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## Modelling and mapping spatio-temporal trends of heavy metal accumulation in moss and natural surface soil monitored 1990–2010 throughout Norway by multivariate generalized linear models and geostatistics



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### HIGHLIGHTS

- Comprehensive analysis of correlation between heavy metal deposition and accumulation.
- Generalized linear models (GLM) can reveal a better fit than respective linear models.
- Integrated use of GLM and geostatistics yield a high spatial resolution.
- Atmospheric deposition, land use, elevation and precipitation are relevant factors.
- From 1995 to 2010 lead concentration in both moss and surface soil decreases.

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### ABSTRACT

**Objective.** This study explores the statistical relations between the accumulation of heavy metals in moss and natural surface soil and potential influencing factors such as atmospheric deposition by use of multivariate regression-kriging and generalized linear models. Based on data collected in 1995, 2000, 2005 and 2010 throughout Norway the statistical correlation of a set of potential predictors (elevation, precipitation, density of different land uses, population density, physical properties of soil) with concentrations of cadmium (Cd), mercury and lead in moss and natural surface soil (response variables), respectively, were evaluated. Spatio-temporal trends were estimated by applying generalized linear models and geostatistics on spatial data covering Norway. The resulting maps were used to investigate to what extent the HM concentrations in moss and natural surface soil are correlated. **Results.** From a set of ten potential predictor variables the modelled atmospheric deposition showed the highest correlation with heavy metals concentrations in moss and natural surface soil. Density of various land uses in a 5 km radius reveal significant correlations with lead and cadmium concentration in moss and mercury concentration in natural surface soil. Elevation also appeared as a relevant factor for accumulation of lead and mercury in moss and cadmium in natural surface soil respectively. Precipitation was found to be a significant factor for cadmium in moss and mercury in natural surface soil. The integrated use of multivariate generalized linear models and kriging interpolation enabled creating heavy metals maps at a high level of spatial resolution. The spatial patterns of cadmium and lead concentrations in moss and natural surface soil in 1995 and 2005 are similar. The heavy metals concentrations in moss and natural surface soil are correlated significantly with high coefficients for lead, medium for cadmium and moderate for mercury. From 1995 up to 2010 the modelled moss and natural surface soil estimates indicate a decrease of lead concentration in both moss and natural surface soil. In the case of the moss data the decrease of accumulation is more pronounced. By contrast, the modelled cadmium and mercury

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concentrations do not exhibit any significant temporal trend. **Conclusions.** In Europe, there is hardly any nation-wide investigation of statistical correlations between the accumulation of heavy metals in moss and natural surface soil and potential influencing factors such as atmospheric deposition. This study could show that assessments of heavy metal concentrations in natural surface soil could complement biomonitoring with moss but should not replace it since the heavy metal concentrations in mosses reliably traces the spatial pattern of respective atmospheric deposition. Generalized linear models extend established methods for estimating spatial patterns and temporal trends of HM concentration in moss and natural surface soil.

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## 1. Introduction

Since 1990, the European Moss Surveys every 5 years provide data on heavy metal (HM) concentration in moss as biomonitors of atmospheric deposition (Harmens et al., 2004, 2008, 2010). The main purpose of this monitoring is to substantiate scientifically environmental policy measures against air pollution through inventorying and mapping atmospheric HM deposition and subsequent bioaccumulation as a serious problem of human health and ecosystem integrity. Moss is used to indicate HM bioaccumulation since metal ions are predominantly absorbed above ground and the annual increment of growth allows temporal allocation of HM concentration in the moss habitus. Every five years accumulation of up to 40 elements in moss is studied according to a standardized protocol (ICP Vegetation, 2010).

In the Norway data on concentrations of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn) in moss have been collected on a nationwide scale since 1977, and mercury (Hg) since 1990. A dense network with 1.5 sample sites per 1000 km<sup>2</sup> was established (Steinnes et al., 2011). For the present investigation data on Pb, Hg, and Cd concentrations collected in 1995, 2000, 2005 and 2010 were used. In parallel to the moss survey data for HM concentrations in natural surface soil were collected in 1995 (Nygård et al., 2012) and 2005 according to the same sampling network. The uppermost 3 cm of the O horizon (predominantly podzols) were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). In the present study data on HM concentrations in natural surface soil for Cd (1995, 2005), Pb (1995, 2005) and Hg (2005) respectively were used.

