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Correlation between atmospheric deposition of Cd, Hg and Pb and their concentrations in mosses specified for ecological land classes covering Europe

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ABSTRACT

Referring to Europe as a whole and to single European countries, previous studies have shown that heavy metal concentrations in mosses (1) are primarily determined by atmospheric deposition of heavy metals; (2) are country and element–specific; and (3) agree well with respect to element–specific spatial patterns and temporal trends of atmospheric deposition of heavy metals. This paper investigates correlations between the concentrations of cadmium, lead and mercury in atmospheric deposition and mosses within the units of an ecological land classification of Europe. To this end, measurements from the 2005/2006 European moss survey and modeled atmospheric deposition in the previous three years were intersected with a map on ecologically defined land classes of Europe. Then, the minimum numbers of sampling sites required within the ecological land classes were computed. Considering spatial auto–correlations, subsequently the correlations between the concentrations of heavy metals in mosses and corresponding deposition were calculated and mapped for each of those ecological land classes containing moss sampling sites. It was concluded that the numbers of sampling sites within Europe and most participating countries as well as within most of the ecological land classes are sufficient for estimating the mean of measurements for the above mentioned three spatial levels within 20% of its true value with 95% confidence. Spatial patterns of correlations between the atmospheric deposition and bioaccumulation were shown to vary by element and ecologically defined land classes.

Keywords: *Bioaccumulation, biomonitoring, ecological land classification, minimum number of sampling sites*

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1. Introduction

The Convention on Long–range Transboundary Air Pollution (LRTAP) from 1979 has been extended with eight protocols aiming at reducing emissions of air pollutants. Amongst them, the 1998 Aarhus Protocol on heavy metals addresses the abatement of cadmium (Cd), lead (Pb) and mercury (Hg) pollution. Within the LRTAP Convention, the European Monitoring and Evaluation Programme (EMEP) collates emission data from parties, measures air and precipitation quality and models atmospheric transport and deposition of air pollutants (Torseth et al., 2012). The EMEP monitoring network for Cd and Pb is scarce or absent in southern and Eastern Europe, whereas Hg is primarily measured in northern Europe.

In addition to EMEP, under the LRTAP–Convention, the Working Group on Effects, established in 1980, provides information on the impacts of air pollutants on the environment and human health, and reports on the deposition of atmospheric pollutants to ecosystems and the exceedances of critical loads or levels. This information is supplemented by the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation, 2005) which has been coordinating the European moss survey since 2000. That survey, conducted every 5 years since 1990, collects data on concentrations of heavy metals (since 1990), nitrogen (since 2005) and persistent organic pollutants (since 2010) in naturally growing mosses (Harmens et al., 2010; Harmens et al., 2013). Compared to the EMEP monitoring network, the spatial resolution of the moss survey in terms of extent, i.e. area covered by sampling sites, and grain, i.e. number of sampling sites, is much higher and spatial and temporal trends are determined for more metals. Although the heavy metal concentrations in mosses provide no direct quantitative measurement of atmospheric deposition, the moss survey data yield a time–integrated measure of the spatial patterns and temporal trends of heavy metal deposition from the atmosphere to terrestrial ecosystems. This was corroborated at the national level by, amongst others, Berg and Steinnes (1997), Berg et al. (2003) and by Harmens et al. (2012), and at the European level by Holy et al. (2009), Schröder et al. (2008) and Schröder et al. (2010).

Referring monitoring data to single countries, such as those participating in the European moss survey, or federations, such as Europe as a whole, may be adequate for environmental reporting and political decisions. Nevertheless, impact assessments would profit from relating monitoring data with information on ecological characteristics of the receiving environmental systems. Additionally, from a review of surface flux modeling approaches it was concluded that, amongst others, “ecoregion information” (Pleim and Ran, 2011) could effectively support deposition modeling. Therefore, the current study investigated the relationship between EMEP modeled atmospheric deposition of Cd, Hg and Pb and their concentration in mosses for up to 40 ecologically defined land classes covering Europe (Hornsmann et al., 2008). Although

previous studies have shown good correlations between both parameters, other factors than atmospheric deposition also contribute to the variation of Cd, Hg and Pb concentrations in mosses (Harmens et al., 2008a; Harmens et al., 2008b; Schröder et al., 2008; Holy et al., 2009; Schröder et al., 2010). As these factors and their influence on the relationship between deposition and bioaccumulation are likely to be different for land classes with different ecological characteristics, we hypothesize that the correlations between both element concentrations in deposition and mosses are land class–specific.

