moss monitoring has a mean variable significance, for Cd (EMEP; 2013–2015) a minor significance and for Pb no significance as a predictor in the statistical models. The mean precipitation sum 2013–2015 can be determined as a significant influencing factor for Cd, Pb and Zn, the 90-day average before sampling for Hg and Pb and subordinate also for Cd and Cu, while the weather (3-day average before sampling) cannot be determined for any element, nor for the local main wind direction. Among the topographic parameters, the orographic height (Cu, Hg, and Ni) and the slope inclination (Cd) are the strongest predictors and the humus form (Cu). In contrast to the MMD 2005, the frequency of moss occurrence does not play a role as a predictor for the elements investigated here. Of the 14 vegetation structure measures studied, the mean distance to adjacent tree populations forms the comparatively strongest predictor (Cd, Cu, Hg, Zn and N), followed by the population height (Cd, Hg, Pb and N), the leaf area index (Cd and N; subordinated for Zn) and finally the degree of coverage of the tree layer (Ni; subordinated for Cd and Hg). In many cases, the spatial density of various land use classes around the moss sampling areas has a high explanatory power for the element concentrations in the mosses. In the case of forests and woods, it is mainly the area portions within radii of 100–300 km that are significant predictors for Cu, Hg, Ni, and N. In the case of urban areas, there are element-specific radii between 25 and 300 km (Cd, Cu, Ni, Pb, and N) and in the case of agricultural areas, there are mostly radii between 50 and 300 km. The population density within the 50 and 100 km radius around the sampling point is a variable with a high explanatory power for all elements except Hg and N. Population density within radius of 5 km is less important. The higher the population density is within radii $\geq$ 50 km, the higher the average concentrations of Cd, Cu, Ni, Pb, and Z in the mosses. Of the numerous potential local emission sources recorded in the MMD 2015, only the distance to federal highways (N; traffic emissions) shows a high variable significance in the RF regression. On the basis of the MMD 2015 data, the distance to the sea is a relevant factor for Ni alone.

