Estimating atmospheric deposition of heavy metals in Germany using LOTOS-EUROS model calculations and data from biomonitoring programmes

Estimation des dépôts atmosphériques de métaux lourds en Allemagne par utilisation du modèle LOTOS-EUROS et des données issues des programmes de biosurveillance

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Abstract

Objectives. Atmospheric deposition of heavy metals (HM) can be determined by use of numeric models, technical devices or measurements on biomonitors such as mosses, leaves or needles. As part of the research and development project *"Impacts of Heavy Metal Emission on Air Quality and Ecosystems across Germany - Sources, Transport, Deposition and potential Hazards"*, commissioned by the Federal Environmental Agency of Germany, the numeric model LOTOS-EUROS was used to calculate data on HM deposition at a spatial resolution of 25 km by 25 km throughout Europe. However, the atmospheric transport model used in the European Monitoring and Evaluation Programme (EMEP) Europe-wide provides a grid of 50 km by 50 km. With respect to monitoring data, the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation Moss Survey) and the German Environmental Specimen Bank (ESB) provide corresponding parameters on HM concentration in various biota. The present study aims at investigating, whether an integrated use of model calculations and monitoring data can extend established methods for estimating and evaluating spatial patterns of atmospheric Pb and Cd deposition across Germany.

Methods. Data from LOTOS-EUROS and EMEP modelling as well as from ESB and ICP Vegetation Moss Survey measurements were spatially joined and then investigated for their statistical relationships between modelled atmospheric deposition of Pb and Cd and respective concentrations in various biomonitors. LOTOS–EUROS and EMEP modelling were evaluated by comparing them with respective biomonitoring data. Associations between modelled and observed data were quantified by regression analysis. Regression equations were applied on geostatistical surface estimations of HM concentration in mosses and then the residuals were interpolated by use of kriging interpolation. Finally, both maps were summed up to a map of atmospheric Pb and Cd deposition across Germany.

Results and conclusions. Data from annual samplings from the German Environmental Specimen Bank (ESB) on HM concentration in tree foliage are suitable, to compare and evaluate deposition estimations from different numeric models. Compared to EMEP, LOTOS-EUROS-model reveals stronger correlations to respective concentration in leaves and needles. The same holds true with respect to data on HM concentration in moss sampled across Europe. Here, the highest correlations were found for the association between geostatistical surface estimations of HM concentration in moss and LOTOS-EUROS model calculations. This could be utilized for data integration by use of Regression-Kriging-Technique, which leads to Cd and Pb deposition maps at a high spatial resolution (3 km x 3 km). This approach should be transferred to future LOTOS-EUROS model calculations with regard to As, Cr, Cu, Ni, V and Zn.

Keywords

biomonitoring, cadmium, deposition modelling, EMEP, Environmental Specimen Bank, European Moss Survey, lead, LOTOS-EUROS.

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Résumé

Objectifs. Le dépôt atmosphérique des métaux lourds (M.L.) peut être déterminé à l'aide de modèles numériques, de dispositifs techniques ou de bioaccumulateurs tels que des mousses, des feuilles ou des aiguilles. Dans le cadre du projet de recherche et de développement « Impacts de l'émission de métaux lourds sur la qualité de l'air et les écosystèmes à travers l'Allemagne - sources, transport, dépôt atmosphérique et risques », commissionnée par l'Agence Fédérale Allemande de l'Environnement (Umweltbundesamt UBA), le modèle numérique LOTOS-EUROS a été utilisé pour calculer des données sur le dépôt d'éléments traces à une résolution spatiale de 25 km par 25 km à travers l'Europe. Toutefois, le modèle numérique appliqué dans le Programme Concerté de Surveillance Continue et d'Évaluation du Transport à Longue Distance des Polluants Atmosphériques en Europe (European Monitoring and Evaluation Programme EMEP*)* fournit une grille de 50 km par 50 km. En ce qui concerne les données de surveillance, le Programme international concerté relatif aux effets de la pollution atmosphérique sur la végétation naturelle et les cultures (ICP Vegetation Moss Survey) et la Banque des Échantillons de l'Environnement Allemand (Umweltprobenbank UPB) fournissent des paramètres sur la concentration d'éléments traces dans divers bioaccumulateurs correspondants.

L'étude suivante présente une utilisation intégrée des calculs de modélisation et des données de biosurveillance pour étendre les méthodes d'estimation et de l'évaluation de la répartition spatiale des dépôts atmosphériques de Pb et de Cd à travers l'Allemagne.

Méthodes. Les données des modèles LOTOS-EUROS et EMEP ont été combinées avec les données de la surveillance des mousses du programme ICP Vegetation/UPB, puis étudiées pour leurs relations statistiques entre les dépôts atmosphériques de Pb et de Cd et les concentrations respectives dans divers bioaccumulateurs.

Une analyse de régression a été réalisée pour étudier les relations entre les données modélisées et observées. Les équations de régression se basent sur des estimations géostatistiques de concentration dans les mousses. Puis les résidus ont été interpolés par la technique du Krigeage. Enfin, les deux cartes se résumaient à une carte de dépôts atmosphériques en Pb et Cd à travers l'Allemagne.

Résultats et conclusions. Les données des prélèvements annuels de la *Banque des Échantillons de l'Environnement Allemand* sur la concentration en éléments traces dans les feuilles des arbres sont tout à fait appropriées pour comparer et évaluer les estimations des dépôts atmosphériques en métaux lourds calculées par différents modèles numériques. Comparé à l'EMEP, LOTOS-EUROS indique de fortes corrélations entre la concentration respective dans les feuilles et les aiguilles des arbres. Il en est de même pour les concentrations en éléments traces dans les mousses prélevées à travers l'Europe. Ici, les corrélations les plus fortes ont été trouvées pour la relation entre les estimations de surface géostatistiques pour la concentration en éléments traces dans les mousses, et les calculs du modèle LOTOS-EUROS. Cela pourrait être utilisé pour l'intégration de données par régression-Krigeage, ce qui permet une cartographie des dépôts de Cd et de Pb pour une résolution spatiale de 3 km par 3 km. Cette approche devrait être transférée aux futurs calculs du modèle LOTOS-EUROS pour As, Cr, Cu, Ni, V et Zn.

Abstract

Banque allemande d'échantillons de l'environnement, biosurveillance par les mousses, cadmium, EMEP, LOTOS-EUROS, modélisation des dépôts, plomb.

1. Introduction

Heavy metals (HM), which are emitted into the atmosphere from natural and anthropogenic sources, are deposited on the ground – after either short or long-range transport – in dependency of their physical and chemical properties, as well as of atmospheric and topographical conditions (Ferrante et al., 2012; Rühling and Tyler, 2001). Total atmospheric deposition of heavy metals encompasses dry, wet and occult deposition, generally leading to various (eco)toxicological hazards (Becker et al., 2013; Truhaut, 1977) and, therefore, are used for assessing environmental quality. Impacts of HM emission on air quality and ecosystems can be assessed by measuring atmospheric HM deposition, sampled by technical devices and biomonitors such as mosses, leaves or needles or by numeric modelling. None of these methods has so far proven to be the best solution, thus all three approaches can complement each other with its specific advantages.

Since 1979 the *Convention on Long-range Transboundary Air Pollution (CLRTAP)* has been endeavouring to limit, reduce and prevent air pollution including long-range trans-boundary air pollution. Under CLRTAP the Aarhus Protocol, last amended in 2012, aims at reducing emissions and immissions of cadmium (Cd), lead (Pb) and mercury (Hg) and its chemical compounds. In this context the European Monitoring and Evaluation Programme (EMEP) collects emission data and measurements of air and precipitation quality from European countries to model atmospheric transport and deposition of air pollutants (Tørseth et al., 2012). The EMEP model has so far produced data at a spatial resolution of 50 km by 50 km. In addition to deposition modelling, since 1990 the European Moss Survey every 5 years provides measurements on concentration of up to 40 metallic elements in moss (Harmens et al., 2010). In Germany, a network with 700-1000 moss sampling sites could be established. All over Europe, up to 7000 sites are sampled (Harmens & Norris, 2008). In the last few years, these monitoring data were used for evaluating the EMEP model and can also be used for mapping deposition of heavy metals (Cd, Pb) at a relatively high spatial resolution of 3 km by 3 km (Schröder et al., 2011). Further data of HM accumulation in biota (i.e. needles or leaves) has been produced in international monitoring programmes (ICP Forests) and on national level (German Environmental Specimen Bank).

Against this background, the research and development project *"Impacts of Heavy Metal Emission on Air Quality and Ecosystems across Germany - Sources, Transport, Deposition and Potential Hazards"*, commissioned by the Federal Environmental Agency of Germany, aims at extending established methods of modelling and mapping heavy metal deposition in Germany and risk assessing, respectively (Builtjes et al., 2014). In this framework, three different groups of HM are investigated: Group A (Cd, Hg and Pb) dealt with highest priority; Group B (As, Cr, Cu, Ni and Zn) considered with medium intensity; Group C comprises other HM (V, Mn, Sb, Ti, Th, Co, Mo and Pt). In this project i.e. the following specific objectives are addressed: 1. Determining the contribution of long-range transport to the current load; 2. Comparing modelled HM deposition with data on HM concentration and other information; 3. Risk assessment; 4. Estimating atmospheric Hg deposition by means of data from a specific water catchment area (case study). The present paper aims at comparing and evaluating different numeric models by use of available data on HM concentration in various biomonitors (mosses, leaves, needles). Furthermore it will be presented, how an integrated use of regression analysis and geostatistical methods can be applied to transform HM concentration in moss (sampled in 2005) into deposition maps (Cd, Pb).

2. Materials

Associations between data on atmospheric deposition derived from numeric models LOTOS-EUROS (Builtjes et al., 2014) and EMEP (Tørseth et al., 2012) and respective data on HM concentrations in biomonitors, such as mosses or tree foliage were examined (Table 1). Spatial information on HM concentration in moss at a spatial resolution of 3 km by 3 km was available through Pesch et al. (2007). Data on HM concentration in leaves and needles, sampled between 2005 and 2011, could be received from the German Environmental Specimen Bank (UBA, 2008).

