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European Heavy Metals in Mosses Survey 1990 – 2005: identification of factors influencing Cd, Hg and Pb concentrations in mosses by means of bi- and multivariate statistics

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Abstract

The aim of this study was to identify the factors influencing Cd, Hg and Pb concentrations in mosses sampled within the framework of the European Heavy Metals in Mosses Surveys 1990 - 2005. The analyses encompassed data from 4661 (1990), 7301 (1995), 6764 (2000) and 5600 (2005) sampling sites. As exemplary case studies revealed that other factors besides atmospheric deposition of metals influence the element concentrations in mosses, the moss datasets of the above mentioned surveys were analysed by means of bi- and multivariate statistics in order to identify factors influencing metal bioaccumulation. In the analyses we used the metadata recorded during the sampling as well as additional geodata e.g. on depositions, emissions and land use. Bivariate Spearman correlation analyses showed the highest correlations between Cd and Pb concentrations in mosses and EMEP modelled total deposition data ($0.62 \leq r_s \leq 0.73$). For Hg the correlations with all the tested factors were considerably lower (e.g. total deposition $r_s \leq 0.24$). Multivariate decision tree analyses by means of Classification and Regression Trees (CART) identified the total deposition as the statistically most significant factor for the Cd and Pb concentrations in the mosses in all four monitoring campaigns. For Hg, the most significant factor

in 1990 as identified by CART was the distance to the nearest Hg source recorded in the European Pollutant Emission Register, in 1995 and 2000 it was the analytical method, and in 2005 CART identified the sampled moss species. The strong correlations between the Cd and Pb concentrations in the mosses and the total deposition can be used to calculate deposition maps with a regression kriging approach on the basis of surface maps on the element concentrations in the mosses.

Introduction

The European moss surveys are based on the basic research conducted by Rühling and Tyler (1968, 1969, 1970), which showed that mosses accumulate heavy metals over several years. Carpet forming, ectohydric mosses obtain most trace elements and nutrients directly from the atmosphere (wet and dry deposition) with little uptake from the substrate and therefore are particularly suitable for monitoring of airborne pollutants. Monitoring the metal concentration of mosses provides a surrogate, time-integrated measure of element deposition from the atmosphere to terrestrial systems. As moss biomonitoring studies are comparably cheap, a higher sampling density can be achieved than with conventional deposition measurements. Since 1990, mosses are used as biomonitors of atmospheric heavy metal deposition at the European scale in a project currently coordinated by the UNECE[1] ICP Vegetation[2] (Harmens et al. 2008a). Four moss surveys have been performed in at least 21 European countries every five years (Harmens et al. 2008a). The aim of these studies is to map spatial and temporal patterns of atmospheric metal accumulation in terrestrial ecosystems by means of ectohydric mosses. In the 2005 European moss survey the mosses have also been applied as biomonitors of atmospheric nitrogen (N) deposition for the first time (Harmens et al. 2008b).

Although mosses proved to be suitable as biomonitors of atmospheric heavy metal deposition at various scales, several studies revealed that element concentrations in mosses can be confounded by factors such as moss species, canopy drip, precipitation, altitude, windblown dust and sea-spray (e.g. Zechmeister et al. 2003). Hence, in Germany the available measurement data and sampling site-describing metadata from the four surveys 1990, 1995, 2000 and 2005 were investigated statistically. Complementary methods were applied to test the hypothesis, if other factors besides the atmospheric deposition affect the spatial patterns of metal and nitrogen accumulation in mosses. The studies were performed with bivariate correlation and contingency analyses (Pesch and Schröder 2006a) and with decision tree models (Kleppin et al. 2008, Pesch and Schröder 2006b, Pesch et al. 2007, Schröder et al. 2008), but did not include data on atmospheric depositions as a possible influence factor. From these studies it was concluded that mainly the moss species and variables associated with canopy drip, elevation, precipitation and the sea-salt-effect seem to influence the spatial variation of the metal concentrations in mosses. These factors proved to be correlated with the metal bioaccumulation as strong as factors related to the degree of urbanisation and pollution around the sampling sites.