Overall, it should be noted that the following predictors stand out in their significance in the set of variables expanded compared to the MMD 2005: Sampled moss species, land use density (percentage of certain land uses) in extended radii between 150 and 300 km, population density in radii between 50 and 100 km, wind erosion hazard of arable land within a radius of 1 km, 3-year and 90-day mean of precipitation total. As in the data of the MMD 2005 [30], the distances to potential emission sources, the background values of the heavy metals concentrations in topsoils, the distance to the sea as well as the local main wind direction will strongly recede in their importance as predictors in 2015. For cross-national analyses with MME 2015 data [12], the inclusion of the mean temperature at the time of sampling [8] as well as the population density/land proportion of different land use classes up to 300 km around the moss sampling area in the predictor set is recommended.
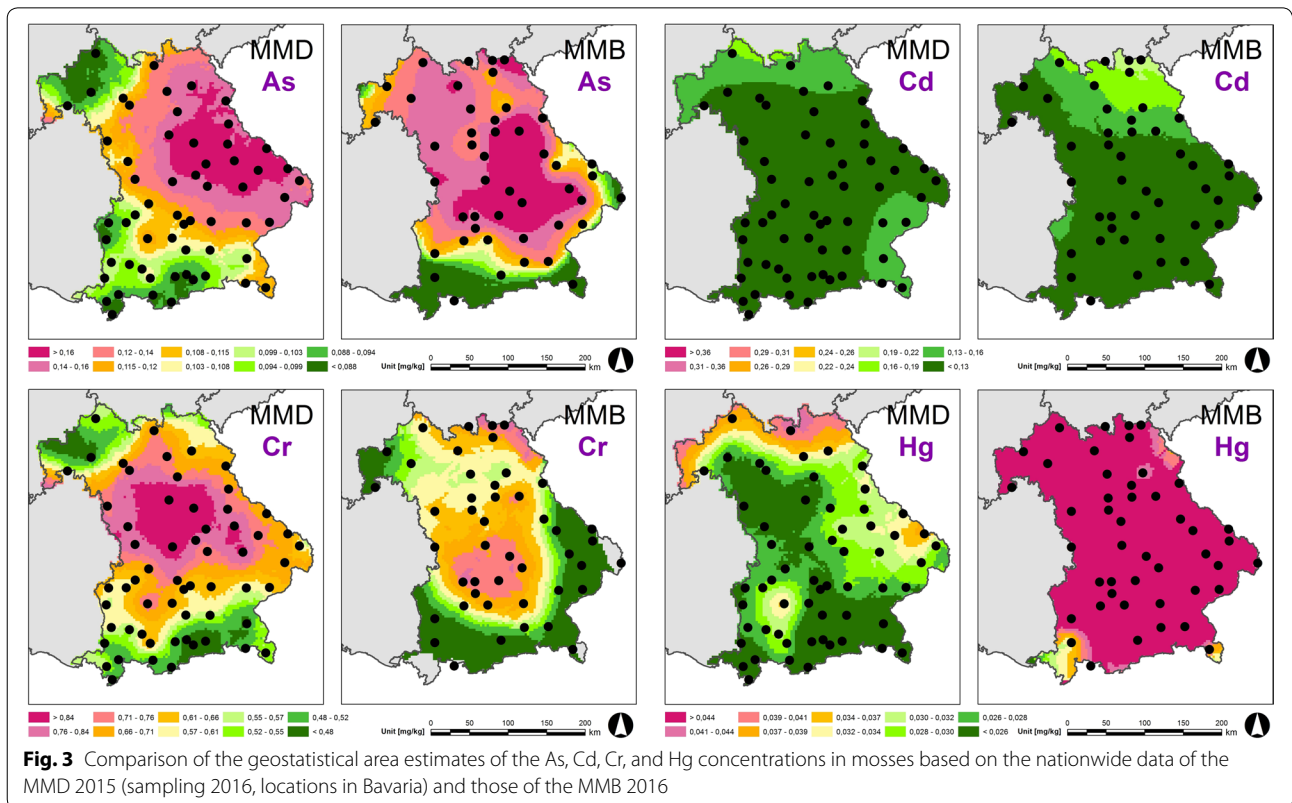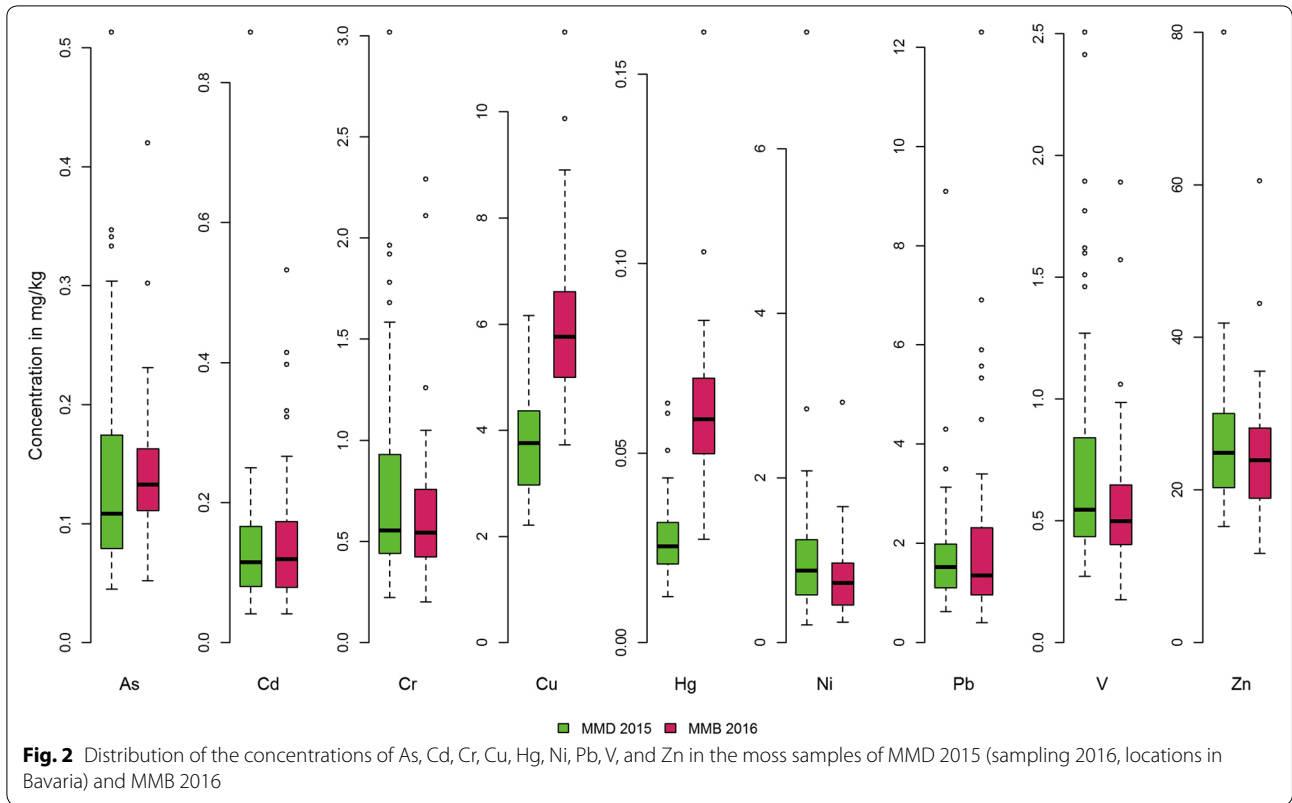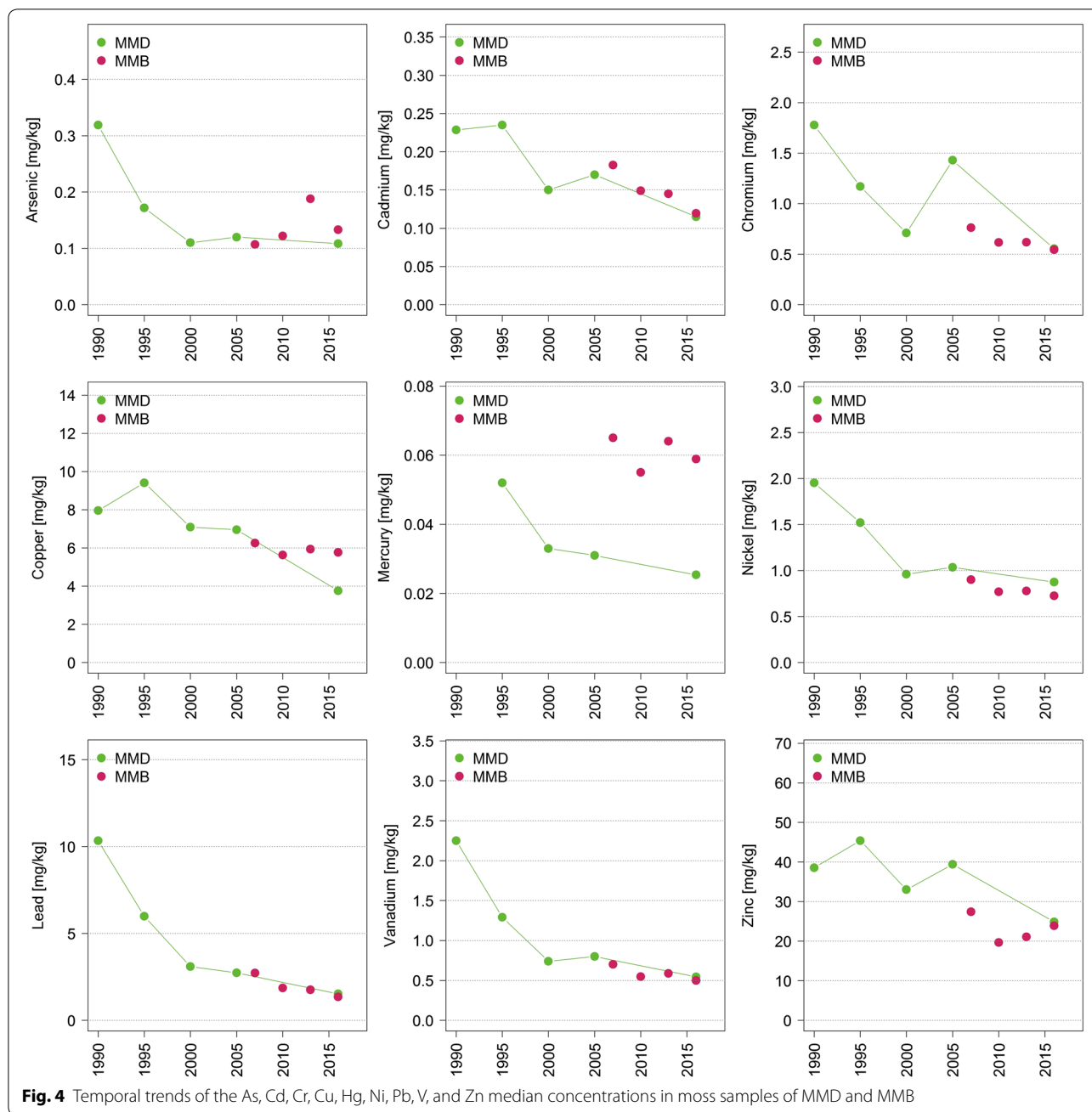
Results MMB and MMD
As
There are no significant differences between the median values of the arsenic content in the moss samples of the MMD 2015 of all sites in Bavaria (0.11 g/kg) and the MMB 2016 (0.13 g/kg) (Fig. 2). With a relative coefficient of variation of 66 %, the dispersion of As concentration in the MMD 2015 is higher than in the MMB 2016 with 44 %. The variogram analysis of the spatial concentration values of MMB 2016 yields an exponential model variogram with a strong, significant spatial autocorrelation within a range of 107 km and a nugget/sill ratio of 0.11. The Morans I statistics indicate a significant spatial autocorrelation ($p < 0.05$). The spatial pattern of the As concentration in *Hc* of the MMB 2016, calculated by Kriging interpolation, graphically matches that of the MMD 2015 (visual estimation) (Fig. 3). The corresponding correlation coefficient as a measure for the similarity of the spatial patterns is $r_s = 0.51$ or $r_p = 0.53$, which is equivalent to a medium–strong match. Compared to the MMD 2015, higher As concentrations can be found in the geostatistical area estimates of the MMB 2016, especially in North-West Bavaria.