2. Materials and Methods

2.1. Moss sampling and chemical analyses

Moss samples were collected at a maximum of 7 300 sites in up to 29 European countries since 1990 every five years. The results of the surveys 1990, 1995, 2000 and 2005 were published by Rühling (1994), Rühling and Steinnes, (1998), Buse et al. (2003), Harmens et al. (2008a), and Harmens et al. (2010), respectively. This investigation relies on the moss survey 2005, conducted according to the guidelines published by ICP Vegetation (2005). Since the sampling sites cover a broad range of ecologically different habitats several carpet–forming moss species were collected. Only the last two to three years' growth of moss material was used for the chemical analyses.

Each sampling site was located at least 300 m from main roads and populated areas and at least 100 m from any road or single house. The majority of mosses were sampled in forests (coniferous, broad–leaved or mixed), followed by "moors and heathland" and natural grassland. In forests, samples were collected as far as possible in small open spaces to preclude any significant effect of canopy drip. Sampling and sample handling were carried out using plastic gloves and bags. Each sample was a composite of about five sub–samples collected in an area of 50 m by 50 m. Dead material and litter were removed from the samples and only the last 2–3 years' growth of moss material was used for the analyses. The concentrations of Cd, Hg and Pb were determined by a range of analytical techniques and quality control exercises were conducted (Steinnes et al., 1997; Harmens et al., 2008a; Schröder et al., 2009; Harmens et al., 2010).

For this investigation we used the data on concentrations of Cd, Hg and Pb in mosses sampled in the European moss survey 2005/6 (from now on referred to as 2005) and spatially connected them with the modeled atmospheric deposition of Cd, Hg and Pb in the previous three years (Section 2.2) and the ecological land classes (Section 2.3) within a GIS. As the last two to three years of moss growth was selected for heavy metal determination, representing the accumulation of atmospheric deposition in mosses in the three years previous to sampling (ICP Vegetation, 2005), EMEP atmospheric deposition data averaged for the years 2003, 2004, and 2005 were included in the statistical analyses.

2.2. Modeling atmospheric deposition

Using EMEP transport models, atmospheric deposition of Cd, Hg and Pb (Travnikov and Ilyin, 2005) are calculated from emission data compiled by EMEP. The modeled data are verified against concentrations in air and precipitation measured at 66 (Cd and Pb) and at 22 (Hg) EMEP sites, respectively (Aas and Breivik, 2009). The EMEP monitoring network for Cd and Pb is scarce or absent in southern and Eastern Europe, whereas Hg is primarily measured in northern Europe. Finally, after validation by measurements, the modeling results are mapped on grids of 50 km by 50 km. The procedure applied and the results are described by Travnikov and Ilyin (2005) and Travnikov et al. (2012). In this investigation we used the modeled EMEP deposition data averaged for the years 2003, 2004, and 2005 and related them to the concentrations of Cd, Hg and Pb in mosses collected in the moss survey 2005 (Section 2.1) and the ecological land classes (Section 2.3) within a GIS.

2.3. Ecological land classification of Europe (ELCE)

The data on atmospheric deposition and the accumulation of trace elements in mosses were connected to a map depicting the geographical distribution of ecological land classes across Europe. This map was calculated by means of Classification and Regression Trees (CART) (Breiman et al., 1984) from 48 digital maps, each visualizing the spatial pattern of one of 48 ecologically relevant land characteristics covering climate, altitude, soil, and potential natural vegetation in Europe (Hornsmann et al., 2008). ELCE subdivides Europe into spatial units mapped on grids of about 20x20 km. Data used for calculating the ELCE unit are data on the potential natural vegetation (Bohn et al., 2005), on altitude (Hastings et al., 1999), on soil texture (FAO, 1996) as well as the monthly averages on air temperature, sunshine duration, relative humidity, and precipitation (New et al., 2002). The potential natural vegetation was set as the target variable whereas the above mentioned data on altitude, soil texture, and climate were chosen as predictors. CART allows the production of several levels of grain, that is in this investigation the numbers of ELCE units differentiated (Lam, 2004), illustrating the spatial patterns of 200 ($ELCE_{200}$) to 40 ($ELCE_{40}$) units. In this investigation $ELCE_{40}$ was used.