[1] United Nations Economic Commission for Europe
[2] International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops

In a recent analysis of the 2005 moss data it could be shown that Cd and Pb concentrations in mosses, in contrast to Hg concentrations, were primarily determined by modelled atmospheric deposition of these metals across Europe (Schröder et al. submitted). The aim of the current study was to validate these findings for previous European moss surveys (1990, 1995, 2000). Bi- and multivariate statistical methods were applied to the moss data and an extensive set of variables assumed to influence metal accumulation in mosses. In the analysis, Cd, Hg and Pb concentrations in mosses were related to point and surface data on, amongst others, EMEP (European Monitoring and Evaluation Programme) modelled emissions and depositions, land use, altitude and the metadata recorded during sampling and determination of heavy metal concentrations in mosses.

Materials and methods

Moss data

In this study moss samples collected across Europe from 4661 sites in 1990/1 (Rühling 1994), 7301 sites in 1995/6 (Rühling and Steinnes 1998), 6764 sites in 2000/1 (Buse et al. 2003) and 5600 sites in 2005/6 (Harmens et al. 2008a) were included in the analysis. Throughout the paper we refer to the years of moss survey as 1990, 1995, 2000 and 2005 respectively. The moss sampling procedure was according to the guidelines described in the monitoring protocol (e.g. ICP Vegetation 2005). Pleurozium schreberi, Hylocomium splendens, Hypnum cupressiforme and Pseudoscleropodium purum were the most frequently sampled moss species. Only the last three years' growth of moss material was used for the determination of heavy metal concentrations. Moss tissue was dried at 40° C (room temperature for Hg) and either dissolved in concentrated nitric acid (with or without hydrogen peroxide or perchloric acid) or not dissolved before analysis (e.g. when neutron activation analysis was used). Acid digestion of samples was performed on a hotplate or in a microwave oven using a range of temperatures. The metal concentrations were determined by use of atomic absorption spectrometry, inductively coupled plasma spectrometry (both ICP optical emission spectrometry and ICP mass spectrometry), fluorescence spectrometry, neutron activation analysis and advanced Hg analysis[3]. All element concentrations (including Hg) were expressed as mg kg^{-1} dry weight at 40° C. In 1995 and 2005, a quality control exercise to assess the analytical performance of the participating laboratories was conducted using the moss reference materials M2 and M3 (Steinnes et al. 1997; Harmens et al. submitted). Some laboratories used additional certified reference material for quality assurance. For the determination of the elemental concentrations in the reference materials the laboratories followed the same analytical procedure as used for the analyses of the moss samples.

Site-describing and regional data

Site-describing data recorded during moss sampling are very sparse for all four surveys and did also not include enough information on relevant factors potentially influencing the heavy metal concentration in the mosses. Therefore,

[3] These advanced techniques include instrumental methods like AMA 245, CV-AAS and PS200 Mercury-Analyser.

additional information from surface maps and point datasets was intersected with the moss sampling sites. To account for the influence of precipitation on the element concentrations in the mosses, long-term monthly means (1961- 1990) from the Global Climate Dataset (CL 2.0), provided by the Climate Research Unit of the School of Environmental Sciences, University of East Anglia, were used in a resolution of 12.5 x 12.5 km². To supplement the site-specific data with regard to information on land use, the proportions of land use were derived from the Corine Land Cover map 2000 (Keil et al. 2005). The area percentage of urban, forested and agricultural land use categories in a radius of 1, 5, 10, 25 km for forests and agriculture or 1, 5, 10, 25, 50, 75 and 100 km for urban areas around each raster cell was calculated and then projected onto either the 1 x 1 or 2 x 2 km² grid cells (Table 2). The sea spray-effect (Berg and Steinnes 1997) was assessed in terms of the distances of the monitoring sites to the coastlines of the Atlantic Ocean and the Baltic, Black and Mediterranean Sea. We further added the distance of each sampling site to the nearest industrial sites recorded in the European Pollutant Emission Register (EPER) and the respective emission values for Cd, Hg and Pb released into the air to the moss datasets. Finally, we intersected the moss sampling sites with data on modelled natural (Cd, Pb), anthropogenic (Cd, Hg, Pb) and total emissions (Cd, Pb) as well as the total deposition (Cd, Hg, Pb) provided by the Meteorological Synthesizing Centre-East (MSC-E) of EMEP. These data with a resolution of 50 x 50 km² are based on the MSCE-HM atmospheric transport model which has been described in detail by Aas and Breivik (2008), Ilyin et al. (2008) and Gusev et al. (2009). For the metal concentrations in mosses the median for each of the 50 x 50 km² EMEP raster cells was used for the correlation analysis. The modelled EMEP emission and deposition data of the year of moss sampling were assigned to the datasets as well as the mean value of the three years before the sampling as the analysed moss shoots represent the recent three years of growth.