The temporal changes of the As concentrations in the moss show an uneven picture: While the As medians of the MMB show no significant differences between the campaigns MMD 2005 and MMD 2015, the MMB shows a significant increase of 24 % between MMB 2007 and MMB 2016, and about 100 % between 2007 and 2013 (Fig. 4).

Cd
The statistical distributions of the MMD 2015 data (median: 0.12 g/kg) and the MMB 2016 (median: 0.12 g/kg) show no significant differences in the Cd concentrations in mosses. A significantly higher 90th percentile of the MMB 2016 (0.30 g/kg) compared to the MMD 2015 (0.19 mg/kg) is striking, i.e. the upper tenth of the sample of the MMB is higher than the respective values from the MMD. The relative coefficient of variation is higher for the MMD 2015 (82 %) than for the MMB 2016 (71 %).

Fig. 2 Distribution of the concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, V, and Zn in the moss samples of MMD 2015 (sampling 2016, locations in Bavaria) and MMB 2016

Fig. 3 Comparison of the geostatistical area estimates of the As, Cd, Cr, and Hg concentrations in mosses based on the nationwide data of the MMD 2015 (sampling 2016, locations in Bavaria) and those of the MMB 2016

Fig. 4 Temporal trends of the As, Cd, Cr, Cu, Hg, Ni, Pb, V, and Zn median concentrations in moss samples of MMD and MMB

The Cd concentration in the samples of MMB 2016 show a weak but significant spatial autocorrelation (range: 300 km; nugget/sill ratio: 0.63) with a p value for the Morans I coefficient of < 0.05. The best possible adaptation to the empirical semi-variogram is reached by a spherical model variogram. The corresponding geostatistical surface estimates of the MMB 2016 show increased Cd concentration compared to those of the MMD 2015, especially in North-West Bavaria (Fig. 3). The correlation between the two geostatistical area estimates is $r_s = 0.31$ and $r_p = 0.50$,

i.e. both spatial patterns correspond low to medium. The inference-statistical analysis of the temporal changes points to significant decreases of the Cd medians by 35 % between 2005 and 2015 (MMD) and significant decreases by 32 % between 2007 and 2016 (MMB).

Cr

The median values of the Cr concentrations in the moss samples of the MMD 2015 (0.55 mg/kg) and the MMB 2016 (0.54 mg/kg) show no significant differences. The

relative coefficient of variation is 6 % higher for the MMD 2015 (70 %) than for the MMB (64 %). The exponential model variogram adapted to the experimental semi-variogram indicates a very weak spatial autocorrelation of the measured data (range 257 km; [40]: Annex A7.3). Morans I statistics ($p = 0.21$) does not indicate a significant spatial autocorrelation. Despite the nugget/sill ratio of 0.67 is below the orientation value of 0.75, the Cr concentrations in mosses were generalised spatially. The calculated maps for the MMB 2016 show lower Cr concentration in the mosses sampled in large parts of Bavaria and higher Cr concentration in the north-east of Bavaria compared to the geostatistical estimates of the MMD 2015 (Fig. 3). The correlations between the two geostatistical estimates are $r_s = 0.50$ and $r_p = 0.45$ [40]: Annex A7.5), indicating a medium spatial correspondence of the spatial distributions compared. The percentage changes in the Cr medians show significant decreases of 61 % between MMD 2005 and MMD 2015 and significant decreases of 29 % between MMB 2007 and MMB 2016.