Table 1. List of data sources used for statistical analysis and data integration.

Liste des sources de données utilisées pour l'analyse statistique et l'intégration de données.

Data	Comment & Source	Unit
HM deposition	Total deposition of Cd and Pb from 2005 and from 2007 to 2011, modelled with LOTOS-EUROS, 25 by 25 km (Builtjes et al., 2014)	µg/m² a
	Total deposition of Cd and Pb from 2005 and from 2007 to 2011, EMEP model calculation, 50 by 50 km (Tørseth et al., 2012)	µg/m² a
HM concentration in foliage	Concentration of Cd and Pb in needles and leaves, measured in 2005 and between 2007 and 2011, held in the German Environmental Specimen Bank (UBA, 2008)	µg/g
HM concentration in moss	Concentration of Cd and Pb in moss, measured in 2005 (Pesch et al., 2007)	µg/g
	Concentration of Cd and Pb in moss, geostatistical surface estimation, 3 by 3 km (Pesch et al., 2007)	µg/g

2.1. Deposition Modelling

2.1.1. European Monitoring and Evaluation Programme (EMEP)

The European Monitoring and Evaluation Programme (EMEP) is part of the UNECE (United Nations Economic Commission for Europe) Convention on Long-range Transboundary Air Pollution (CLRTAP). EMEP serves to collect reported spatial emission data from European countries to model atmospheric transport and deposition of air pollutants (Tørseth et al., 2012). The EMEP model provides data on Europe-wide atmospheric deposition of Pb, Cd and Hg calculated with a grid size of 50 km by 50 km. In this study data for the total atmospheric deposition of Cd and Pb (2005, 2007-2011) were used as a corresponding parameter to the HM concentration in tree foliage and moss, respectively. The EMEP grid consists of 204 cells across Germany with Cd total deposition between 15,45 and 181,13 µg/m² a and a median amounting to 35,59 µg/m² a (2007-2011). For Pb, the values came out to be between 571,18 and 4087,26 µg/m² a (median 1245,08 µg/m² a).

2.1.2. LOTOS-EUROS deposition modelling

The second dataset relies on the chemical transport model LOTOS-EUROS (Builtjes et al., 2014). The total deposition is estimated based on separate assessments for dry and wet deposition fluxes ($F_{tot} = F_{wet} + F_{dry}$). The numeric model is used to calculate land use dependent dry deposition distributions across Germany for the metals that allow explicit modeling (As, Cd, Cr, Cu, Pb, Ni, V and Zn). Calculations are performed using existing emission databases or through the modeling of particulate matter (PM) in combination with metal contents. With respect to the wet deposition flux, data on rain water composition from available deposition networks are used. For the present study, Cd and Pb simulations were performed for the years 2005 and 2007-2011 with a spatial resolution of 25 km by 25 km Europe-wide (Figure 1). For Cd, the median of the time period 2007-2011 account for 25,70 µg/m² a. The range of variation is between 13,98 und 51.96 µg/m² a. For Pb, the values are between 334,65 and 1567,63 µg/m² a, the median amounts to 604,62 µg/m² a.

2.2. European Moss Survey

The EMEP/ECE-Project Atmospheric Heavy Metal Deposition in Europe - estimations based on moss analysis (European Moss Survey) is associated with the Convention on Long-range Transboundary Air Pollution (CLRTAP). Since 1990 the Europe-wide Moss Survey has been providing data on HM concentrations in naturally growing moss following a harmonized methodology (ICP Vegetation, 2005; Harmens et al., 2004, 2008 and 2010). Moss is predominantly used to determine spatial distribution and temporal trends of HM pollution as a serious problem of human health. Metal ions are predominantly absorbed above ground and the annual increment of growth allows temporal allocation of HM concentration in the moss habitus. In the year 2005 moss

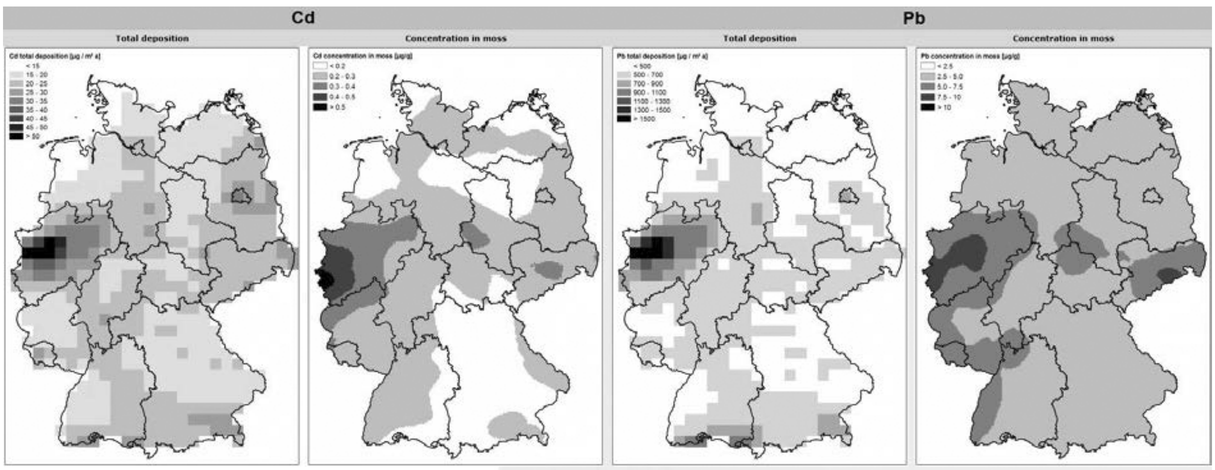


Figure 1. Spatial distribution of LOTOS-EUROS modelled Cd and Pb total deposition [µg/m² a] and respective measured HM concentration in moss [µg/g] for the year 2005.

Répartition spatiale des dépôts totaux de Cd et de Pb [µg/m² a] calculée avec LOTOS-EUROS et les concentrations en éléments traces mesurées dans les mousses [µg/g] pour l'année 2005.

specimens were collected at 728 sample sites across Germany. Further data derived from moss specimen collected at 41 plots in the year 2004; two regions in the North West and Middle East Germany (Schröder et al. 2007) were added. The sampling sites were at least 300 m away from major roads and 100 m away from any road or houses. Samples of the species Hypnum cupressiforme, Pleurozium schreberi and Scleropodium purum were collected. The majority of samples were taken in broad-leaved and coniferous forests. Other sites included moor, grassland and park areas. Concentrations of up to 40 elements in moss were studied according to a standardized protocol (ICP Vegetation, 2005). For Cd, these 769 samplings reveal concentrations in moss between 0,06 und 1,71 µg/g (median 0,20 µg/g). The Pb concentration varies between 1,19 und 40,41 µg/g (median 3,70 µg/g). On this basis, Germany-wide maps on HM concentrations in moss were calculated by use of geostatistical methods (Pesch et al., 2007). These geostatistical surface estimations for the year 2005 were computed with a grid size of 3 km by 3 km and are available for the elements As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Ti, V and Zn.

2.3. Environmental Specimen Bank (ESB)

Data on HM concentrations in tree foliage (leaves and needles) were received from the *German Environmental Specimen Bank (ESB)*. Spatio-temporal data from the years 2005 and 2007 through 2011 in representative terrestrial ecosystems (agrarian, urban-industrial, forestry and nearly natural) were acquired. In particular, these data comprise annual samplings of leaves from beech *(Fagus sylvatica)* and poplar *(Populus nigra 'Italica')* and 1-year old shoots from spruce *(Picea abies)* and pine *(Pinus sylvestris)*. All samples are annually analyzed for As, Cd, Co, Cr, Cu, Hg, Mo, Nk, Pb, Ti and Zn concentrations in the biomonitors according to a strictly applied standardized guideline for sampling and sample treatment (UBA, 2008). Thus, ESB can be considered as a reliable data source. However, contrary to the European Moss Survey, the ESB network of foliage specimen is not very dense and encompasses merely 20 sampling plots. For the time period 2007-2011, Cd concentrations in leaves and needles came out to be between 0,01 and 1,75 µg/g (median 0,12 µg/g). For Pb, the median amounts to 0,46 µg/g within a range of between 1,14 and 1,95 µg/g (N = 87). All station data[1] and measurements[2] are freely provided via Internet.

1) http://www.env-it.de/stationen/public/open.do
2) http://www.umweltprobenbank.de/de/documents/investigations/analytes

3. Methods

The following methods serve for integrating and comparing atmospheric deposition of heavy metals from LOTOS-EUROS model with measured HM concentrations in tree foliage and moss. All analyses were implemented in R (R Development Core Team, 2011). Strength of the correlation was classified as very weak if r < 0,2, weak if r is between 0,2 and 0,4, moderate if r is between 0,4 and 0,6, strong if r is between 0,6 and 0,8 and very strong if r > 0,8 (Brosius, 2013). Comparisons of correlation coefficients (LOTOS-EUROS vs. biomonitors, EMEP vs. biomonitors) were done according to Formula 3.1 (Sachs & Hedderich, 2009):

$$x^2 = \sum_{i=1}^{k} (n_i - 3)(z_i - z)^2 \qquad \text{Formula 3.1}$$

with:
χ^2 = Test value
k = Degree of freedom (number of coefficients)
n_i = Number of samplings
z_i = Transformed correlation coefficient according to Fisher
z = Hypothetical z-value according to Sachs & Hedderich (2009)

On this basis, homogeneity of correlation coefficients were tested at a significance level of $\alpha = 0{,}05$. Significance of homogeneity increases with the similarity of correlation coefficients and also in particular with the number of samplings. If χ^2 is lower than the hypothetical z-value according to Sachs & Hedderich (2009), the homogeneity of correlation coefficients can be considered as significant.