The statistical analyses were performed using the Cd, Hg and Pb concentrations in mosses, the EMEP modelled data and the additional data are listed in Table 1. The analyses were limited to the above metals as these are the only metals for which atmospheric deposition is modelled by EMEP. The additional data sets include site-specific characteristics as documented by the participating countries and also regional characteristics which might influence the heavy metal accumulation in mosses (Berg and Steinnes 1997; Herpin et al. 2004; Schröder et al. 2008; Zechmeister et al. 2003). In the following, these site-specific and regional characteristics are referred to as predictors.

Table 1: Predictor variables for the metal accumulation in mosses

Statistical analyses

Bivariate correlation analysis was used to analyse the strength and direction of the statistical relationship between the metal concentrations in mosses and the predictors. We decided to compute the Spearman rank correlation coefficient r_s because the metal concentrations mostly proved to be not normally distributed. Although this non-parametric correlation method is less powerful than parametric methods if the assumptions underlying the latter are met, it is less likely to give distorted results when the assumptions fail. The coefficient r_s equals -1 if the two

rankings are completely contrary, 0 if the rankings are completely independent and +1 if there is an outright agreement between the two rankings. Within the interval [-1,+1] the strength of correlation was classified according to Hagl (2008): r_s values < |0.2| are very low, between |0.2| and |0.5| low, from |0.5| to |0.7| moderate, between |0.7| and |0.9| high and > |0.9| very high. In this context statistical significance refers to how general a relationship is and the likelihood that the observed relationship occurred by chance.

In addition to the correlation analysis, Classification and Regression Trees (CART, Breiman et al. 1984) were used to analyse the multivariate correlations between the metal concentrations in the mosses and the predictor variables. CART can use an explanatory variable more than once, so it is able to work with multiple interrelated data. CART can reveal hierarchical and non-linear relationships among one dependent variable (metal concentration in the mosses) and several describing variables (regional characteristics of the sampling sites such as depositions and land cover data) by sub-dividing a heterogeneous data set into more homogeneous sub-sets (classes or nodes) by a series of nested binary 'if-then-else' splits. Each split maximises the homogeneity of the dependent variable. Each possible binary split for all variables is evaluated recursively for the best class separation until homogeneous end nodes are reached. The predictor selected is the one for which the two new classes have the greatest within-group similarity for the response variable. The two new classes are then examined separately, with respect to each of the predictor variables, to see if they can be split again. The resulting dendrogram can have multiple branches, each of which represents a path to a particular combination of independent variables defining variable sub-spaces.

Results

The EMEP modelled total deposition of Cd and Pb and their concentrations in mosses were moderately to highly correlated (Table 2): the maximum correlation coefficients for Cd were 0.69 for the year of sampling and 0.68 for the 3-year accumulation period repectively (moss survey 2000, $p < 0.001$). For Pb, the highest correlation coefficient was 0.73, both for the year of sampling and the 3 year accumulation period (moss survey 2005, $p < 0.001$). Hardly any difference were found when relating moss concentrations to EMEP modelled deposition for either the year of sampling or the three years previous to sampling the mosses. In contrast, the correlations between EMEP modelled total Hg deposition and concentrations in mosses were either not significant or low to very low. The highest correlation was found for the moss survey 2000; year of sampling: r_s = 0.22, 3 year accumulation period: $r_s = 0.24$ ($p < 0.001$).