2.4. Calculation of minimum number of sampling sites needed for reliable statistics

Measurement values should be meaningful not only for one certain point in space and time. Measurements taken in a geographically specified area should rather allow for generalizetions so that, e.g., their mean value is reliable with respect to variability and number of measurements covering that region. The number of samples required is to be based on a specified confidence interval about the mean of the variable considered (Nelson and Ward, 1981). Therefore, in this investigation the minimum number of sampling sites needed for reliable statistics were calculated prior to the calculation of correlations between the concentrations of Cd, Hg and Pb in atmospheric deposition and in mosses. Hox (2010) provides an overview of sample size issues with regard to minimum sample sizes (MSS) needed. In this investigation, the minimum number for estimating the mean of measurements within 20% of its true value with 95% confidence was computed using this formula:

$$MSS = \left(\frac{Stdev \times 1.96}{0.2 \times Mean}\right)^2 \quad (1)$$

Calculations were processed for (a) Europe in terms of the sum of the territories of countries which participated in the moss survey 2005; (b) each of the participating countries; (c) each of the 40 ecological land classes of Europe covered by the survey network. For the countries (b) and the land classes (c) both, the percentage of countries and classes with missing monitoring sites and the percentage of area covered were calculated. Since contrary to the countries, ELCE units are not necessarily spatially contiguous, the percentage was only calculated for those parts of land classes covered by moss survey sampling sites buffered by the minimum auto–correlation range of elements dealt with. Compared to Hg and Pb, for Cd the smallest auto–correlation range, amounting by 62.5 km, was calculated with the help of Variogram Analysis (Schröder et al., 2010).

2.5. Correlations between modeled deposition and measured concentrations in mosses

As a widespread phenomenon in environmental systems, auto–correlation of a random process is defined as the similarity of, or correlation between, values of a process at neighboring points in time or space. Positive autocorrelation means that the

individual observations contain information which is part of other, timely or spatial neighboring, observations. By this, subsequently, the effective sample size will be lower than the number of realized observations. Thus, positive spatial auto–correlation enhances type I errors, so that parametric statistics such as Pearson correlation coefficients are declared significant when they should not be (Nelson and Ward, 1981). Therefore, spatial auto–correlations of both EMEP deposition data and moss data across Europe were calculated according to Dutilleul et al. (1993) and Schröder et al. (2012).

Then, for each ecologically defined land class Spearman rank correlations between EMEP modeled atmospheric dry, wet and total deposition and concentrations in mosses for Cd, Hg and Pb were determined. In this investigation, Spearman rank correlation coefficients r_s were calculated because the measured concentrations mostly proved not to be 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 in opposite to each other, r_s equals 0 if the rankings are completely independent and +1 if there is complete agreement between the two rankings. Within the interval [−1, +1] the strength of correlation can be classified as follows: r_s values <0.2 are very low, between 0.2 and 0.49 low, from 0.5 to 0.69 moderate, between 0.7 and 0.89 high and ≥0.9 very high (Schröder et al., 2010). Moss data outside the mean ±3 standard deviations were eliminated from the analysis leading to exclusion of 2–3% of the moss data.

3. Results and Discussion

3.1. Reliability of atmospheric pollution data

Deposition data (EMEP). The deposition data comprise uncertainties of data collected from emission inventories, monitoring and modeling. The uncertainty of emission data is difficult to quantity since the national emission inventories do not provide respective information. Travnikov et al. (2012) assumed "a relatively high level of uncertainty for all metal emissions". The uncertainty of country–specific totals of heavy metal emission might range between 30 and 60% (Harmens et al. 2012). Thus, analyses of data consistency revealed that data on anthropogenic emissions officially submitted cannot explain observed levels of Pb and Cd wet deposition in Europe (Pacyna et al., 2009). "Based on observations of these metals in the EMEP monitoring network one can expect 2–3 fold underestimation of emission data in Europe" (Travnikov and Ilyin, 2005).