3.1. Correlating modelled HM deposition with HM concentration in tree foliage

One step in the investigation was to correlate modelled HM deposition (EMEP, LOTOS-EUROS) with respective measurements on HM concentrations in tree foliage from ESB. As LOTOS-EUROS model calculations were calculated with emissions for 2005, the results for different years only show the inter-annual variability due to meteorology, but not any trend. Thus, data from the ESB were firstly detrended with regard to LOTOS-EUROS comparisons, whereby the slope of the trend model was used, therefore (Formula 3.2).

$$F = (a * J_b + b) / (a * J_p + b) \qquad \text{Formula 3.2}$$

with:
F = Conversion factor
J_b = Base year
J_p = Sampling year
a = Slope oft the trend model
b = Intercept of the trend model

Geographical information on modelled atmospheric Cd and Pb deposition and concentrations in leaves (beech, poplar) and 1-year old shoots (spruce, pine) from the years 2005 and 2007-2011 were combined by means of GIS functions (overlay, spatial join). Based on this matrix, diagnostic plots were used to identify and, if necessary, exclude outliers. Homogeneity of data was assessed by plotting residuals against fitted values. Quantile-quantile plots (QQ Plots) were used to assess, whether residuals were normally distributed. Afterwards, the association between data on atmospheric HM deposition and respective concentration in the tree foliage were quantified by use of Kendall correlation coefficient $r_{(k)}$. Significance was tested according to Mann-Kendall, also due to small sample size. Correlations were evaluated, whether they are specific for metals, specimen types or ecosystem types (agrarian, forestry, urban-industrial, near natural). Finally, the results of the correlation analyses were used to compare both LOTOS-EUROS and EMEP model calculations in relation to available measurements of bioaccumulation (according to Formula 3.1).

3.2. Correlating modelled HM deposition with HM concentration in moss

Geostatistical surface estimations of Cd and Pb concentrations in moss (2005/2006) were spatially combined with model calculations (LOTOS-EUROS, EMEP) for preprocessing. The respective median of HM concentration within each cell of LOTOS-EUROS grid (25 km by 25 km) and EMEP grid (50 km by 50 km) was calculated. Additionally, moss sampling sites from the years 2004 and 2005/2006 were joined with modelled data. Again, QQ Plots and scatterplots (residuals vs. fitted) were used to exclude outliers and assess homogeneity of data. For correlation analysis, we used Spearman's rank coefficient $r_{(s)}$, because sampling sizes were relatively high, but data on HM concentration in moss were not normally distributed and, thus, did not meet the assumptions for parametric statistics. Correlations were evaluated, whether they are specific for land-use classes (open landscape, forests) or various HM loads areas. Afterwards, LOTOS-EUROS and EMEP model calculations and their associations to respective moss data were compared according to Formula 3.1. Reflecting to the strongest correlations, relationships between model calculations and data on bioaccumulation in moss were quantified by building linear regression models, whereby non-normal distributed data were transformed. Finally, explained variance or goodness-of-fit were measured by calculating the R-squared value.

3.3. Integrating LOTOS-EUROS model calculations on HM concentration in bio-monitors

This method aims at integrating two sources of information, i.e. numeric modelling and moss monitoring data, for computing deposition maps of Cd and Pb across Germany at a high spatial resolution. This approach for mapping atmospheric deposition by use of Regression-Kriging-Techniques (Hengl et al., 2004; Odeh et al., 1995) has proven successfully in similar cases (Schröder et al., 2011). The procedure encompasses following steps: (1) applying regression models (Formula 4.1 and 4.2) to available geostatistical surface estimations on HM concentration in moss (regression maps as result), (2) analyzing and interpolating residuals (regression model vs. LOTOS-EUROS) by use of geostatistical methods (residual maps as result) and (3) a final summation of both (HM deposition maps as result). E.g., for 2005, regression models were applied to spatial data on Cd and Pb concentration in moss (predictors) to compute a corresponding number of regression maps with Cd and Pb concentrations in atmospheric deposition (response variables). Residuals of regression functions, which represent the unexplained variation after fitting the linear models, were determined, exponentiated and then interpolated for each centerpoint of the corresponding LOTOS-EUROS grid. Results were investigated for their spatial auto-correlation using variogram analysis. Spatial auto-correlation is defined as the similarity of, i.e. correlation between values of a process at neighboring points (Johnston et al., 2001). A semi-variogram describes the spatial auto-correlation of point measurements. Relevant parameters for evaluating the semi-variogram are the so-called nugget, sill and major range. The nugget effect is defined by the intercept of the semi-variogram model with the ordinate. Additionally, the nugget effect is determined by confounding factors such as measurement errors or high spatial variability within the interval encompassing the smallest spatial distances between measurement points or underneath the mesh size. The major range is the distance in between point measurements showing high spatial auto-correlation. The value at which the fitted variogram curve attains this range is called the sill. A high partial sill, also called a sill-nugget, indicates a positive auto-correlation within the major range which enables to calculate comprehensive residual maps by use of kriging interpolation. Based on the data-driven geostatistical model, kriging takes into account weighted distances between a measurement point and its neighboring points as well as between the neighboring points themselves. At the end of the process, the regression and residual maps were summed up to several maps of Cd and Pb deposition (2005) on a grid of 3 km x 3 km.

4. Results

4.1. Correlating modelled HM deposition with HM concentration in tree foliage

Correlations were only calculated for specimen types with more than 10 samplings over the whole time period, i.e., data of 1-year old shoots from pine were excluded due to small sampling size (N = 6). The number of samplings between 2005 and 2011 amounted to 28 (beech), 17 (poplar) and 35 (spruce). Metal specific correlations could be determined as follows.

Cadmium. For Cd, the association between measured Cd concentration in leaves and LOTOS-EUROS modelled deposition reveal significant positive correlations ($p < 0{,}05$). For LOTOS-EUROS, Kendall's correlation coefficients amounts to $r_{(k)} = 0{,}31$ (beech) and $r_{(k)} = 0{,}37$ (poplar). By contrast, correlations based on EMEP data are non-significant and somewhat lower to LOTOS-EUROS ($r_{(k)} = 0{,}23$ for beech and $r_{(k)} = 0{,}26$ for poplar). Correlations between Cd concentration in 1-year old shoots from spruce and modelled deposition were ecosystem type-specific. For LOTOS-EUROS, significant strong and moderate correlations ($p < 0{,}05$) were achieved for 1-year old shoots from spruce in forest ecosystems ($r_{(k)} = 0{,}64$) and near natural terrestrial ecosystems ($r_{(k)} = 0{,}49$). Again, EMEP data showed non-significant and lower correlations compared to LOTOS-EUROS ($r_{(k)} = 0{,}40$ in forestry ecosystems and $r_{(k)} = 0{,}36$ in near natural terrestrial ecosystems). For spruce in urban-industrial ecosystems, we found non-significant correlations of $r_{(k)} = 0{,}33$ (LOTOS-EUROS) and $r_{(k)} = 0{,}29$ (EMEP). Negative correlations in agrarian ecosystems for both LOTOS-EUROS and EMEP did not look plausible.

Lead. For Pb, we found significant moderate and very strong relationships between measured Pb concentration in leaves and LOTOS-EUROS model calculations ($p < 0{,}01$). Coefficients according to Kendall amounts to $r_{(k)} = 0{,}48$ (beech) and $r_{(k)} = 0{,}81$ (poplar). The association between LOTOS-EUROS data and Pb concentrations in 1-year old shoots from spruce also revealed a moderate coefficient ($r_{(k)} = 0{,}41$, $p < 0{,}01$). Again, the correlation between EMEP data and Pb concentration in beech foliage is relatively low compared to LOTOS-EUROS, but appeared to be significant ($r_{(k)} = 0{,}43$, $p < 0{,}01$). Same holds true for poplar ($r_{(k)} = 0{,}44$, $p < 0{,}05$) and 1-year old shoots from spruce ($r_{(k)} = 0{,}27$, $p < 0{,}05$). To summarize, LOTOS-EUROS model calculations of Pb deposition related to data from ESB revealed correlation coefficients, which were relatively high in contrast to EMEP. According to Formula 3.1, merely Pb concentrations in poplar's specimen showed significant differences of both correlation coefficients. This is in particular due to small sample sizes.

In view of these correlations, regression analyses were carried out with respect to the association between LOTOS-EUROS model calculations and respective data on HM concentration in biomonitors. The results, calculated separately for various specimen types, are depicted in Figure 2.

4.2. Correlating modelled HM deposition with HM concentration in moss

The relationships between atmospheric Cd and Pb deposition, modelled with LOTOS-EUROS and EMEP, and respective data from the European Moss Survey (samplings and geostatistical surface estimations) can be characterized as follows.

Cadmium. For Cd, the association between measured Cd concentration in moss samplings and respective atmospheric deposition from LOTOS-EUROS model revealed significant statistical association in terms of Spearmans's rank coefficient of $r_{(s)} = 0{,}32$ ($p < 0{,}01$). By contrast, the coefficient with respect to EMEP data is lower ($r_{(s)} = 0{,}27$, $p < 0{,}01$). According to Formula 3.1, the differences between the two coefficients were significant ($p < 0{,}05$). This is due to the relatively high number of sample sites (N = 769). Correlations between LOTOS-EUROS modelled data and measured accumulations in moss were land-use-specific. For plots in forest areas, a low correlation ($r_{(s)} = 0{,}7$, N = 741) was determined, sample sites in open landscape showed a significant high correlation ($r_{(s)} = 0{,}65$, N = 28). Relating 25 km by 25 km LOTOS-EUROS model calculations with corresponding medians of 3 km by 3 km surface estimations of Cd concentration in moss (N = 573), the coefficient amounts to $r_{(s)} = 0{,}39$ ($p < 0{,}01$).

