Integrative evaluation of heavy metals concentrations in atmospheric deposition and biomonitors

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Abstract This paper aims at evaluating heavy metals (HM) concentrations in modelled atmospheric deposition and biomonitors. The model LOTOS-EUROS (LE) yielded data on HM deposition at a spatial resolution of 25 km by 25 km throughout Europe. The European Monitoring and Evaluation Programme (EMEP) provided model calculations on 50 km by 50 km grids. Corresponding data on HM concentration in moss, leaves, needles and soil were derived from the European Moss Survey (EMS), the German Environmental Specimen Bank (ESB) and the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests). The modelled HM deposition and respective concentrations in moss (EMS), leaves and needles (ESB, ICP Forests) and soil (ICP Forests) were investigated for their statistical relationships. Regression equations were applied on geostatistical surface estimations of HM concentration in moss and then the residuals were interpolated by use of Kriging interpolation. Both maps were summed up to a map of cadmium (Cd) and lead (Pb) deposition across Germany. Biomonitoring data were stronger correlated to LE than to EMEP. For HM concentrations in moss, highest correlations were found between geostatistical surface estimations of HM concentration in moss and deposition (LE).

Keywords: Deposition modelling; EMEP; Environmental Specimen Bank; European Moss Survey; ICP Forests; LOTOS-EUROS**.**

1. Introduction

Since 1979 the United Nations Economic Commission for Europe (UN-ECE) Convention on Long-range Transboundary Air Pollution (CLRTAP) has been seeking to limit, reduce and prevent long-range transboundary air pollution. Under CLRTAP, the Aarhus Protocol aims at reducing emission of cadmium (Cd), lead (Pb) and mercury (Hg). The assessment of ecotoxicological effects of HM emission includes measurements of atmospheric HM deposition, derived by complementary methods such as technical devices (bulk deposition or wet deposition samplers) and biomonitors as for instance mosses, leaves, needles, and soils or by numeric modelling. This paper aims at comparatively evaluating results from atmospheric deposition modelling and data on HM concentration in moss, tree foliage, and soils by means of correlation analysis (Nickel and Schröder 2016)[1].

2. Materials and Methods

2.1. Data

EMEP collects emission data and measurements of air and precipitation quality from European countries to model atmospheric transport and deposition of air pollutants. The model results are validated against standardised wet deposition measurements at, depending from the respective element, around 70 sites across Europe. The EMEP model has so far produced data at a spatial resolution of 50 km by 50 km (Tørseth *et al*. 2012). LOTOS-EUROS (LE; Builtjes *et al*. 2014; Schaap *et al*. 2008) calculates deposition values on a 25 km by 25 km grid covering Europe and on a 7 km by 7 km grid for Germany.

The EMEP model provides data on Europe-wide atmospheric deposition of Pb, Cd and Hg calculated by use of emission and meteorological data (Tørseth *et al*. 2012). In this study data for the total atmospheric deposition of Cd and Pb (2005, 2007-2011) and land use-specific data (Cd and Pb, 2011) for 3 of 18 classes comparable with LE were used: grassland as well as for deciduous and coniferous forests. The EMEP grid consists of 204 cells across Germany. For each EMEP raster grid the median and other descriptive statistical measures from the respective LE-grids were calculated. Using emission data and meteorological data, LE produces total deposition values for arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), vanadium (V), and zinc (Zn) for 2009-2011 and, respectively, Cd and Pb for 2005 with a spatial resolution of 25 km by 25 km for Europe and deposition data for Cd and Pb (2007-2011) on a grid of 7 km by 7 km covering Germany (9 land-use classes, averaged over the land-use classes in each grid cell). The modelled deposition values rely on meteorological data 2009-2011 (Europe) and 2007-2011 (Germany) respectively and

[1]All references cited in this extended abstract are included in:

Nickel S. and Schröder W. (2016), Integrative evaluation of data derived from biomonitoring and models indicating atmospheric deposition of heavy metals. Environmental Science and Pollution Research, 1-21 DOI 10.1007/s11356-015-6006-1 [Published online 2016.01.07].

emission data for 2000 (As, Cr, Cu, Ni, V, Zn) and 2005 (Cd, Pb) so that they do not contain any emission trend, contrary to the EMEP modelling results.