The correlations with anthropogenic emissions were generally moderate for Cd and Pb, reaching correlation coefficients of up to 0.68 for Pb in the moss survey 2005. For Hg, again the correlations were either not significant or very low ($r_s <$ 0.20). For natural emissions, data were only available for Cd and Pb and the correlation coefficients ranged between 0.40 and 0.60. For total emissions Spearman correlation coefficients of up to 0.65 were found (Pb, moss survey 2005).

Table 2: Spearman rank correlation coefficients between Cd, Hg, and Pb concentrations in mosses and modelled EMEP data; n.a. = not available, n.s. = not significant.

The correlations with the site-describing variables were generally low to very low with the exception of the proportion of urban land uses in the surroundings of the sampling sites, which is in case of Cd and Pb and large radii were often moderately correlated (Table 3). There appears to be a trend of increasing correlation coefficients with increasing radii of land use proportions.

Table 3: Correlation between concentrations of Cd, Hg, and Pb in mosses and site or regional characteristics.

The results of the decision tree analyses were further processed on the basis of a weighted index as presented by Kleppin et al. (2008). This index uses the frequency of selection of each predictor and weighs it by the tree level it was chosen in, so that a predictor chosen in a lower tree level is weighted less than a predictor chosen as often but in higher tree levels. For Cd, the most important predictor as indicated by the calculated index (5.0) was the total EMEP modelled deposition in the year of sampling (yos), followed by the analytical method applied (1.33) and the moss species (1.0; Table 4). All other predictors have index values below 1.0. The most important predictor for Hg were the analytical method (3.17), the sampled moss species (2.0), the distance to the nearest Hg emission source recorded in the European pollutant Emission Register (EPER) (1.33) and the share of forested areas in the surroundings of the sampling sites (1.16). As for Cd, the total EMEP modelled deposition in the year of sampling was identified as the most important predictor for Pb (4.33), followed by the 3 years mean of the total EMEP modelled deposition (1.5) and the distance to the nearest Pb source recorded in the EPER (1.33).

Table 4: Index values calculate from decision tree analyses using CART.

Discussion

For Cd and Pb, the results of the current study show a moderate to high and significant positive correlation between the EMEP modelled total deposition and concentrations in mosses for all the moss survey years. This is in agreement with the results previously reported for 2005 (Schröder et al. submitted) and results reported for individual countries. For example, for Cd Berg and Steinnes (1997) and Berg et al. (1995) found a significant positive correlation between the concentration in the moss H. splendens and P. schreberi and wet deposition (r^2 = 0.82 - 0.84), for Pb the correlation was even higher (r^2 = 0.98 - 1.00). The correlation coefficients in the current study are not as strong, because they are not based on deposition measurements and moss sampling at identical sites, as was the case for the studies by Berg et al. (1995) and Berg and Steinnes (1997). We related the modelled emission and deposition data to the medians of all moss sampling sites located within the respective 50 x 50 km² EMEP grid cells. Hence, we investigated the association between deposition and moss accumulation at a broader spatial scale. Nevertheless, the modelled deposition data shows the highest correlations with the Cd and Pb concentrations in the mosses and is the most significant predictor in the decision trees calculated for these metals. Therefore, mosses are a valuable tool for determining spatial and temporal variations in atmospheric depositions at a high spatial resolution across Europe for Cd and Pb.

In an investigation in Germany (Pesch et al. 2007), positive low to moderate correlations between the metal concentration in mosses and in bulk deposition measured in the open field (ICP Forests Level II 1998, 1999, 2000) were found for Cd ($0 < r_s \leq 0.5$, n = 18), Cu ($0 < r_s \leq 0.5$, n = 17), Pb ($0.3 \leq r_s \leq 0.5$, n = 18), and Zn ($r_s = 0.5$, n = 27). For throughfall deposition and the moss concentrations the correlations were very low for Cd ($0 < r_s \leq 0.2$, n = 20) and Pb ($0 < r_s \leq 0.1$, n = 21), low for Cu ($r_s = 0.3$, n = 17), and low to moderate in case of Zn ($0.3 \leq r_s \leq 0.6$, n = 32). Furthermore, for Cd in mosses a correlation of 1.0 was found with wet only deposition data from the air monitoring network of the Federal Environment Agency (FEA) (Σ 2004-2005, n = 6).