Taking the data with the strongest correlations (LOTOS-EUROS and surface estimations of Cd concentration in moss), Scatterplot and QQ-Plot indicate a positive, non-linear association between both variables. Thus, the response variable was logarithmized

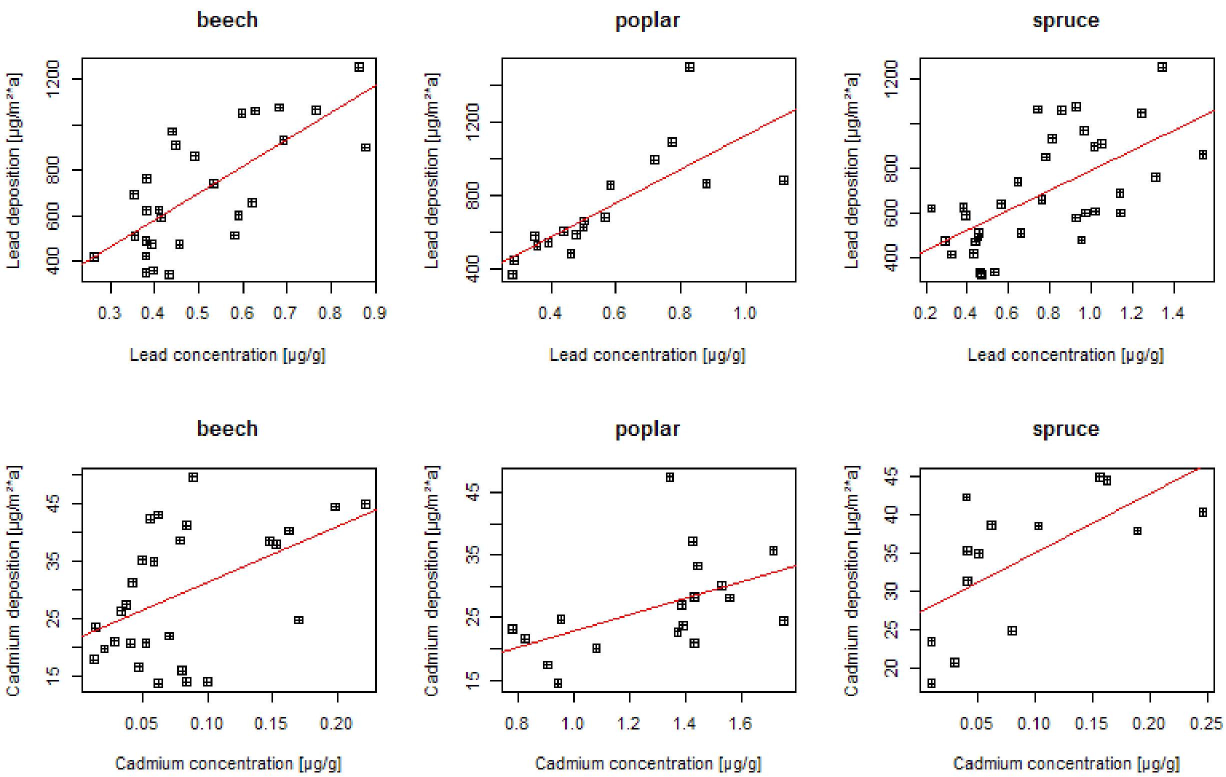


Figure 2. Regression analysis of the association between atmospheric Cd and Pb deposition [µg/m²a] and respective concentration in tree foliage [µg/g] (detrended) for the period 2005 - 2011 related to various specimen types.

Analyses de régression entre les dépôts atmosphériques de Cd et de Pb [µg/m²a] et les concentrations dans le feuillage des arbres [µg/g] (corrigé de la tendance sous-jacente) pour la période 2005-2011 relatifs à divers types d'échantillons.

to get a log-linear model (Figure 3). Following regression equation could be extracted for further analysis:

$y = 1.788x + 2.633$ Formula 4.1

with:
y = ln Cd total deposition (LOTOS-EUROS) [µg/m²a]
x = Cd concentration in moss [µg/g]

The coefficient of determination amounts to R^2 = 0,26, i.e. the regression model explains 26 % of the variance. Within the range of validity (0,01 – 0,55 µg/g Cd in moss) Cd deposition can be determined with deviation of +/- 7,93 µg/m² a from LOTOS-EUROS data. In open landscape, the deviation is somewhat lower at +/- 5,06 µg/m² a (N = 28). The range of variation of LOTOS-EUROS is wider than the range of statistical model (Table 2), i.e., the regression equation causes a smoothing effect on the response variable.

σ = standard deviation

Compared to the regression model, median of LOTOS-EUROS is somewhat higher (118 %). Examining medians in various Cd load areas (< 20 µg/m² a = low; 20 – 30 µg/m² a = intermediate; > 30 µg/m² a = high), zones with low und intermediate Cd loads revealed similar values (97 - 108 %), whereas high levels of Cd deposition correspond with significantly higher deposition rates in the LOTOS-EUROS model calculations (142 %).

Lead. For Pb, again modelled atmospheric deposition was significantly associated with respective concentration in moss. Data from LOTOS-EUROS and the moss samplings (N = 769) revealed a Spearman's correlation coefficient of $r_{(s)}$ = 0,35 (p < 0,01). Based on EMEP modelled data, a similar coefficient of $r_{(s)}$ = 0,.31 (p < 0,01) could be determined. Again, according to Formula 3.1, the differences between the two coefficients were significant (p < 0,05). Plots of open landscape showed a significant moderate correlation coefficient of $r_{(s)}$ = 0,48 (N = 28). Again, for

Table 2. Statistical characteristics of LOTOS-EUROS modelled Cd deposition compared to calculated Cd deposition according to Formula 4.1 (N = 769).

Valeurs statistiques caractéristiques des dépôts totaux de Cd modélisées avec LOTOS-EUROS et calculées selon la formule 4.1 (N = 769).

Variable	Unit	Min	Max	Median	Mean	σ
Cd deposition 2005 (according to Formula 4.1)	µg/m² a	15,49	35,89	19,89	20,96	3,46
Cd deposition 2005 (LOTOS-EUROS model)	µg/m² a	9,35	85.11	23,57	24.77	7,25

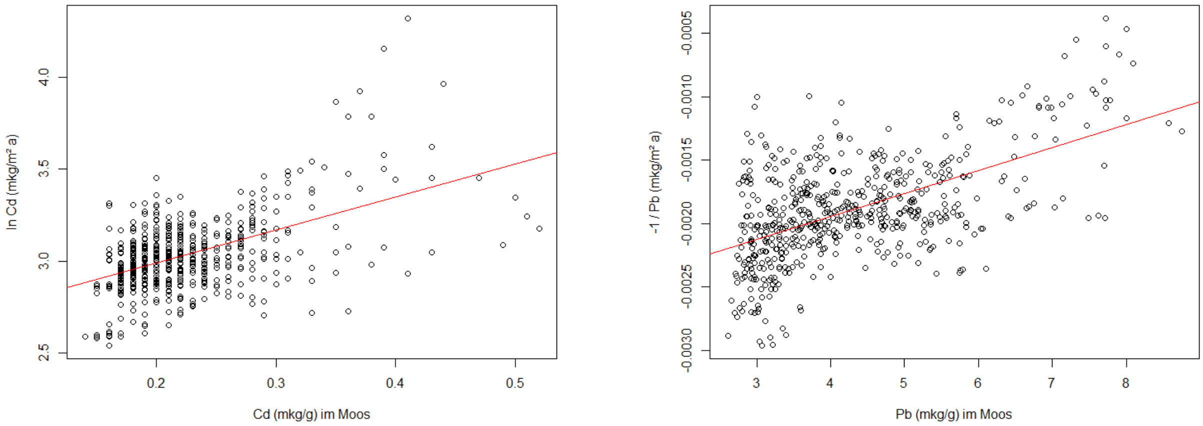


Figure 3. Regression models for the association between Cd concentration in moss (left) and Pb concentration in moss (right) and respective atmospheric deposition derived from LOTOS-EUROS model calculations for the year 2005.

Modèles de régression entre la concentration de Cd dans les mousses (à gauche) et la concentration de Pb dans les mousses (à droite) et les dépôts atmosphériques, calculés avec LOTOS-EUROS pour l'année 2005.

samplings in forestry areas, a relatively low correlation $r_{(s)}$ = 0,28 (N = 741) was calculated. The relation between Pb concentration in moss (3 km by 3 km grid) and LOTOS-EUROS indicated a significant correlation amounting to $r_{(s)}$ = 0,48 (p < 0,01). Compared to Cd, the correlation is somewhat stronger, but still moderate.

A non-linear relationship between both variables was found. Model linearization was carried out by transforming the response variable with 1 / y corresponding to a cubic function (Figure 3):

$$y = 0.0001813x - 0.0026695 \qquad \text{Formula 4.2}$$

with:
y = -1 / Pb (µg/m² a) total deposition (LOTOS-EUROS) [µg/m²a]
x = Pb concentration in moss [µg/g]

The coefficient of determination, R^2 = 0,30 indicates, that the regression model explains about 30 % of the variance. The range of validity is between Pb concentrations of 2,5 – 9,0 µg/g in moss. Within this range, atmospheric Pb deposition can be estimated with a deviation of +/- 279 µg/m² a, compared to LOTOS-EUROS. Sample sites of open landscape reveal a relatively low root mean square error of +/- 156,29 µg/m² a (N = 16).

σ = standard deviation

With respect to LOTOS-EUROS, the range of variation is wider and the median is higher (116 %) than the respective values of the statistical model (Table 3). Again, within modelled zones of low und intermediate contamination, similar Pb deposition rates were calculated (99 - 116 %). By contrast, areas with high levels of HM deposition indicated significantly higher deposition rates by use of LOTOS-EUROS model (143,6 %).

Table 3. Statistical characteristics of LOTOS-EUROS modelled Pb deposition compared to calculated Pb deposition according to Formula 4.2 (N = 561).

Valeurs statistiques caractéristiques des dépôts totaux de Cd modélisées avec LOTOS-EUROS et calculées selon la formule 4.2 (N = 561).