Cu
The Cu median in the moss samples of MMB 2016 (5.77 mg/kg) is significantly higher compared to MMD 2015 (3.76 mg/kg). The coefficients of variation are almost identical (MMD 2015: 24 %; MMB 2016: 27 %). Both variogram analysis and Moran's I statistics show no spatial autocorrelation for the Cu concentrations measured at the 46 sites in MMB 2016. Between sampling in MMB 2007 the Cu content has decreased significantly by 8 %, between MMD 2005 and MMD 2015 it is 46 % ($p < 0.05$). This less pronounced decline in the MMB pattern is also reflected in the MMB 2010 and MMB 2013 findings (Fig. 4).

Hg
At 0.059 mg/kg, the Hg median of the MMB 2016 is more than twice as high as in the same sampling year of the MMD 2015 (0.025 mg/kg). A similar relation results from the comparison of the campaigns MMB 2007 (0.065 mg/kg) and MMD 2005 (0.031 mg/kg). The relative coefficients of variation in MMD 2015 (35 %) and MMB 2016 (36 %) are almost identical. The exponential model variogram adapted to the experimental semi-variogram by the least squares method shows a clear spatial autocorrelation with a nugget/sill ratio of 0.30 within a range of 137 km. However, the significance of the spatial autocorrelation is not confirmed by the Morans I statistics. Due to the sufficient nugget/sill ratio, the Hg concentration in the mosses was interpolated using universal kriging (1st order). Compared to the MMD 2015 area estimate, the map calculated for the MMB 2016 shows significantly higher values in almost all parts of Bavaria, mostly above

0.044 mg/kg (Fig. 3). With correlation coefficients of $r_s = 0.14$ and $r_p = 0.07$) the similarities of the spatial patterns prove to be very weak. The changes in Hg accumulation over time between MMB 2007 and MMB 2016 are characterised by significant decreases of 9 % and between MMD 2005 and MMD 2015 by significant decreases of 18 %. These declining trends in the Hg concentrations in the mosses, which can be observed in both monitoring programmes, are, however, apparent at very different accumulation levels (Fig. 4).

Ni
The Ni concentrations in the moss samples of the MMD 2015 (0.87 mg/kg) do not differ significantly from those of the MMB 2016 (0.73 mg/kg). The relative coefficients of variation differ by 32 % (MMB 2016: 60 %; MMD 2015: 92 %). The measured values of the MMB 2016 are not spatially auto-correlated, which is why a spatial generalisation was not carried out. Between the sampling year 2006 of the MMD 2005 and the sampling year 2016 of the MMD 2015, there is a significant decrease of 16 % in the Ni content in Bavaria. By way of comparison, MMB fell significantly by 20 % between 2007 and 2016. The good agreement of these trend statements is reflected, as it were, in Fig. 4.

Pb
There are no statistically significant differences between the annual medians of the Pb concentration in the mosses sampled within the MMD 2015 (1.5 mg/kg) and the MMB 2016 (1.4 mg/kg) [39]: Annex A7.2). The measured values of the MMD 2015 [39]: Appendix A5.9) scatter with a relative coefficient of variation of 68 % weaker than those of the MMB 2016 (101 %). The MMB 2016 data do not show any spatial autocorrelation. The temporal trends of the Pb concentration in the moss samples of both monitoring programmes are in good agreement (Fig. 4). The median differences result in significant decreases in Pb concentrations of 44 % (MMD 2005 to MMD 2015) and 51 % (MMB 2007 to MMB 2016).

V
The V concentrations in the moss samples of the MMD 2015 (0.55 mg/kg) and MMB 2016 (0.50 mg/kg) are significantly at the same level. The 90th percentile of the MMD 2015 (2.32 mg/kg) is significantly higher compared to the MMB 2016 (1.60 mg/kg). The dispersion of values from the MMD is 13 % higher than for the MMB (relative coefficient of variation (MMB 2016: 55 %; MMD 2015: 68 %). Variogram analysis and Moran's I statistics on MMB 2016 provide no evidence of spatial autocorrelation, which is why geostatistical mapping was not carried out. When comparing the line diagrams in Fig. 4,

the patterns of the temporal changes of the V medians between 2005 and 2016 agree well. Significant decreases of 32 % (MMD 2005–MMD 2015) and 29 % (MMB 2007–MMB 2016) are characteristic.