In addition to the total deposition which primarily determines the Cd and Pb concentrations in the mosses, other factors contribute to the scatter in the relationships observed. The correlation analyses show significant, however, mostly very low, low or moderate relationships with numerous factors, of which the proportion of urban land uses shows the highest association with the element concentrations in the mosses. The influence of urban emissions on the bioaccumulation of Cd, Hg and Pb in mosses has also been observed by Aničić et al. (2007), Coşkun et al. (2005), Figueira et al. (2002), and Gramatica et al. (2006). In the framework of analyses of the German data from the moss survey 2005, Pesch et al. (2007) also found highly significant correlations of the concentrations of As, Cd, Cr, Cu, Fe, Ni, Pb, Sb and Zn in mosses and the proportion of urban areas in a radius of 5 km around the sampling sites. For Cd and Pb significant negative correlations with the proportion of forested areas in the surroundings of the sampling sites have been found. Here, the forests may indicate background areas with a low influence of urban emissions but may also relate to the fact that forests filter heavy metals out of the air. The proportion of agricultural areas is positively correlated with the Cd and Pb concentrations in mosses which is in contrast to the results of Pesch et al. (2007), who found negative correlations for Cd, Ni, Pb and Sb as well as a positive correlation for Cr in Germany. However, Figueira et al. (2002) mention agricultural practices as a source of Cd in the environment. Except for Cd in 2005, precipitation is positively, but generally very low correlated with the Cd and Pb bioaccumulation in mosses, which may be caused by increased wet deposition (Čeburnis and Valiulis 1999, Frahm 1998, Herpin et al. 1996, Schröder et al. 2008, Zechmeister 1995). In addition, metals deposited on trees and shrubs growing above the mosses may rinse onto the mosses and accumulate in them (Couto et al. 2004, Fernandez and Carballeira 2002, Okland et al. 1999, Schröder et al. 2008, Zechmeister et al. 2003) or soil particles containing metal elements may be splashed onto the mosses at sites with low soil coverage (Aničić et al. 2007, Bargagli 1995, Coşkun et al. 2005, Fernandez and Carballeira 2002). In contrast, Berg and Steiness (1997), Couto et al. (2004), Herpin et al. (1996) and Sharma (2007) report lower element concentrations in mosses as a consequence of a leaching of accumulated elements from the mosses or a wash-off of deposited materials from the mosses. These contrasting results reported on the influence on precipitation on heavy metal concentrations in mosses might well explain the very low correlations observed in this study. The distance to the sea is positively correlated with the Cd and Pb concentrations in the mosses. This is in accordance with Berg et al. (1995) who reported on the influence of sea salt cations (Ca, Mg) on the bioaccumulation of As, Cd, Cu, Pb, V and Zn; these sea salt cations

compete with heavy metals for the same cation exchange sites in the mosses. When atmospheric deposition of metals was not taken into account, Kleppin et al. (2008) found the distance to the sea to be the third most important predictor in decision tree analyses of German moss survey data from 1990, 1995 and 2000. Pesch et al. (2007) found negative correlations with the distance to the sea for Cr and V, but reported positive correlations for As, Cd, Cu, Fe, Hg, Ni, Pb, Sb, Ti and Zn for Germany.