Variable	Unit	Min	Max	Median	Mean	σ
Pb deposition 2005 (according to Formula 4.2)	µg/m^2 a	451,58	961,89	514,32	547,86	96,66
Pb deposition 2005 (LOTOS-EUROS model)	µg/m^2 a	261,06	2968,32	596,15	650,96	263,66

4.3. Integrating LOTOS-EUROS model calculations and HM bioaccumulation

The surface estimations of atmospheric Cd and Pb deposition as result of Regression-Kriging computations are as follows (figure 4).

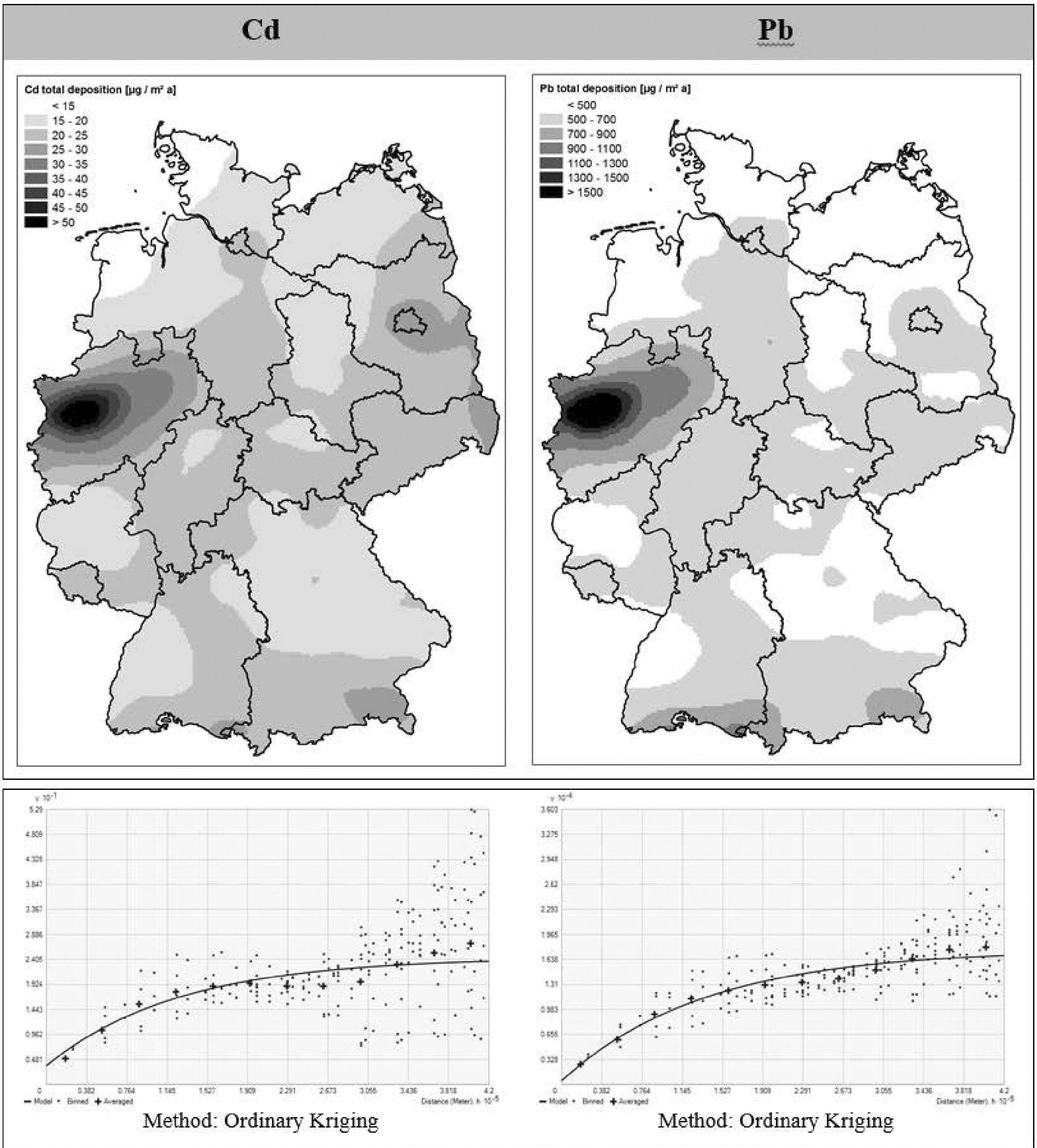
Cadmium. For Cd, variogram model revealed a nugget / sill ratio of 15 % and a major range of 375 km, within which point estimations are significant. Based on the spatial distribution depicted in Figure 4 the Cd deposition is between 12,09 and 60,44 µg/m^2 a. Arithmetic mean of the regression-kriging data amounts to 21,30 µg/m^2 a (= 4,79). The ratio between the median of the regression-kriging data (20,60 µg/m^2 a) and the median of LOTOS-EUROS deposition data (20,43 µg/m^2 a) is near 1. Variability of the LOTOS-EUROS modelled Cd deposition is relatively high compared to the regression-kriging data. Core areas with Cd total deposition above 25,3 µg/m^2 a (= 90th percentile) are located in North Rhine-Westphalia, Berlin, in the east of Saxony and in Bavaria close to the border with Austria.

Lead. For Pb, the nugget / sill ratio amounts to 10 % and the major range to 420 km, respectively. The total deposition is in a range of 330,70-2147,98 µg/m^2 a. Again, modelled deposition showed a higher variability (337,57-2626,44 µg/m^2 a). The arithmetic mean of the regression-kriging data on total deposition amounts to 563,05 µg/m^2 a (= 176,39). The median of data corresponding to Figure 4 (520,11 µg/m^2 a) and the median of modelled distribution (517,65 µg/m^2) revealed a ratio near 1. Centers with values > 704,27 µg/m^2 a (= 90th percentile) have been detected in North Rhine-Westphalia and the south of Bavaria and Baden-Württemberg in the year of 2005.

5. Discussion and Conclusions

Data from annual samplings on HM concentration in tree foliage from the German Environmental Specimen Bank (ESB) are suitable for comparison with model calculations of atmospheric HM deposition (i.e. LOTOS-EUROS, EMEP). Due to the use of standard operating procedures at the ESB (sampling, transport, sample preparation, analytics), a high degree of data quality is guaranteed (UBA, 2008). Based on this, predominantly significant correlations between ESB data on HM concentration in leaves and needles and respective modelled deposition ($p < 0,05$) could be proved. For Pb, correlations were specific for specimen types, and for Cd, additionally ecosystem type-specific. Compared to EMEP, correlations with respect to LOTOS-EUROS were higher. By contrast, the differences between the coefficients were predominantly not significant, except Pb concentrations in poplar's leaves. This was in particular due to the small number of samplings in the ESB (N = 87 between 2005 and 2011). The low number and, thus, spatial coverage of 20 sample sites also may imply a low spatial representativity. Since ESB samplings are taken annually, they are predestined in particular for trend analysis. Here, these advantages could not be optimally utilized, because LOTOS-EUROS model calculations were based on emission data from 2005, so the different years only show the inter-annual variability due to meteorology and not any trend.

By comparison, the data from the European Moss Survey 2005 reveal a relative high spatial representativity with a site density of 2.0 sites / 1000 km^2 (Pesch et al., 2007). Due to a harmonized methodology (ICP Vegetation 2005), the data from the Moss Survey can be considered as a reliable data source allowing for spatial and temporal comparisons. Corresponding to this, it could be indicated, that the correlations of



Lag Size	35 km	***Lag Size***	35 km
Nugget/Sill Ratio	15 %	***Nugget/Sill Ratio***	10 %
Range	375 km	***Range***	420 km
Mean Error	0.00285	***Mean Error***	0.4629
Model Type	Exponential	***Model Type***	Exponential

Figure 4. Regression-Kriging-Maps and results of geostatistical analyses for atmospheric Cd deposition (left) and Pb deposition (right) calculated for the year 2005 with HM concentration in moss as predictor variable.

Cartes de régression-Krigeage et résultats des analyses géostatistiques pour les dépôts totaux de Cd (à gauche) et les dépôts de Pb (à droite) calculés pour l'année 2005 avec la concentration en éléments traces dans les mousses comme variable explicative.

HM concentrations in moss and respective LOTOS-EUROS model calculations were highly significant, with Pb being higher compared to Cd. Correlations based on geostatistical surface estimations were relatively strong compared to those based on the moss samplings. These results are in line with earlier Europe-wide studies, dealing with HM deposition values from EMEP model (Schröder et al., 2011). Correlations between moss data and LOTOS-EUROS were relatively high compared to EMEP. It has to be noticed, that validating the absolute values of both models is not possible, but spatial patterns of HM deposition and accumulation can be compared.

Based on data integration by use of Regression-Kriging-Technique (surface estimations of HM concentration in moss and LOTOS-EUROS) Cd and Pb deposition maps were calculated on a 3 km by 3 km grid. Specific advantages of model calculations (thematic information on deposition rates) and monitoring data (measurements at a relatively high spatial resolution) can be combined. However, for LOTOS-EUROS (25 km by 25 km), the positive effects of data integration were less pronounced compared to EMEP (50 km by 50 km). The most recent data for Germany were only available for the year 2005. In the sense of an improved integrative analysis it would be highly beneficial, if Germany participates in the next monitoring campaign planned for 2015/2016.

Research and development project *"Impacts of Heavy Metal Emission on Air Quality and Ecosystems across Germany - Sources, Transport, Deposition and Potential Hazards"*, which is going to run until 2016, should model other metals with LOTOS-EUROS such as As, Cr, Cu, Ni, V and Zn. These deposition data should be compared as well with data from the European Moss Survey, Environmental Specimen Bank and, additionally, ICP Forests Level II. It also should be determined, to what extent Regression-Kriging leads to higher thematic accuracy. This could be done by a comparative analysis of the different deposition maps with respective deposition measurements.

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Authors' contributions

MS supplied the LOTOS-EUROS data. WS headed the investigation and the computations executed by SN. All authors participated in writing the article and read and approved the final manuscript.