The uncertainty of modeling results includes the estimation of intrinsic model uncertainties, the overall model uncertainty and the comparison of modeled values with field observations. The intrinsic model uncertainty abstracts form the influence of emission data and amounts for the total deposition of Cd and Pb by 33% and for Hg by 39% on average. The overall model uncertainty is about 58% for the total deposition of Cd and Pb and 46% for Hg (Ilyin et al., 2005; Travnikov et al., 2012). The agreement of modeled and monitoring data covering the period between 1990 and 2010 was proved to be element–specific: for wet deposition of Cd the observed levels are underestimated by the model in all years of the considered period. Nevertheless, modeled and measured concentrations of Cd in wet deposition were correlated with r=0.59 (number of model/measurement pairs=772). The discrepancies between modeled and measured data are assumed to be caused by uncertainties in emission data (see above) and in measurements (see below). Concentrations of Cd in precipitation are much lower than those of Pb, hence, the reliability of analytical detection is more challenging compared to the measurement of higher concentrations that are, e.g., due to bio–accumulation found in mosses. The correlation between modeled and measured Hg wet deposition accounted for 0.73 (number of model/measurement pairs=163). However, the correlation between modeled and measured Hg concentrations in air (r=0.24; number of model/measurement pairs=99) indicates that spatial and temporal variability of Hg background concentrations in air is low. Modeled concentrations of Pb agree well with the measured concentrations in wet deposition as indicated by a correlation of about 0.76 (number of model/measurement pairs=796) (Travnikov et al., 2012).

The uncertainty of monitoring data includes the estimation of the uncertainty caused by analytical methods. Accordingly, most of the national laboratories participating in the analysis of Cd and Pb sampled at the EMEP stations met the data quality objective criteria meaning that the accuracy in the laboratory should be better than 15% and 25% for high and low concentrations of heavy metals, respectively (Travnikov et al., 2012). While laboratory comparisons provided estimations of the accuracy of analytical methods, overall measurement accuracy was estimated by field campaigns. Field comparison of measurements of Hg concentrations in precipitation accounted for ±40% (Aas, 2006; UBA, 2006). Uncertainty of wet deposition of Pb and Cd, estimated from the results of 2006–2007 field campaign, was around 20% (Travnikov et al., 2012).

Moss data. The moss sampling and chemical analysis was according to the guidelines described by ICP Vegetation (2005). Quality control exercises were conducted in 1995 (Steinnes et al., 1997) and 2005 (Harmens et al., 2008a; Harmens et al., 2010; Harmens et al., 2012) with moss reference material being distributed amongst participating laboratories. In addition, some laboratories used other certified reference material for quality assurance, and in Germany moss data was checked for plausibility site–specifically (Schröder et al., 2009). Recommended values were established in 1995 for moss reference material. For example, the recommended values for Cd, Hg and Pb for moss reference M2 were 0.454±0.019, 0.058±0.005 and 6.37±0.43 mg kg^{-1} (mean±standard deviation), respectively, and 0.106±0.005, 0.035±0.004 and 3.33±0.25 mg kg^{-1}, respectively, for moss reference M3 (Steinnes et al., 1997). In 2005, the mean values of M2 and M3 were generally in good agreement with the recommended values (Steinnes et al., 1997): the M2–recovery was 95, 94 and 103% of recommended values for Cd, Hg and Pb and the M3–recovery amounted for 102, 117 and 104% of respective recommended values. Thus, the quality control of the moss survey data yielded satisfying results (Harmens et al. 2008a; Harmens et al., 2010).

3.2. Minimum number of sampling sites

Table 1 contains the results of calculated minimum number of moss sampling sites for each of those 40 ELCE units which were covered by the European moss survey network 2005. Accordingly, in most cases the number of sampled sites exceeds the number of sites required for estimating the mean of measurements for the above mentioned three spatial levels within 20% of its true value with 95% confidence. For Hg measurements, the minimum number of sampling sites required failed in 3 out of 26 ELCE units (11.5%) where Hg was determined in mosses: in land class $ELCE_{40}D\_22$ (located in Central Sweden and Northwest Russia), 23 sites instead of 3 should have been sampled, 47 instead of 35 sites in $ELCE_{40}G1\_0$ (mainly located in Italy and Southeast Europe–Hungary, Romania, Serbia, Macedonia, Albania, Greece, Bulgaria and Turkey and covering small areas of Northeast Austria, the Czech Republic and Central Poland), and 48 instead of 22 sites in $ELCE_{40}S\_0$ (occurs in Ireland and Northern Great Britain, Iceland, Scandinavia and Northeast Europe, i.e. Northwest Russia, Estonia, Latvia and Belarus). In case of Pb and Cd measurements, the percentage of ELCE units with less sampling sites than needed was 9 out of 29 (31%) and 7 out of 29 (24.1%), respectively.