In addition to deposition modelling, biomonitoring programmes provide data on HM concentrations potentially correlated with atmospheric deposition of HM. Data on HM concentration in tree foliage, sampled between 2005 and 2011, were received from ESB and iCP Forests. ESB is an archive for samples documenting environmental quality. The specimens are collected in 13 areas representing specific ecosystem types at regular time intervals. They allow monitoring changes in the concentration of various substances in specimens across time (Rüdel *et al*. 2009). In this investigation HM concentrations in leaves and needles collected at ESB sites were included. From the ESB, foliage chemistry data for 2005 and 2007-2011 collected in representative terrestrial ecosystems (agrarian, urban-industrial, forestry and nearly natural) were acquired. These data comprise annual leaves collected from beech (*Fagus sylvatica*) and poplar (*Populus nigra* 'Italica') and 1-year old shoots from spruce (*Picea abies*) and pine (*Pinus sylvestris*). All samples were analysed annually for As, Cd, cobalt (Co), Cr, Cu, Hg, molybdenum (Mo), Ni, Pb, Ti and Zn concentrations according to standardized guidelines for sampling and sample treatment (UBA 2008). Contrary to EMS, the ESB foliage database encompasses merely 20 sampling sites.

Respective data from 103 German ICP Forests Level 2 plots were considered as well as data on HM concentrations in surface soil. An overview of the ICP Forests monitoring design is given by Ferretti and Fischer (2013). Data on foliar chemistry collected at roughly 1900 sites of the nation-wide soil monitoring (Hilbrig *et al*. 2014) could not be included, yet, but are intended to be.

Since 1990 the EMS every 5 years has been providing data on concentrations of up to 40 metallic elements in moss, concentrations of nitrogen since 2005 and persistent organic pollutants since 2010. In Germany, during 1990-2005 moss was sampled at roughly 700-1000 sites. All over Europe, up to 7300 sites were sampled (Harmens *et al*. 2015). The EMS provides data on HM concentrations in naturally growing moss following a harmonized methodology (iCP Vegetation 2014) enabling to map spatial patterns and temporal trends of HM pollution. In 2005 moss specimens were collected at 728 sample sites across Germany. Further data derived from moss specimen collected at 41 plots in the year 2004 in 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 analysed according to iCP Vegetation (2014). On this basis, Germany-wide maps on concentrations of As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Ti, V, and Zn in moss were calculated by use of geostatistical methods on a grid size of 3 km by 3 km. For analysing correlations between HM concentrations in moss and modelled atmospheric deposition (EMEP, LE) Cd and Pb concentrations in moss collected at 5776 sites across Europe were additionally integrated. Data on HM concentration in moss was derived from Pesch *et al*. (2007) as site-specific values and geostatistical surface estimations (Schröder *et al*. 2011) and included in this investigation together with the above mentioned data of HM accumulation in needles and leaves collected by ICP Forests and ESB and in surface soil specimens sampled by ICP Forests.

2.2. Statistics

The statistical analyses were performed by using R (R Development Core Team 2011). The calculations comprised Spearman rank correlation coefficents (r_s) and Kendall rank correlation coefficients (r_τ) as implemented in the R Package 'Kendall'. The significance of differences between mean values was examined by application of the Wilcoxon signed-rank, and the significance of differences between correlation coefficients was calculated according to Sachs and Hedderich (2009).

On this basis, research hypothesis 'correlation coefficients are different' were tested. Significance of differences increases with the dissimilarity of correlation coefficients and also in particular with the number of samplings. If χ^2 exceeds the hypothetical z-value according to Sachs and Hedderich (2009), the difference of correlation coefficients can be considered as significant. This were calculated at a significance level of $\alpha = 0.05$. For interpreting the results of the correlation analyses it should be noted that enhanced robustness is connected to lower precision (Hennemuth *et al*. 2013; Kendall and Gibbons 1990). To enable comparing the spatial patterns of modelled deposition of As, Cr, Cu, Ni, V, and Zn (LE, 2009-2011, 25 km by 25 km), Cd and Pb (LE, 2007-2011, 7 km by 7 km) and geostatistically mapped concentrations of respective HM in moss collected 2005 in Germany the data were normalized.

For computing Cd and Pb deposition maps for Germany at a high spatial resolution Regression Kriging (Hengl *et al*. 2004; Odeh *et al*. 1995; Schröder *et al*. 2011) was used. This procedure encompassed following steps: (1) applying regression models to geostatistical surface estimations of HM concentration in moss (regression maps as result), (2) analysing and interpolating residuals (regression model vs. LE and EMEP) by use of geostatistical methods (residual maps as result) and (3) summation of both (HM deposition maps as result). For 2005, regression models were applied to spatial data on Cd and Pb concentrations 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 centre point of the corresponding LE and EMEP grids. Results were investigated for their spatial auto-correlation using variogram analysis. Finally, the regression and residual maps were summed up to maps of Cd and Pb deposition (2005) on a grid of 3 km by 3 km.