Références bibliographiques

Becker K., Schroeter-Kermani C., Seiwert M. et al. (2013). German health-related environmental monitoring: Assessing time trends of the general population's exposure to heavy metals. *International Journal of Hygiene and Environmental Health* 2013, n° 216(3), p. 250-254.

Brosius F. (2013). SPSS 21. *Mitp/bhv, Heidelberg*. 1054 p.

Builtjes P., Schaap M., Wichink Kruit R. et al. (2014). Impacts of heavy metal emissions on air quality and ecosystems in Germany. *1st Progress Report on behalf of the German Federal Environmental Agency,* Dessau. April 2014.

Ferrante M., Fiore M., Oliveri Conti G. et al. (2012). Old and new air pollutants: An evaluation on thirty years experiences. In: Haryanto B. (ed) Air pollution - a comprehensive perspective. InTech 2012:1-26, DOI: 10.5772/47820. Available at: http://www.intechopen.com/books/air-pollution-a-comprehensive-perspective/old-and-new-air-pollutants-an-evaluation-on-thirty-years-experiences .

Harmens H., Buse A., Büker P. et al. (2004). Heavy Metal Concentrations in European Mosses: 2000/2001 Survey. *Journal of Atmospheric Chemistry* n° 49, p. 425-436.

Harmens H., Norris D. & the participants of the moss survey. (2008). Spatial and temporal trends in heavy metal accumulation in mosses in Europe (1990-2005). Programme Coordination Centre for the ICP Vegetation, Centre for Ecology and Hydrology, Bangor, UK.

Harmens H., Norris D., Steinnes E. et al. (2010). Mosses as biomonitors of atmospheric heavy metal deposition: Spatial patterns and temporal trends in Europe. *Environmental Pollution*, n° 158, p. 3144-3156.

Hengl T., Heuvelink G.B.M., Stein A. (2004). A generic framework for spatial prediction of soil variables based on regression-kriging. *Geoderma* n° 120 (1-2), p. 75-93.

Johnston K., Ver Hoef J.M., Krivoruchko K., Lucas N. (2001). Using ArcGIS *Geostatistical Analyst. Redlands*, 300 p.

ICP Vegetation (2005). Heavy Metals in European Mosses: 2005/2006 Survey. In: Monitoring Manual, ICP Vegetation Programme Coordination Centre, p. 18. CEH Bangor.

Odeh I.O.A., McBratney A.B., Chittleborough D.J. (1995). Further results on prediction of soil properties from terrain attributes: heterotopic cokriging and regression-kriging. *Geoderma* n° 67 (3-4), p. 215-226.

Pesch R., Schröder W., Genssler L. et al. (2007). Moos-Monitoring 2005/2006: Schwermetalle IV und Gesamtstickstoff [Heavy metals IV and total nitrogen]. - Berlin (Umweltforschungsplan des Bundesministers für Umwelt, Naturschutz und Reaktorsicherheit. FuE-Vorhaben 205 64 200, Abschlussbericht, im Auftrag des Umweltbundesamtes [Environmental Research Plan of the Federal Minister for the Environment, Nature Conservation and Nuclear Safety. R & D projects 205 64 200, Final report, commissioned by the Federal Environment Agency]); 90 S., 11 Tab., 2 Abb. (Texteil); 51 S. + 41 Karten, 34 Tabellen, 46 Diagramme (Anhangsteil) (ID: 189)

R Development Core Team (2011). R: A language and environment for statistical computing. R Foundation for Statistical Computing. Vienna.

Rühling A., Tyler G. (2001). Changes in atmospheric deposition rates of heavy metals in Sweden. *Water, Air, Soil Poll,* Focus 1, p. 311-323.

Sachs L., Hedderich J. (2009). Angewandte Statistik [Applied Statistics]. Methodensammlung mit R. Springer-Verlag, Berlin, Heidelberg. 813 p.

Schröder W., Hornsmann I., Pesch R. et al. (2007). Nitrogen and metals in two regions in Central Europe: Significant differences in accumulation in mosses due to land use?. *Environmental Monitoring and Assessment* n° 133, p. 495-505.

Schröder W., Holy M., Pesch R. et al. (2011). Mapping atmospheric depositions of cadmium and lead in Germany based on EMEP deposition data and the European Moss Survey 2005. *Environmental Sciences Europe*, n° 23, p. 19.

Tørseth K., Aas W., Breivik K. et al. (2012). Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972-2009. *Atmos. Chem. Phys*., n° 12, p. 5447-5481.

Truhaut R. (1977). Ecotoxicology: objectives, principles, and perspectives. *Ecotoxicol Environ Saf,* n° 1, p. 151-173.

UBA (2008). Umweltprobenbank des Bundes – Konzeption (Stand: Oktober 2008). Available at: http://www.umweltprobenbank.de/upb_static/fck/download/Konzeption_ Okt_2008_de.pdf

Annexes

Supplemental material

Objectives for statistical analysis and data integration

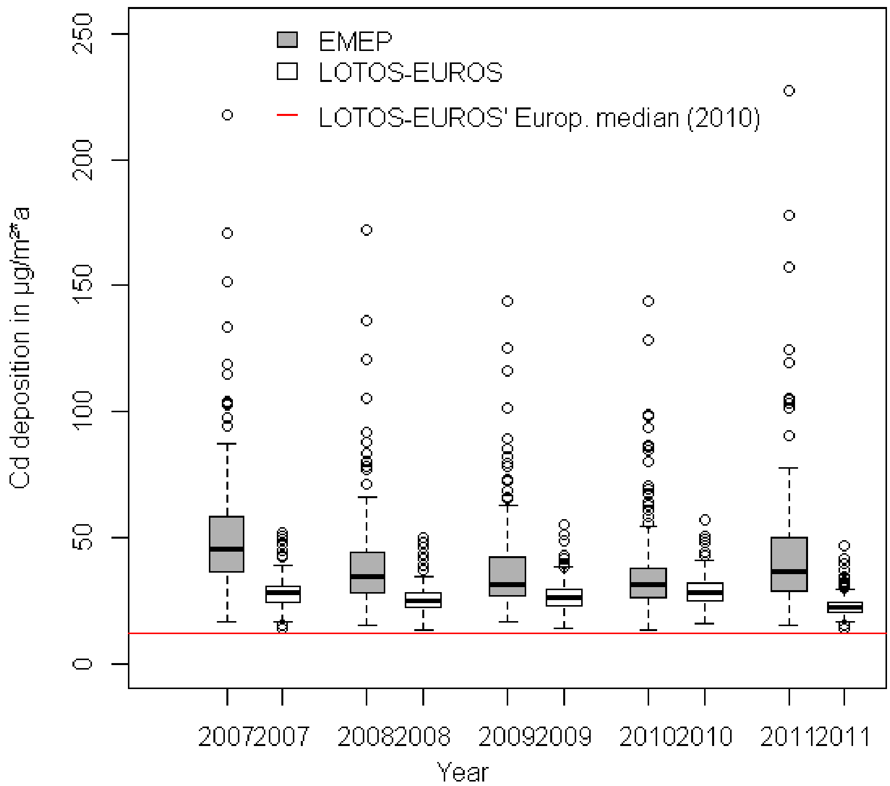
Data	①		②		③	
	Cd	Pb	Cd	Pb	Cd	Pb
EMEP (50 km by 50 km)	✓	✓	✓	✓		
LOTOS-EUROS (25 km by 25 km)	✓	✓	✓	✓	✓	✓
Moss Survey			✓	✓		
Moss estimations (3 km by 3 km)			✓	✓	✓	✓
ESB	✓	✓				

✓ = used data

① = Comparing LOTOS-EUROS and EMEP model calculations with data from the ESB

② = Comparing LOTOS-EUROS and EMEP model calculations with data from the European Moss Survey

③ = Mapping atmospheric HM deposition integrating LOTOS-EUROS and accumulation data from the European Moss Survey



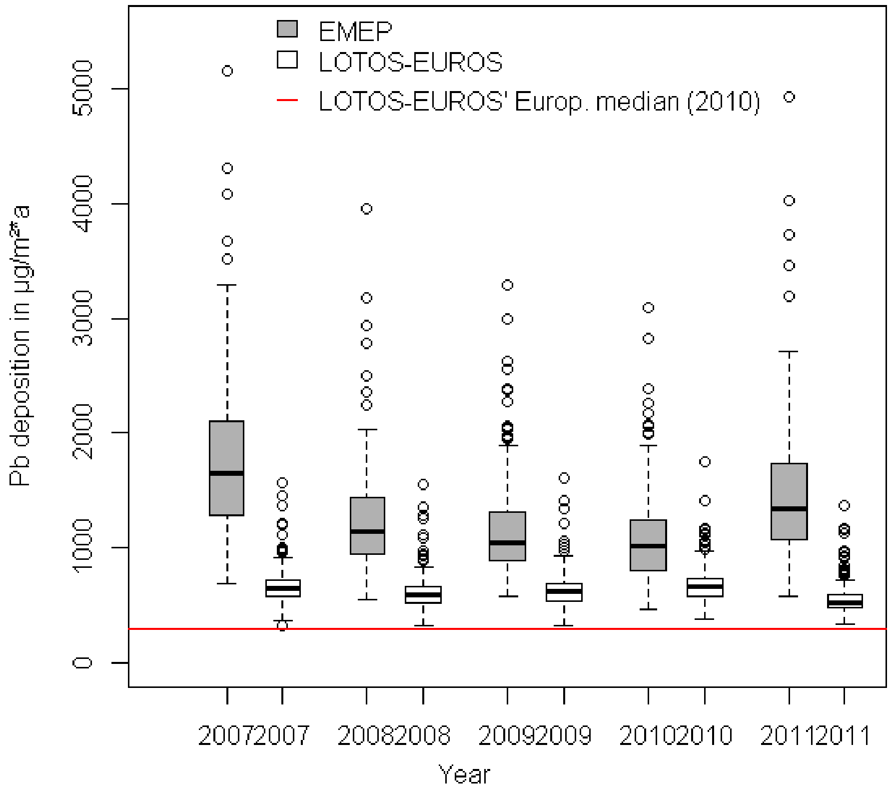


Figure 1. Comparing total modelled Cd and Pb deposition for the time period between 2007 and 2011 across Germany (EMEP, LOTOS-EUROS) with LOTOS-EUROS' European median for the year 2010.