The determination of minimum numbers of sampling sites needed for calculating reliable mean values for each of the 25 countries participating in the European moss survey 2005 revealed a similar picture as found for ecologically defined land classes as spatial reference system: 7 out of 25 (28%), 1 out of 14 (7.1%) and 2 out of 26 (8.7%) of the countries participating in the European moss survey 2005 did not sample mosses from a sufficient number of sites to estimate reliable mean values for the bioaccumulation of Pb, Hg and Cd, respectively.

Comparing the percentage of number and of area covered by countries and ELCE units with missing moss sampling sites enables ranking the elements monitored according to the need for enhancing the spatial resolution of the survey network: Pb>Cd>Hg. The results for the minimum sample size needed give reason to discuss whether the network should be adjusted accordingly. Pesch and Schröder (2006) developed a methodology how to optimize the moss monitoring network by example of Germany without reduction of statistical power. Accordingly, the German moss survey network 2005 was designed. Hornsmann et al. (2008) complemented that approach for Europe by use of ELCE.

3.3. Correlations between concentrations in atmospheric deposition and in mosses specified for ecologically defined land classes

Positive spatial auto–correlations could be proved and accounted for in the calculation of statistical correlations between atmospheric deposition and bioaccumulation within ELCE units. The results showed that the auto–correlation considerably reduces the degrees of freedom. Despite this, the correlations remained statistically significant (Schröder et al., 2012).

Harmens et al. (2012) correlated metal concentrations in deposition and mosses for single European countries. This is reasonable in terms of environmental policies but should be supplemented with correlation analyses within the spatial framework of ecologically defined land classes. Such spatial units are, contrary to species which are used to indicate single aspects of habitat quality including pollution, complex indicators comprehending the ecological coverage of land in terms of, e.g., soil, vegetation, elevation and climate (Aspinall and Pearson, 2000; Wallace et al., 2004). Figures 1–3 depict the spatial structures of Spearman Rank correlation coefficient between concentration of Cd, Pb and Hg in atmospheric deposition and mosses calculated and mapped for each of the $ELCE_{40}$ units for the moss survey of 2005.

Correlation coefficients were calculated only for those ELCE units containing more than 10 observation sites. Therefore, the number of ELCE units accounted for in the correlation analysis (e.g. 28 for Cd) does not automatically match the number of ELCE units considered within the analysis of the minimum number of sampling sites (e.g. 29 for Cd).

For Cd in 8 out of 28 ELCE units (28.6%) the r_s values are below 0.2 (20.2% of area of ELCE units covered by moss sampling sites). In a further 12 out of 28 ELCE units (42.9%) r_s values range between 0.2 and 0.49 (40.8% of total area). In Figure 1 they are colored in green and located in Great Britain, Scandinavia and Iceland and in some parts of France as well as Central and Eastern Europe. Finally, in the remaining 8 out of 28 ELCE units the r_s values are moderate with values between |0.5| and |0.69| (28.6 % of total area) (7 out of 28 = 25 %) and, respectively, high with values above |0.7| (2 % of total area) (1 out of 28 = 3.6%). In Figure 1 they are coloured in yellow and orange, respectively, and occur from the North and South Downs (England) to Normandy, covers the Pyrenees as well as parts of the Alps, the Carpathian Mountains, the Dinaric Alps, the Balkan Mountains and parts in Eastern Germany, Poland, southern Belarus and the North of the Ukraine.

Compared to the Cd correlation pattern, the spatial structure for Pb is different: the correlations between deposition and accumulation of Pb lower than 0.2 (21.3% of total area) occur in ELCE units mainly located in Great Britain and within a corridor that ranges from Central Norway through northern parts of Sweden and Finland as well as in parts of Central and Eastern Europe (grey colored in Figure 2). Correlations between 0.2 and 0.49 (38.4% of total area) dominate continental Europe, especially parts in Central Europe, the Balkans, the Baltic States and Sweden (green colored in Figure 2). Correlation values from 0.5 to 0.69 (34.9% of total area) are clearly clustered in Iceland, western and northern parts of Scandinavia, Finland, the Alps, the Pyrenees and in low mountain ranges in Eastern Europe as for example the Carpathian Mountains (yellow colored in Figure 2).