A further step in the investigation was to correlate modelled HM deposition (EMEP, LE) with respective yearly measurements on HM concentrations in tree foliage from ESB. As LE deposition values were calculated with emissions for 2000 (As, Cr, Cu, Ni, and Zn) and 2005 (Cd,

Pb), the results for different years only show the inter-annual variability due to meteorology, but not any trend. Thus, data from the ESB were detrended with regard to LE comparisons, whereby the slope of the trend model was used

In addition to the correlation of HM concentrations in biomonitors sampled for the ESB, concentrations of Cd, Cu, Pb and Zn in leaves and needles and of Cd and Pb in soil specimens collected on ICP Forests plots across Germany were correlated with respective HM concentrations in atmospheric deposition modelled with LE (Cd, Pb: 2007-2011, 7 km by 7 km; Cu, Zn: 2009-2011, 25 km by 25 km) and EMEP (Cd, Pb, 2007-2011, 50 km by 50 km). The results were compared to results presented by Meyer *et al*. (2015) and Nickel *et al*. (2014) who found strong (Pb) and moderate (Cd) correlations between natural surface soils sampled across Norway and respective atmospheric deposition (EMEP). HM concentrations in leaves and needles, respectively, were determined in specimens collected from *Fagus sylvatica*, *Quercus robur*, *Quercus petraea*, *Picea abies*, *Pinus sylvestris*, and up to four organic soil layers according to BMVEL (2006). Since the LE modelling was based on emission data only for 2000 (Cu, Zn) and 2005 (Cd, Pb) and for meteorological data covering 2007-2011 the HM concentrations in leaves, needles and soils were detrended.

3. Results

This investigation quantified correlations of 1. LE and EMEP modelled HM deposition values; 2. EMEP and LE modelled HM deposition values and respective HM concentrations measured in moss 2005 and spatially estimated for unsampled locations; 3. LE and EMEP modelled HM deposition with HM concentration in tree foliage (ESB); 4. EMEP and LE modelled HM deposition values and respective HM concentrations in tree foliage and surface soil specimens (ICP Forests). For a detailed presentation of respective results, which cannot be given in this paper due to place restrictions, please refer to Schröder *et al*. (2016, footnote 1). In the following, the results of the above mentioned correlation analyses are discussed comprehensively.

As far as authors kept track of biomonitoring, modelling and mapping, the investigation at hand is the first one integrating data not only from different deposition models but also data derived by different biomonitoring approaches. Therefore, the result cannot be compared meaningfully to other studies. Based on a unique data base, the study investigated integratively whether different models calculate similar HM deposition values and how well the modelled values agree with HM measured and, in case of moss, spatially estimated HM concentrations in biomonitors such as moss, tree foliage and surface soils. EMEP and LE modelled HM deposition values were correlated showing differences in maximum values and geographical structure in some regions. The differences between EMEP and LE are much more pronounced for Pb than for Cd. The correlation of EMEP and LE modelled HM deposition values and, both, respective HM concentrations measured in moss 2005 and spatially estimated for unsampled locations show corroborate that moss concentrations indicate fairly well atmospheric deposition high spatial resolution.

The spatial patterns of modelled atmospheric deposition of Cd and Pb show that the differences between EMEP and LE results are strongly correlated with EMEP deposition values ($r_s > 0.9$), i.e. the differences are high where EMEP values are high as for instance in North Rhine-Westphalia. LE calculates higher deposition where wet deposition is high and where the EMEP values are low (e.g. in Bavaria). Consistent high correlations were computed by both EMEP and LE for coniferous forests while for grassland the spatial patterns derived by both models differ clearly. However, the median values calculated by both models are similar for grassland but rather different for coniferous forests. These striking differences may be due to different emission data used for modelling. Where needed, EMEP modelling encompasses expert judgements modifying emission data which seem to be unreasonable. Thus, in the future, common work of modellers, deposition and biomonitoring experts is needed to harmonize and validate the data used for estimation of atmospheric deposition.

Comparing the ratio of deposition values modelled for forests and grassland with respective values derived by moss analyses, the Cd and Pb deposition values calculated with LE differ less from biomonitoring results than it is the case for EMEP. **Table 1** contains a compilation of predominantly significant correlations between data derived by biomonitoring and modelling ($p < 0.05$). Accordingly, the correlation coefficients r_s range between 0.31 and 0.81. In 5 out of 8 cases LE results are stronger with moss values compared to EMEP. Higher correlations between moss and EMEP result exist only where the median moss concentration was exceeded. This is consistent with the fact that the major differences of spatial patterns computed based on EMEP and LE were observed in regions with high HM deposition.