Zn

The medians of the Zn concentrations of MMD 20015 (24.9 mg/kg) and MMB 2016 (23.9 mg/kg) show no significant differences. The characteristic values of the scatter are almost the same. The Zn concentration measured in MMB 2016 is not spatially auto-correlated. Between the campaigns of the MMD 2005 and MMD 2015, there are significant negative median differences of − 37 % and between the MMB 2007 and MMB 2016 of − 13 %. Figure 4 illustrates a typical fluctuation range in the time series of both biomonitoring programmes and a corridor of about ± 5 mg/kg emerging from past fluctuations. The changes in the Zn year medians since 1990 and 2007, respectively, were within this corridor.

The analyses of the data from the MMD and the MMB open up the possibility of identifying and quantifying differences and thus uncertainties in the empirical findings or data derived from them. As in earlier studies [26], the spatial generalisations were able to contribute to the merging and integrative evaluation of the findings from different monitoring programmes.

The median values of heavy metal accumulation in moss samples collected at 60 MMD 2015 sites in Bavaria (sampling year 2016) and the 46 MMB 2016 sites show no significant median differences for 7 of the 9 elements studied (As, Cd, Cr, Ni, Pb, V and Zn). Significant means that this statement can be transferred to the population with a probability of error of less than 5 %.

This finding is remarkable in that, unlike the MMB, the MMD includes two further moss species *Ps* and *Sp* in addition to *Hc,* and the descriptive-statistical characteristic values differ significantly from moss species to moss species. In addition, some of MMB's sampling sites do not meet the essential criteria of the MMD experimental protocol [15] for background load monitoring (300 m minimum distance between sampling sites and major state and federal roads or motorways, settlement areas and industrial facilities; 100 m minimum distance to individual houses and smaller roads) [19]. This means that although not all MMB sites are sufficiently distant from potential local emission sources, as opposed to the MMD, the measured value distributions in the data collectives of both biomonitoring programmes are significantly the same in 7 out of 9 cases.

The hypothesis that the variance of bioaccumulation due to the use of different moss species in MMD is fundamentally higher than when using only one moss species (here: *Hypnum cupressiforme*) seems to be indicated

in 4 of the 9 investigated elements (As, Cd, Ni, V). With Pb, the variance in the MMD is even significantly higher than in the MMB. Nor can the large difference between the Hg values of the two monitoring programmes be explained by the fact that different moss species were collected in the MMD, because the MMD 2015 also provides significantly lower median values for P_s and S_p (median $H_c = 0.0281$ mg/kg; median $P_s = 0.0238$ mg/kg; median $S_p = 0.0231$ mg/kg) than for H_c in the MMB 2016 (media$n = 0.0589$ mg/kg). Rather, the deviations could be due to different analytical methods (MMD 2016: ISO 2005; MMB 2016: Direct analyzer according to EPA method 7473 [19].

With regard to the temporal trends of bioaccumulation since 2005, the moss data from both monitoring programmes for 4 of the 9 heavy metals (Cd, Cr, Pb and V) investigated show significant decreases of more than 20 %. For Cd, Ni, Pb and V, the time trends of the MMD since 1990 match those of the MMB well. This also applies to a limited extent to As and Cr, provided that the campaign year 2010 for As and the campaign year 2005 for Cr are excluded from consideration as exceptional years. In the case of Cu and Zn, larger fluctuations in the time series for bioaccumulation are discernible in comparison with the other metals. Within this fluctuation corridor, however, the Cu and Zn trends of both monitoring programmes are well in line.

The accumulation data of MMB 2016 showed spatial autocorrelations in 4 of the 9 investigated HM (As, Cd, Cr and Hg). The comparison of the corresponding geostatistical area estimates with those of the MMD2015 showed good similarities of the spatial patterns with correlation coefficients of $0 \geq 0.5$ for As, Cd and Cr. Hg showed very clear differences between the two spatial patterns. The lack of spatial autocorrelation among the other five HM in the MMB suggests that the number of samples is too small ($n = 46$) for geostatistical surface estimation. For future measurement network planning in the MMB, a stronger consideration of geostatistical validity in site selection is, therefore, recommended.