The spatial pattern of the correlation between atmospheric deposition and accumulation of Hg in mosses clearly differs from that found for Cd and Pb. Correlations coefficients <0.2 (53.9% of total area) including negative values are widespread in Europe (grey colored in Figure 3). However, r_s values between 0.2 and 0.49 (38.1% of total area) were measured in ELCE units covering parts of the Balkan Peninsula, Scandinavia, Iceland and in some regions of Central Europe (green colored in Figure 3). Correlations between 0.5 and 0.69 are restricted to occur in one ELCE unit (2.5% of total area) located in western and Central Europe.

Gaseous elemental Hg constitutes more than 95% of the mass of atmospheric mercury. Additionally, Hg can also be found oxidized, both in gaseous and aqueous phases and possibly linked to the particulate matter. Atmospheric residence times of Hg species vary from one year for gaseous elemental Hg (Lindqvist and Rodhe, 1985), days to weeks for Hg adsorbed to particulate matter, and hours to days for oxidized gaseous species (Seigneur et al., 2003). These very different life times are due to the rates of dry and wet deposition which are in turn governed by physical and chemical properties of the species. Owing to the long life time of the dominant Hg component in the atmosphere, gaseous elemental Hg, Hg is considered as a global pollutant (Roustan and Bocquet, 2006), meaning that the source–sink relationship is rather weak due to both, long residence time of Hg in the atmosphere and long–range transport. Therefore, the statistical correlation between the Hg concentration in atmospheric deposition and mosses, acting as biological sinks, is lower than that of Cd and Pb in most ELCE units.

Table 1. *Minimum sample size needed for Europe, participating countries and ELCE units covered by the survey network with regard to mean and standard deviation of Cd, Hg and Pb concentrations in mosses in 2005*

	Cd	Hg	Pb
Number of sites missing for adequate coverage of Europe	53	4	268
Area of Europe covered by countries with missing sites (km^2)	668 672.5 (6.5%)	262 04.1 (1.1%)	1 725 928.2 (28.9%)
Number of ELCE units with missing sites	7/29 (24.1%)	3/26 (11.5%)	9/29 (31.0%)
Area covered by ELCE units with missing sites (km^2)	498 186.7 (12.3%)	105 844.8 (4.2%)	858 911.5 (21.5%)
Number of countries with missing sites	2/26 (7.7%)	1/14 (7.1%)	7/25 (28.0%)
Area covered by countries with missing sites (km^2)	668 672.5 (6.5%)	26 204.1 (1.1%)	1 725 928.2 (28.9%)