For Hg, the correlations between its concentrations in mosses and EMEP modelled total deposition was low to very low. As Hg in ambient air is predominantly found in the vapour phase and has a residence time of the order of one year it has to be considered as a "global pollutant" (Schroeder and Munthe 1998) without distinct spatial deposition patterns. Multivariate analysis indicated that the Hg concentration in mosses is primarily determined by the analytical technique, but the sampled moss species plays also a major role (Table 4). The former might reflect that the determination of Hg is analytically still more challenging than that of Cd and Pb. It seems likely, however, that the lack of correlation between modelled deposition values for Hg and observed concentrations in moss may relate to the specific chemistry of Hg and corresponding interactions with the moss. Hg is believed to be taken up primarily in its gaseous form, at least in plants (De Temmerman et al. 2007, 2009). For Norway it was reported that mosses are able to retain dry deposited gaseous Hg to a significant extent (e.g. Steinnes et al. 2003). It might well be that the deposition pattern depicted by the moss survey is a better measure of the net Hg supply to the terrestrial ecosystem than that indicated by EMEP modelled calculations (Harmens et al. submitted; Schröder et al. submitted).

Conclusions

Considering the intrinsic uncertainties of the EMEP model (Ilyin and Travnikov 2005) and uncertainties associated with heavy metal emission data, and potential limitations in the use of moss data as monitors of atmospheric deposition (Harmens et al. 2008a), the moss and deposition data agree reasonably well, at least for Cd and Pb. The statistical analyses confirmed that the concentrations of these elements in the mosses are primarily determined by the atmospheric deposition and that mosses can therefore be used as biomonitors for these elements. For Hg, the use of mosses at biomonitors of atmospheric deposition requires further investigation, however, it might well be that the mercury concentration in mosses better reflects the actual deposition to vegetation than that modelled by EMEP model. Correlations can not be expected to equal 1 since deposition and bioaccumulation are not identical but coupled processes in the complex chain of emission, transportation, deposition and accumulation (Lindberg and Turner 1988). This chain of processes and especially the deposition and accumulation processes show distinct differences over time and also across spatial scales (Fränzle et al. 1995).

For Cd and Pb, the strong correlations between the element concentrations in the mosses and the total deposition can be used to calculate deposition maps with a regression kriging approach on the basis of surface maps on the element concentrations in the mosses (Hengl et al. 2007, Odeh et al. 1995).

The moss survey is the only European environmental programme that enables detecting the spatial variability of heavy metal deposition in terrestrial ecosystems in a way that can be proven to be geostatistically valid. In this context, the moss survey features a range of advantages in comparison with other monitoring approaches: readily identifiable in the field; widely distributed; easy to sample repeatedly throughout time to capture temporal variability and cheap, where the cost of sampling and the cost of the following laboratory analyses should be such that sufficient replicates and statistical rigour can be obtained (Osborn et al. 2000; Pakeman et al. 2000).

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Tables

Table 1: Predictor variables for the metal accumulation in mosses

Predictor	Resolution	Data Source
Moss species	site-specific	
Altitude	site-specific	
Analytical method	site-specific	
Sea distance	site-specific	
Precipitation	12.5 km x 12.5 km	CRU[1]
Population density	100 m x 100 m	EEA[2]
Agricultural land uses (1, 5, 10, 25 km radius)	1 km x 1 km	EEA[2]
Forestal land uses (1, 5, 10, 25 km radius)	1 km x 1 km	EEA[2]
Urban land uses (1, 5, 10, 25, 50 km radius)	1 km x 1 km	EEA[2]
Urban land uses (75, 100 km radius)	2 km x 2 km	EEA[2]
Distance to Cd, Hg, Pb emission source (EPER[3])	site-specific	EEA[2]
Total deposition Cd,Hg and Pb	50 km x 50 km	MSC-East[4]
Natural emissions Cd and Pb	50 km x 50 km	MSC-East[4]
Anthropogenic emissions Cd, Hg and Pb	50 km x 50 km	MSC-East[4]
Total emissions Cd and Pb	50 km x 50 km	MSC-East[4]

[1]Climatic Research Unit, http://www.cru.uea.ac.uk
[2]European Environment Agency, http://www.eea.europa.eu
[3]European Pollutant Emission Register
[4]Meteorological Synthesizing Centre-East of EMEP, http://www.msceast.org

Table 2: Spearman rank correlation coefficients between Cd, Hg, and Pb concentrations in mosses and modelled EMEP data; n.a. = not available, n.s. = not significant.