Comparaison des dépôts atmosphériques totaux de Cd et de Pb (2007-2011) à travers l'Allemagne (EMEP, LOTOS-EUROS) et les médianes européennes (2010) modélisés avec LOTOS-EUROS.

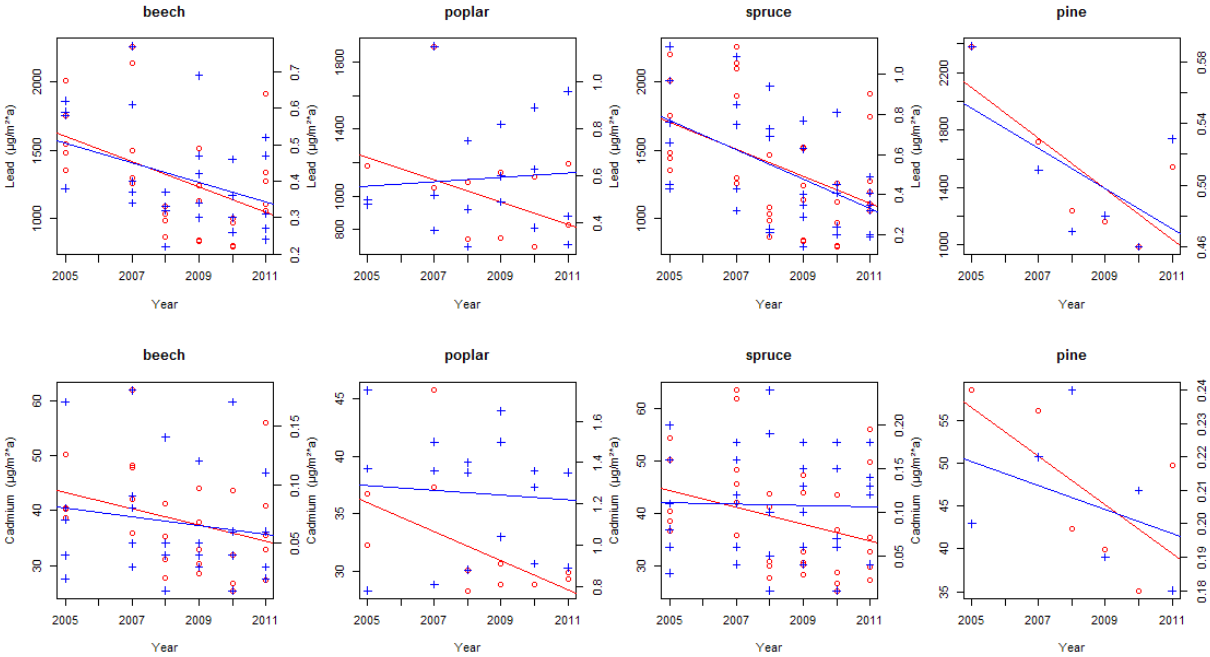


Figure 2. Comparing temporal trends of atmospheric Cd and Pb deposition (circles) [µg/m² a] and respective concentration in tree foliage (crosses) [µg/g] between 2005 and 2011 related to various specimen types.

Comparaisons des tendances temporelles des dépôts totaux de Cd et de Pb (cercles) [µg/m² a] et des concentrations respectives dans le feuillage des arbres (croix) [µg/g] pour la période 2005-2011 relatifs à divers types d'échantillons.

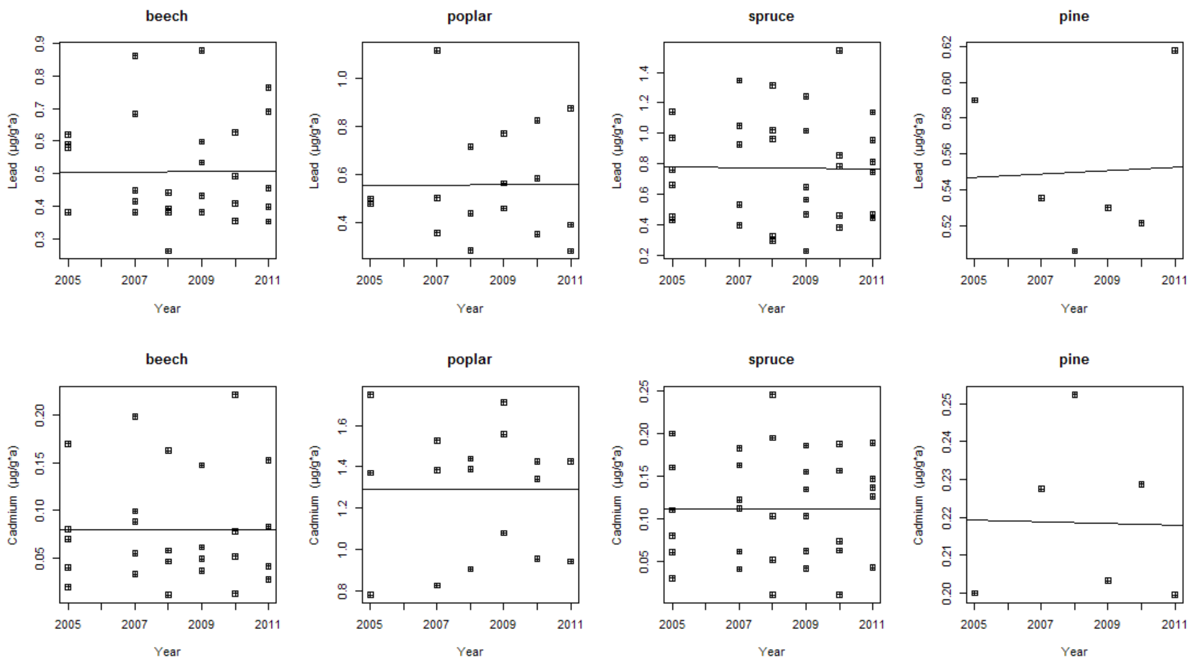


Figure 3. Detrended data on Cd and Pb concentration in tree foliage [µg/g] between 2005 and 2011 related to various specimen types.

Correction de la tendance sous-jacente pour les concentrations de Cd et de Pb dans le feuillage des arbres [µg/g] pour la période 2005-2011 relatifs à divers types d'échantillons.

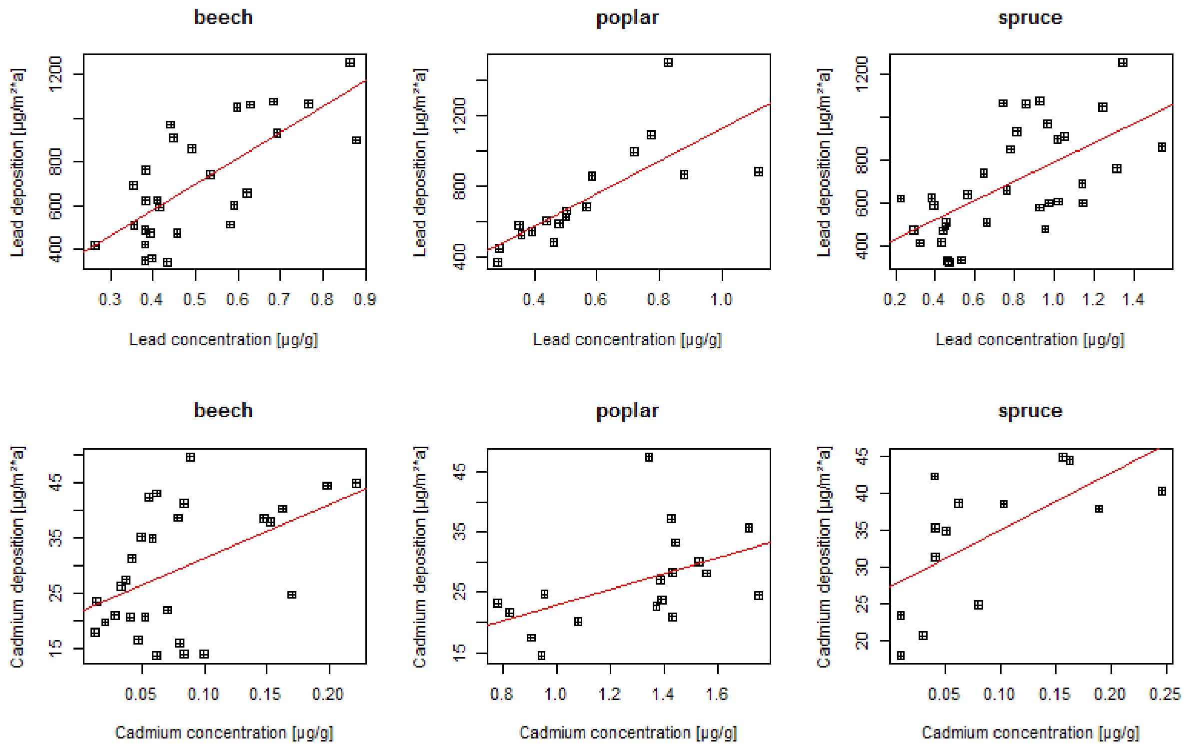


Figure 4. Regression analysis of the association between atmospheric Cd and Pb deposition [µg/m²a] and respective concentration in tree foliage [µg/g] for the period 2005 - 2011 related to various specimen types.

Analyses de régression entre les dépôts atmosphériques de Cd et de Pb [µg/m²a] et les concentrations respectives dans le feuillage des arbres [µg/g] (corrigé de la tendance sous-jacente) pour la période 2005-2011 relatifs à divers types d'échantillons.

Table 1. Descriptive statistics of the total modelled deposition of Cd and Pb across Germany (EMEP, LOTOS-EUROS) and respective concentrations in moss, leaves and needles (2005-2011).