The coefficients of correlation between modelled total deposition of As, Cd, Cr, Cu, Ni, Pb, V, and Zn and respective element concentrations in moss are predominantly higher for geostatistical surface estimations than for sampling site specific measurement values from which the estimations were derived (**Figure 1**). The correlation coefficients of spatially estimated moss values are moderate for As and Pb ($p < 0.01$) and low for Ni, Cd, Cu, and V. **Figure 2** shows that the coefficients of correlation between LE results and geostatistically estimated moss concentrations are mostly higher for dry deposition than for wet deposition. For Cr, unreasonable correlations were found which probably are due to emissions from the Kola Peninsula which were not reported but measured as a striking increase of Cr concentration in moss of about 100-200 % (Mohr and Schröder 2014). In Germany, moss specimens sampled in the Northeast were highly contaminated.

The HM concentrations in leaves and needles (ESB) could be proved to correlate with modelled deposition. The interpretation of this correlation should consider that, contrary to moss, element concentrations in leaves and needles are not only due to atmospheric deposition but potentially to element uptake by roots (Ceburnis and Steinnes 2009). The relations were found to be specimen specific and in case of Cd concentrations in one year old

spruce needles ecosystem type specific. The LE correlation exceeded those calculated for EMEP. However, these differences could not be proved to be significant. A drawback to be considered is the low spatial density of ESB data.

Contrary to the ESB data, the ICP Forests Level II data (2007-2011) reveal in 6 out of 7 cases stronger correlations to the deposition modelled with EMEP. The respective coefficients are lower than those for the relation between LE data and ESB results. Rather clear correlations could be found between Pb deposition (LE) and two years old needles of pine and spruce ($0.56 \leq r_\tau \leq 0.58$, $p < 0.01$). Highest and significant correlations ($p < 0.01$) between deposition of Cd (LE) and Oh soil horizons and between Pb deposition (LE) and L and Oh horizons were detected.

To conclude, spatial patterns of HM concentration in biomonitors (moss, leaves, and needles) and organic surface soil layers are predominantly higher correlated to deposition modelled by LE compared to EMEP (**Table 1**). For Cd, strongest correlations could be found between deposition data calculated by LE and concentrations in moss (Europe, geostatistically estimated) and needles (Germany). For Pb, the coefficients of correlation came out to be the highest for EMEP deposition and element concentrations in moss (Europe, geostatistically estimated) and leaves from ICP Forests Level II (Germany) and, respectively, LE deposition and leaves from ESB (Germany).

The LE deposition values of As, Cd, Ni, and Pb and respective geostatistically estimated concentrations in moss explained 17-30 % of the variance. The residuals of the four statistical models potentially could be reduced through considering environmental characteristics such as precipitation or land use (Nickel *et al*. 2014). The most severe drawback of the presented comparison of modelling and monitoring data indicating atmospheric deposition was the missing moss data for 2010. This is especially true since the surface estimations of HM concentrations in moss derived from moss sampled in 2005 could be corroborated as peculiarly appropriate for comparison with results from deposition modelling and for improving respective models. Thus, future moss survey designs should ensure spatial validity of measurements. This could be supported by integrating biomonitoring programmes such as EMS, ICP Forests and ESB.

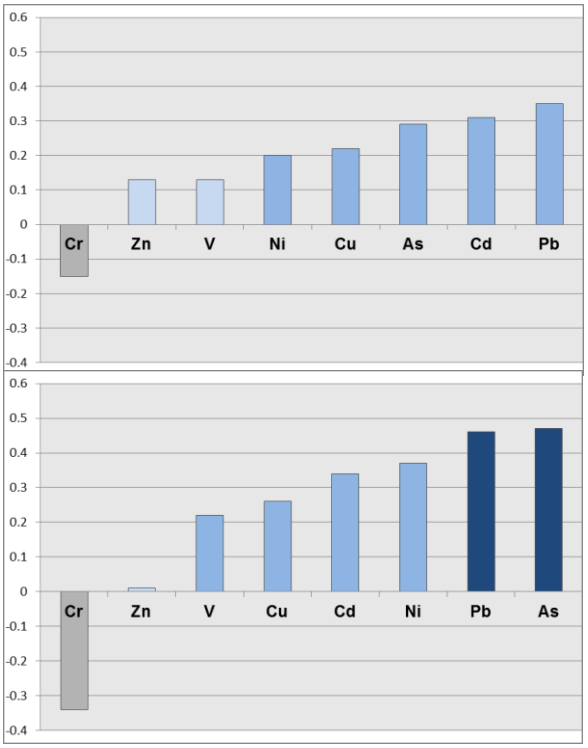

Figure 6. Coefficients (Spearman) of correlation between total deposition of As, Cd, Cu, Cr, Ni, Pb, V and Zn modelled with LE (Germany: 2009-2011) and site specific measurements of respective HM concentrations in moss 2005 (at the top) and derived geostatistical surface estimations of HM concentrations in moss 2005 (at the bottom)

Comparing both deposition models could not yield a reasonable statement on which tool was more suitable for this analysis. This is due to the fact that to that aim a rigorous and systematic comparative analysis based on same emission and meteorological data would be needed.