Conclusions

The requirement of the [15] regarding a calibration of element accumulation in mosses when using other species than the recommended *Ps* or *Hylocomium splendens* (outside Germany) currently cannot be fully met. Nevertheless, it remains necessary to determine existing uncertainties in the bioindication of atmospheric deposition by comparing the different moss species in order to be able to take these into account in the interpretation of the results. The fact that the sampled moss species is statistically significantly associated with the element concentrations in the mosses was indicated by the multivariate

statistical analyses at least for Cd, Cu, Ni, Pb, Zn, and N outlined here [39]. The species comparison in the preliminary work by Schröder et al. [37, 38] already showed that *Hc* in Germany in all three campaigns examined in 1990, 1995 and 2000 mostly had higher heavy metals concentrations in comparison to *Ps* and *Sp,* whereby measured value distributions from different spatial samples were used. Relevant studies on the 1990 and 1995 campaigns [14, 41] already suggested the recommendation not to use correction and conversion factors. Leblond and Meyer [20] arrived at similar conclusions on the basis of moss species collected at identical sites in France in 2006 (15 sites), 2011 (20 sites) and 2016 (32 sites). The reasons given for this were insufficient correlations between the various moss species and the fact that no significant influences could be detected in comparisons at the federal state level (medians) [14, 41]. The latter is confirmed by the comparisons made in this study between the MMD in Bavaria and the MMB. For example, the heavy metal concentrations in the moss samples from 60 sites of the MMD 2015 in Bavaria (sampling year 2016) and 46 sites of the MMB 2016 at seven of the nine investigated elements (As, Cd, Cr, Ni, Pb, V and Zn) show no significant differences in their respective median values. This finding is remarkable in that, in contrast to the MMB, the MMD, in addition to *Hypnum cupressiforme,* includes two other moss species *Pleurozium schreberi* and *Scleropodium purum* and, in addition, a large proportion of the MMB's sampling sites do not fulfil the MMD's essential criteria for monitoring background pollution (300 m minimum distance between sampling points and larger state and federal roads or motorways, settlement areas and industrial plants; 100-m minimum distance from individual houses and smaller roads). Even if the natural diversity of the moss species recommended by the ICP Vegetation [15] in most participating States does not allow to restrict the homogeneity of the sampled species to only one species future MMD or MME campaigns should ensure that the same species as in the previous campaign is always collected at the individual sites and that the geostatistical validity of the measured values, i.e. their spatial autocorrelation through an appropriately dense measurement network.

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: element dependent up to 20 %) and different adsorption, accumulation and leaching properties of mosses (moss species variability) in the same range. To verify/falsify moss species-specific accumulation of atmospheric deposition, different moss species should be taken in parallel at the same site, what is not possible across Europe and Germany without a remarkable loss of spatial density, or analysed in laboratory studies which, so far, are very rare. Therefore, we recommend until further notice not to use conversion/correction factors.

Abbreviations
Al: aluminium; As: arsenic; Ba: barium; CA: commonality analysis; Ca: calcium; Cd: cadmium; Cr: chromium; Cu: copper; EMEP: European Monitoring and Evaluation Programme; Fe: iron; Hc: *Hypnum cupressiforme*; Hg: mercury; HM: heavy metals; ICP: International Cooperative Programme; ISO: International Organization for Standardization; K: potassium; LE: LOTOS-EUROS; Mg: magnesium; MLR: multiple linear regression; MMB: Bavarian Moss Monitoring; MMD: German Moss Monitoring; MME: European Moss Monitoring; Mn: manganese; MSC-E: meteorological synthesising center-east; MSC-W: meteorological synthesising center-west; n: sample size; Ni: nickel; p: level of significance; Pb: lead; Ps: *Pleurozium schreberi*; RF: random forest; r_p: correlation coefficient (Pearson); r_s: correlation coefficient (Spearman); Sb: antimone; Sp: *Scleropodium purum*; Sr: strontium; Ti: titanium; V: vanadium; Zn: zinc.

Authors' contributions
WS headed the computations executed by SN. WS wrote the article. Both authors read and approved the final manuscript.

Availability of data and materials
The datasets generated and/or analysed during the current study are not publicly available due to copyright but are available from the corresponding author on reasonable request.

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Competing interests
The authors declare that they have no competing interests

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