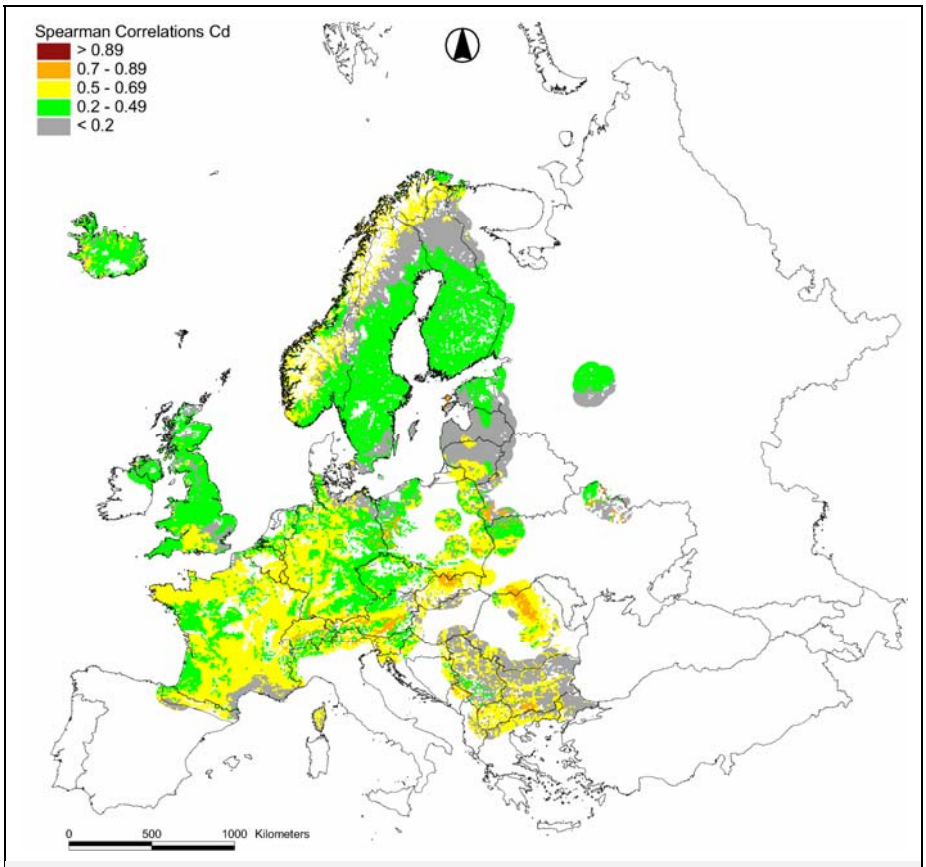

Figure 1. *Correlations of modeled Cd concentrations in total atmospheric deposition (2005) and in mosses (2005) within ELCE units.*

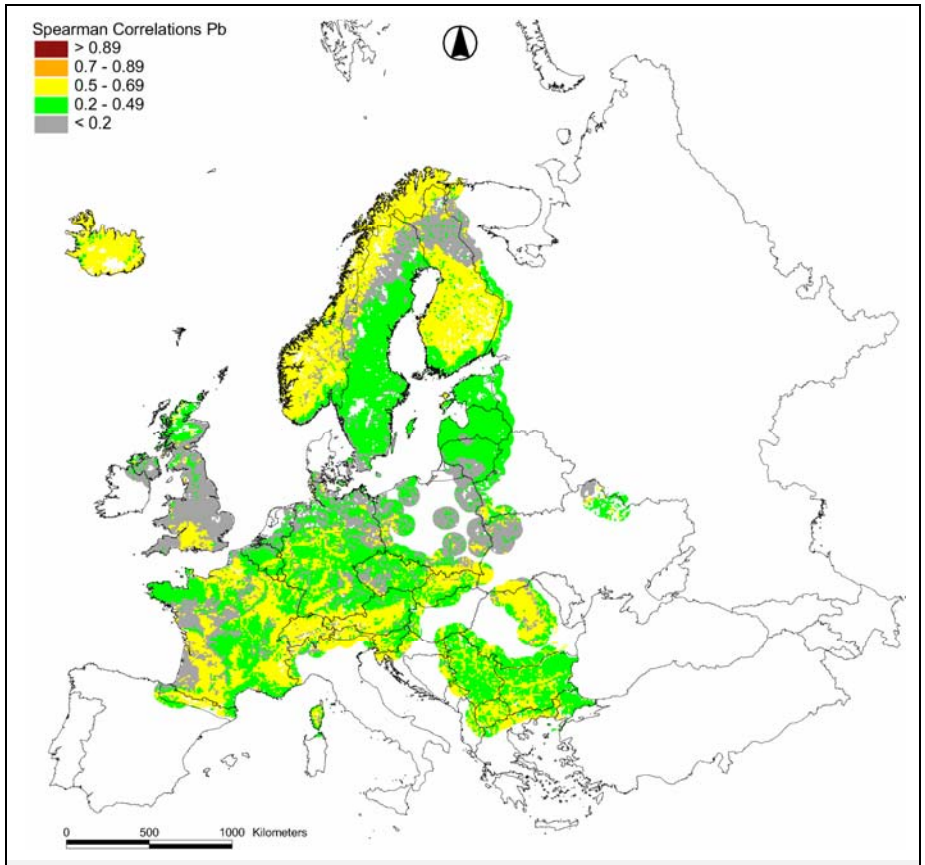

Figure 2. *Correlations of modeled Pb concentrations in total atmospheric deposition (2005) and in mosses (2005) within ELCE units.*