Total deposition	**1990***	**1995**	**2000**	**2005**
Cd (year of sampling)	0.62	0.64	0.69	0.65
Cd (3 years mean)	n.a.	0.64	0.68	0.63
Hg (year of sampling)	n.s.	0.09	0.22	0.17
Hg (3 years mean)	n.a.	0.10	0.24	0.20
Pb (year of sampling)	0.68	0.68	0.68	0.73
Pb (3 years mean)	n.a.	0.67	0.67	0.73
Anthropogenic emissions	**1990**	**1995**	**2000**	**2005**
Cd (year of sampling)	0.54	0.48	0.53	0.49
Cd (3 years mean)	n.a.	0.48	0.54	0.51
Hg (year of sampling)	n.s.	n.s.	0.18	0.14
Hg (3 years mean)	n.a.	n.s.	0.19	0.14
Pb (year of sampling)	0.57	0.61	0.58	0.63
Pb (3 years mean)	n.a.	0.61	0.56	0.68
Natural emissions	**1990**	**1995**	**2000**	**2005**
Cd (year of sampling)	0.48	0.46	0.56	0.40
Cd (3 years mean)	n.a.	0.48	0.56	0.40
Pb (year of sampling)	0.60	0.57	0.58	0.54
Pb (3 years mean)	n.a.	0.58	0.57	0.54
Total emissions	**1990**	**1995**	**2000**	**2005**
Cd (year of sampling)	0.58	0.56	0.61	0.49
Cd (3 years mean)	n.a.	0.56	0.61	0.49
Pb (year of sampling)	0.60	0.63	0.62	0.65
Pb (3 years mean)	n.a.	0.63	0.60	0.65

$p < 0.001$

* In 1990 moss data on Hg was only available from two countries (Austria and Switzerland) from a total of 167 sampling sites.

Table 3: Correlation between concentrations of Cd, Hg, and Pb in mosses and site or regional characteristics (n.s.: $p > 0.05$; italics: $0.01 < p \leq 0.05$; bold: $p \leq 0.01$)