Statistiques descriptives des dépôts totaux de Cd et de Pb (LOTOS-EUROS, EMEP) et des concentrations respectives dans les mousses, les feuilles et les aiguilles d'arbres à travers l'Allemagne (2005-2011).

Variable	Unit	N	Min	Max	Median	Mean	StDev
Cd total deposition 2005 (LOTOS-EUROS)	µg/m² a	204	9,35	81,11	23,57	24,77	7,25
Cd total deposition 2007-2011 (LOTOS-EUROS)	µg/m² a	204	13,98	51,96	25,70	26,34	5,31
Cd total deposition 2005 (EMEP)	µg/m² a	204	19,59	98,13	41,29	44,15	14,55
Cd total deposition 2007-2011 (EMEP)	µg/m² a	204	15,45	181,13	35,59	41,32	20,80
Cd conc. in moss 2005 (measured values)	µg/g	769	0,06	1,71	0,20	0,24	0,14
Cd conc. in moss 2005 (geostatistical surface estimation)	µg/g	527	0,06	0,60	0,21	0,23	0,06
Cd conc. in 1-year old shoots from spruce 2007-2011 (ESB)	µg/g	35	0,01	0,24	0,11	0,11	0,06
Cd conc. in 1-year old shoots from pine 2007-2011 (ESB)	µg/g	6	0,18	0,24	0,21	0,21	0,02
Cd conc. in leaves from beech 2007-2011 (ESB)	µg/g	28	0,01	0,18	0,05	0,07	0,05
Cd conc. in leaves from poplar 2007-2011 (ESB)	µg/g	18	0,78	1,75	1,35	1,25	0,29
Pb total deposition 2005 (LOTOS-EUROS)	µg/m² a	204	261,06	2968,32	596,15	650,96	263,66
Pb total deposition 2007-2011 (LOTOS-EUROS)	µg/m² a	204	334,65	1567,63	604,62	629,90	161,32
Pb total deposition 2005 (EMEP)	µg/m² a	204	634,72	3244,38	1660,33	1692,04	539,45
Pb total deposition 2007-2011 (EMEP)	µg/m² a	204	571,18	4087,26	1245,08	1333,56	489,12
Pb conc. in moss 2005 (measured values)	µg/g	769	1,19	40,41	3,70	4,54	3,28
Pb conc. in moss 2005 (geostatistical surface estimation)	µg/g	527	2,50	11,95	4,00	4,32	3,28
Pb conc. in 1-year old shoots from spruce 2007-2011 (ESB)	µg/g	35	0,14	1,95	0,45	0,57	0,37
Pb conc. in 1-year old shoots from pine 2007-2011 (ESB)	µg/g	6	0,46	0,59	0,49	0,51	0,05
Pb conc. in leaves from beech 2007-2011 (ESB)	µg/g	28	0,22	0,77	0,37	0,42	0,14
Pb conc. in leaves from poplar 2007-2011 (ESB)	µg/g	18	0,30	1,89	0,51	0,66	0,39

Table 2. Kendall correlation coefficients for the relation between LOTOS-EUROS model calculations and data from the Environmental Specimen Bank (2005-2011).

Coefficients de corrélation de Kendall entre les calculs du modèle LOTOS-EUROS et les données de la Banque des échantillons de l'environnement (2005-2011).

Heavy Metal	Specimen Type	N	$r_{(k)}$	p
Pb	beech	28	0,42	< 0,01
Pb	poplar	17	0,79	< 0,01
Pb	spruce	34	0,31	0,01
Pb	pine	6	-0,60	0,13
Cd	beech	28	0,29	0,03
Cd	poplar	18	0,39	0,03
Cd	spruce	35	0,06	0,65
Cd	pine	6	0,33	0,45

Table 3. Kendall correlation coefficients for the relation between LOTOS-EUROS model calculations and data from the Environmental Specimen Bank (2005-2011, detrended).

Coefficients de corrélation de Kendall entre les calculs du modèle LOTOS-EUROS et les données de la Banque des échantillons de l'environnement (2005-2011, corrigé de la tendance sous-jacente).

Heavy Metal	Specimen Type	N	$r_{(k)}$	p
Pb	beech	28	0,48	< 0,01
Pb	poplar	17	0,81	< 0,01
Pb	spruce	34	0,41	< 0,01
Pb	pine	6	-0,37	0,45
Cd	beech	28	0,31	0,02
Cd	poplar	18	0,37	0,03
Cd	spruce	35	0,09	0,48
Cd	pine	6	0,33	0,45

Table 4. Kendall correlation coefficients for the relation between EMEP model calculations and data from the Environmental Specimen Bank (2005-2011).

Coefficients de corrélation de Kendall entre les calculs du modèle de l'EMEP et les données de la Banque des échantillons de l'environnement (2005-2011).

Heavy Metal	Specimen Type	N	$r_{(k)}$	p
Pb	beech	28	0,43	< 0,01
Pb	poplar	17	0,44	0,02
Pb	spruce	34	0,27	0,03
Pb	pine	6	0,73	0,06
Cd	beech	28	0,23	0,09
Cd	poplar	18	0,26	0,15
Cd	spruce	35	0,19	0,1
Cd	pine	6	-0,07	1,00

Table 5. Kendall correlation coefficients for the relation between LOTOS-EUROS model calculations and data from the Environmental Specimen Bank (2005-2011).

Coefficients de corrélation de Kendall entre les calculs du modèle LOTOS-EUROS et les données de la Banque des échantillons de l'environnement (2005-2011).

Heavy Metal	Specimen Type	Ecosystem Type	N	$r_{(k)}$	p
Pb	beech	agrarian ecosystems	6	-0,20	0,70
Pb	beech	forestry ecosystems	8	0,50	0,11
Pb	beech	near-natural ecosystems	14	0,25	0,23
Pb	poplar	urban-industrial ecosystems	17	0,79	< 0,01
Pb	spruce	agrarian ecosystems	6	0,07	1
Pb	spruce	urban-industrial ecosystems	6	-0,33	0,45
Pb	spruce	forestry ecosystems	8	0,29	0,39
Pb	spruce	near-natural ecosystems	14	0,19	0,38
Pb	pine	urban-industrial ecosystems	6	-0,60	0,13
Cd	beech	agrarian ecosystems	6	-0,20	0,71
Cd	beech	forestry ecosystems	8	0,57	0,06
Cd	beech	near-natural ecosystems	14	0,56	0,01
Cd	poplar	urban-industrial ecosystems	18	0,39	0,03
Cd	spruce	agrarian ecosystems	6	-0,87	0,02
Cd	spruce	urban-industrial ecosystems	7	0,08	1
Cd	spruce	forestry ecosystems	8	0,57	0,06
Cd	spruce	near-natural ecosystems	14	0,52	0,01
Cd	pine	urban-industrial ecosystems	6	0,33	0,45

Table 6. Kendall correlation coefficients for the relation between LOTOS-EUROS model calculations and data from the Environmental Specimen Bank (2005-2011, detrended).

Coefficients de corrélation de Kendall entre les calculs du modèle LOTOS-EUROS et les données de la Banque des échantillons de l'environnement (2005-2011, corrigé de la tendance sous-jacente).

Heavy Metal	Specimen Type	Ecosystem Type	N	$r_{(k)}$	p
Pb	beech	agrarian ecosystems	6	0,47	0,26
Pb	beech	forestry ecosystems	8	0,64	0,04
Pb	beech	near-natural ecosystems	14	0,56	0,01
Pb	poplar	urban-industrial ecosystems	17	0,44	0,02
Pb	spruce	agrarian ecosystems	6	0,07	1,00
Pb	spruce	urban-industrial ecosystems	6	0,33	0,45
Pb	spruce	forestry ecosystems	8	0,43	0,17
Pb	spruce	near-natural ecosystems	14	0,21	0,32
Pb	pine	urban-industrial ecosystems	6	0,73	0,06
Cd	beech	agrarian ecosystems	6	0,07	1,00
Cd	beech	forestry ecosystems	8	0,69	0,02
Cd	beech	near-natural ecosystems	14	0,43	0,04
Cd	poplar	urban-industrial ecosystems	18	0,26	0,15
Cd	spruce	agrarian ecosystems	6	-0,73	0,06
Cd	spruce	urban-industrial ecosystems	7	0,29	0,45
Cd	spruce	forestry ecosystems	8	0,40	0,21
Cd	spruce	near-natural ecosystems	14	0,36	0,08
Cd	pine	urban-industrial ecosystems	6	-0,07	1,00

Table 7. Kendall correlation coefficients for the relation between EMEP model calculations and data from the Environmental Specimen Bank (2005-2011).

Coefficients de corrélation de Kendall entre les calculs du modèle de l'EMEP et les données de la Banque des échantillons de l'environnement (2005-2011).

Heavy Metal	Specimen Type	Ecosystem Type	N	$r_{(k)}$	p
Pb	beech	agrarian ecosystems	6	0,47	0,26
Pb	beech	forestry ecosystems	8	0,64	0,04
Pb	beech	near-natural ecosystems	14	0,56	0,01
Pb	poplar	urban-industrial ecosystems	17	0,44	0,02
Pb	spruce	agrarian ecosystems	6	0,07	1,00
Pb	spruce	urban-industrial ecosystems	6	0,33	0,45
Pb	spruce	forestry ecosystems	8	0,43	0,17
Pb	spruce	near-natural ecosystems	14	0,21	0,32
Pb	pine	urban-industrial ecosystems	6	0,73	0,06
Cd	beech	agrarian ecosystems	6	0,07	1,00
Cd	beech	forestry ecosystems	8	0,69	0,02
Cd	beech	near-natural ecosystems	14	0,43	0,04
Cd	poplar	urban-industrial ecosystems	18	0,26	0,15
Cd	spruce	agrarian ecosystems	6	-0,73	0,06
Cd	spruce	urban-industrial ecosystems	7	0,29	0,45
Cd	spruce	forestry ecosystems	8	0,40	0,21
Cd	spruce	near-natural ecosystems	14	0,36	0,08
Cd	pine	urban-industrial ecosystems	6	-0,07	1,00