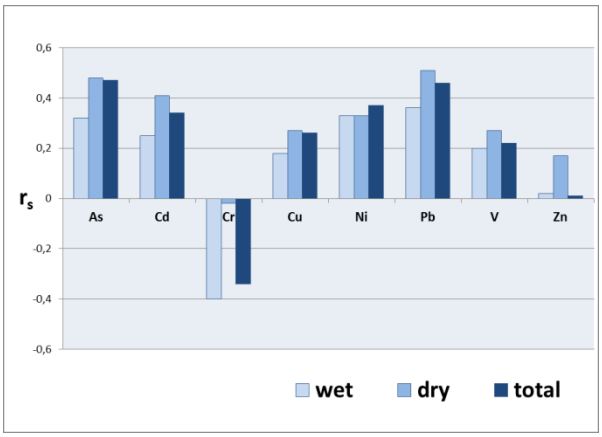

Figure 7. Coefficients (Spearman) of correlation between dry, wet and total deposition of As, Cd, Cr, Cu, Ni, Pb, V, and Zn modelled with LE (Germany: 2009-2011) and geostatistically estimated concentrations of respective HM (2005)

Table 1. Coefficients of correlation of Cd and Pb concentrations in biomonitors and respective total atmospheric deposition *(LE, EMEP)* in Europe and Germany

Biomonitoring network / Specimen type	Element	$r_{(LE)}$	$r_{(EMEP)}$
European Moss Survey (2005/2006)			
Moss, measured conc. (Germany)	Cd	0.31	0.27
Moss, measured conc. (Europe)	Cd	0.66	0.59
Moss, measured conc. (Germany)	Pb	0.35	0.31
Moss, measured conc. (Europe)	Pb	0.56	0.65
Moss, geostatistically estimated conc. (Germany)	Cd	0.37	0.43
Moss, geostatistically estimated conc. (Europe)	Cd	0.81	0.70
Moss, geostatistically estimated conc. (Germany)	Pb	0.49	0.44
Moss, geostatistically estimated conc. (Europe)	Pb	0.42	0.57
German Environmental Specimen Bank (2007-2011)			
Beech (*Fagus sylvatica*)	Cd	0.29	0.23*
Poplar (*Populus nigra 'Italica'*)	Cd	0.36	0.26*
Spruce (*Picea abies*), nearly natural ecosystems	Cd	0.49	0.36*
Spruce (*Picea abies*), forestry ecosystems	Cd	0.64	0.40*
Beech (*Fagus sylvatica*)	Pb	0.44	0.43
Poplar (*Populus nigra 'Italica'*)	Pb	0.63	0.44
Spruce (*Picea abies*)	Pb	0.29	0.27
ICP Forest Level II (2007-2011)			
Beech (*Fagus sylvatica*)	Cd	-0.03*	0.21
Spruce (*Picea abies*)	Cd	0.21	0.28
Pine (*Pinus sylvestris*)	Cd	0.34	0.08*
Beech (*Fagus sylvatica*)	Pb	0.26	0.40
Spruce (*Picea abies*)	Pb	0.19	0.30
Pine (*Pinus sylvestris*)	Pb	0.18	0.20
L – Litter layer	Cd	-0.04*	0.09*
Of – Fermentation layer	Cd	0.12*	0.04*
Ofh – Fermentation/Humus layer	Cd	0.02*	-0.06*
Oh – Humus layer	Cd	0.31	0.27
L – Litter layer	Pb	0.38	0.24
Of – Fermentation layer	Pb	0.21*	0.15
Ofh – Fermentation/Humus layer	Pb	-0.20*	0.26*
Oh – Humus layer	Pb	0.32	0.23

N = Sample size; r = Spearman's correlation coefficient (EMS) Kendall's correlation coefficient (ESB, ICP Forests); (LE) = with regard to comparisons with LOTOS-EUROS; (EMEP) = with regard to comparisons with EMEP; * = not significant ($p > 0.05$)