	Cd 1990	Cd 1995	Cd 2000	Cd 2005	Hg 1990**	Hg 1995	Hg 2000	Hg 2005	Pb 1990	Pb 1995	Pb 2000	Pb 2005
Altitude*	**-0.14**	**-0.25**	**0.10**	**0.14**	**n.s.**	-0.16	**-0.28**	**-0.07**	-0.04	-0.13	**0.08**	**0.18**
Population density	**0.31**	**0.40**	**0.36**	**0.19**	**n.s.**	**0.13**	**n.s.**	**n.s.**	**0.37**	**0.36**	**0.34**	**0.16**
Distance to EPER source	-0.04	**-0.22**	**-0.17**	**-0.06**	**-0.32**	**n.s.**	**-0.04**	**n.s.**	**-0.30**	**-0.30**	**-0.12**	**-0.15**
EPER emission	**0.13**	**0.19**	**0.11**	**0.11**	**n.s.**	**n.s.**	**n.s.**	**n.s.**	**-0.14**	**-0.09**	**-0.04**	**-0.07**
Precipitation	**0.07**	**0.20**	**0.05**	**-0.05**	**n.s.**	**0.18**	**0.10**	**0.17**	**0.14**	**0.27**	**0.08**	**0.11**
Sea distance	**0.21**	**0.21**	**0.23**	**0.33**	**n.s.**	**-0.18**	**-0.06**	**-0.18**	**0.11**	**0.17**	**0.25**	**0.31**
Agriculture 1 km	**0.21**	**0.22**	**0.21**	**0.09**	**n.s.**	-0.03	**n.s.**	**n.s.**	**0.19**	**0.17**	**0.17**	**0.18**
Agriculture 5 km	**0.32**	**0.36**	**0.32**	**0.14**	**-0.20**	**n.s.**	**n.s.**	**n.s.**	**0.29**	**0.30**	**0.27**	**0.25**
Agriculture 10 km	**0.35**	**0.41**	**0.35**	**0.17**	**-0.21**	**0.05**	**n.s.**	**n.s.**	**0.32**	**0.35**	**0.31**	**0.28**
Agriculture 25 km	**0.38**	**0.44**	**0.39**	**0.20**	**-0.23**	**0.05**	**0.06**	**n.s.**	**0.35**	**0.38**	**0.35**	**0.31**
Forests 1 km	0.04	**-0.04**	**n.s.**	**n.s.**	**n.s.**	**0.05**	**n.s.**	**n.s.**	**0.05**	**n.s.**	**n.s.**	**-0.06**
Forests 5 km	**n.s.**	**-0.13**	**-0.09**	**n.s.**	**n.s.**	**n.s.**	**n.s.**	**n.s.**	0.03	**-0.05**	**-0.04**	**-0.09**
Forests 10 km	**n.s.**	**-0.16**	**-0.12**	**n.s.**	**n.s.**	**n.s.**	**n.s.**	**n.s.**	**n.s.**	**-0.09**	**-0.07**	**-0.11**
Forests 25 km	-0.04	**-0.18**	**-0.14**	-0.03	**n.s.**	**n.s.**	**n.s.**	-0.04	**n.s.**	**-0.11**	**-0.10**	**-0.14**
Urban areas 1 km	**0.12**	**0.14**	**0.14**	**0.10**	**n.s.**	**0.04**	**n.s.**	**n.s.**	**0.15**	**0.13**	**0.16**	**0.09**
Urban areas 5 km	**0.29**	**0.37**	**0.36**	**0.23**	**n.s.**	**0.08**	**n.s.**	**-0.07**	**0.35**	**0.31**	**0.35**	**0.24**
Urban areas 10 km	**0.39**	**0.44**	**0.42**	**0.30**	**n.s.**	**0.11**	0.03	**-0.09**	**0.43**	**0.38**	**0.41**	**0.30**
Urban areas 25 km	**0.44**	**0.50**	**0.48**	**0.34**	**n.s.**	**0.08**	0.04	**-0.11**	**0.48**	**0.44**	**0.48**	**0.36**
Urban areas 50 km	**0.45**	**0.54**	**0.51**	**0.37**	**n.s.**	**0.08**	0.03	**-0.15**	**0.48**	**0.48**	**0.50**	**0.39**
Urban areas 75 km	**0.46**	**0.56**	**0.52**	**0.39**	**n.s.**	**0.07**	**n.s.**	**-0.16**	**0.49**	**0.49**	**0.50**	**0.41**
Urban areas 100 km	**0.46**	**0.57**	**0.51**	**0.40**	0.17	**0.06**	**n.s.**	**-0.17**	**0.48**	**0.51**	**0.51**	**0.41**

*** In 1990 altitude data was taken from Global Land One-km Base Elevation Project (GLOBE). In the other years the site specific data on altitude (as documented by the moss samplers) was used.**

**** In 1990 measurement data on Hg was only available from two countries (Austria and Switzerland) from a total of 167 sampling sites.**

Table 4: Index values calculate from decision tree analyses using CART.

Cd		Hg		Pb	
Predictor	**Index value**	**Predictor**	**Index value**	**Predictor**	**Index value**
Total deposition (yos)	5.00	Analytical method	3.17	Total deposition (yos)	4.33
Analytical method	1.33	Moss species	2.00	Total deposition (3 years)	1.50
Moss species	1.00	Distance to EPER source	1.33	Distance to EPER source	1.33
Total deposition (3 years)	0.83	Forested areas	1.16	Analytical method	0.67
Urban areas	0.67	Total deposition (yos)	0.83	Moss species	0.67
Total emissions (yos)	0.50	Digestion method	0.83	Urban areas	0.67
Precipitation	0.50	Urban areas	0.66	total emissions (3 years)	0.50
Sea distance	0.50	Sea distance	0.50	Sea distance	0.50
Total emissions (3 years)	0.33	Altitude	0.33	Digestion	0.50
Anthropogenic emissions (3 years)	0.33	Precipitation	0.33	Precipitation	0.33
Distance to EPER source	0.33				
EPER emission value	0.33				