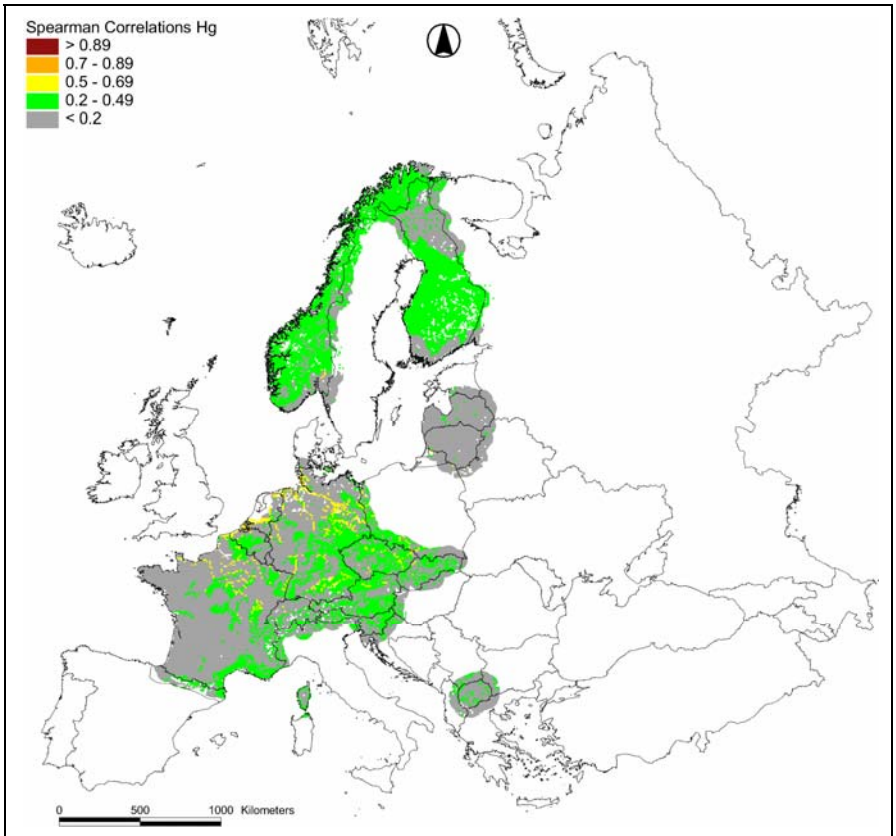

Figure 3. *Correlations of modeled Hg concentrations in total atmospheric deposition (2005) and in mosses (2005) within ELCE units.*

Considering the uncertainties in the EMEP modeled deposition data (Section 2.2) and the potential limitations and confounding factors in the use of mosses as monitors of atmospheric deposition (Harmens et al., 2008b; Aboal et al., 2010), the spatial patterns and temporal trends of both data sets agree reasonably well for Cd and Pb. The results specified for ecological land classed confirm that metal concentrations in mosses can serve complementing deposition monitoring and modeling to determine spatial patterns and temporal trends of Cd, Pb deposition (Aboal et al., 2010; Harmens et al., 2010).

4. Conclusions

From the current investigation the following conclusions can be drawn: for Cd, Hg and Pb the correlations between concentrations in mosses and the EMEP modeled total atmospheric deposition are land class–specific and metal–specific. However, significant positive correlations were found for about 71% (Cd), 35% (Hg) and 75% (Pb) of the ELCE units. Non–significant or significant low negative correlations were found in ecological land classes where mosses were sampled in a relative small number of EMEP grid squares. Correlations were generally not affected by using EMEP modeled deposition data for the year previous to sampling (data not shown) or averaged over three years previous to sampling of the mosses. For the majority of land ecological classes across Europe, the moss biomonitoring could be corroborated as a valid, complementary method for assessing spatial patterns and temporal trends of atmospheric deposition of metals across Europe.

To further investigate the relationship between atmospheric deposition of metals and their concentrations in mosses and the robustness of this relationship, we recommend that countries sample mosses at EMEP monitoring stations and/or national deposition monitoring stations. The presence of a dense national heavy metal deposition monitoring network and measurement of concentrations in mosses at the same sites is likely to reduce the uncertainty in modeled deposition data and might provide further insight into why in some of the ecological land classes correlations were not significantly positive between the two data sets. In a more general perspective this study allows concluding that moss surveys may complement monitoring and modeling atmospheric deposition of heavy metals. This is especially helpful in cases such as Hg with spatially scarce monitoring networks (Sprovieri et al., 2010). Advancements in land surface and chemical surface flux modeling are assumed to depend on improved descriptions of land use and vegetation characteristics. Combining them with "ecoregion information" (Pleim and Ran, 2011) should help for better defining key parameters.

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