In previous investigations close statistical relationships between Pb and Cd concentrations in moss and data from the EMEP-model for atmospheric fall out in Europe have been shown (Schröder et al., 2011). EMEP, the European Monitoring and Evaluation Programme, is part of the UNECE (United Nations Economic Commission for Europe) Convention on Long-range Transboundary Air Pollution (CLRTAP) and serves to collect emission data from European countries to model atmospheric transport and deposition of air pollutants (Tørseth et al., 2012). EMEP provides data on Europe-wide atmospheric deposition of Pb, Cd and Hg calculated with a grid size of 50 km by 50 km. We used data for the total deposition over three years as a corresponding parameter to the HM concentration in moss (e.g. the period of 2003–05 represents the base year of 2005).

The following study aims at modelling spatial patterns and dynamics of HM concentrations in moss and natural surface soil across Norway. This was done by extending well established Regression-Kriging-Techniques (Hengl et al., 2004; Odeh et al., 1995) with multivariate generalized linear models (GLM) (Madsen and Thyregod, 2011; Nelder and Wedderburn, 1972) instead of simple linear regression models as basis. Using the above

data from Norway, the statistical correlation of a set of potential predictor variables (elevation, precipitation, distribution of different kinds of land use, population density, and physical properties of surface soil) with response variables (HM concentration in natural surface soil and moss respectively) were evaluated using GLM's. Then the regression functions in conjunction with a Geographic Information System (GIS) were used to transform spatial information of the independent variables to time-discrete maps of HM concentration in moss and natural surface soil, and kriging interpolation methods were applied to fit these regression maps onto the residuals. Based on the HM maps of Norway calculated as briefly described above, the correlation of HM concentration in moss and natural surface soil were analyzed statistically.

## 2. Methods

### 2.1. Statistical modelling

Generalized linear models (GLM) are parametric statistics not assuming a normal error distribution (Madsen and Thyregod, 2011; Nelder and Wedderburn, 1972). By specifying the assumed error distribution of the response variable, which has to be from the family of exponential distributions, data transformation can be avoided. Additionally, a function linking expected values to explanatory variable has to be determined (link function). GLM make use of maximum likelihood tests instead of least squares estimators to assess statistical relations of explanatory variables with response variables. Therefore, deviances but not sums of squares are the criterion to measure the fit of a model (Dalgaard, 2002). For various kinds of data specific error distributions with matching link functions are usually assumed (Zuur et al., 2009). Due to the assumption of the error distribution, the regression of residuals does not follow a straight line but a distribution specific shape. Contrary to linear regression models GLM do not calculate a direct measure of explained variance or goodness-of-fit (UCLA, 2011).

The data examined here are concentrations of Cd, Hg and Pb, which are continuous data with positive values. Therefore either a Gamma distribution with inverse link and lognormal function respectively or a Gaussian distribution with identity as link function can be assumed. The latter gives results identical to those of a linear regression. We inspected the diagnostic plots to decide which model gives the best fit for the data at hand. Diagnostic plots were also used to identify and, if necessary, exclude outliers. Homogeneity of data was assessed by plotting residuals against fitted values and square roots of standardized residuals against fitted values. For both plots a regularly distributed scatter diagram is expected. Clustering of points is a hint for violation of homogeneity. A quantile–quantile plot (QQ Plot) was used to assess whether residuals were normally distributed. Standardized residuals in linear models and standardized deviance residuals in generalized linear

**Table 1**

Potential predictors for HM concentration in moss and natural surface soil in 1995, 2000, 2005 and 2010.

Variables	Comment & source	Unit	1	2	3	4
Sea distance	Derived from administrative borders	km	p	p	p	p
Elevation	World digital elevation model (ETOPO5)	m. a. s. l	p	p	p	p
Precipitation	1991–2002	mm/month	p	p	p	p
Density of agricultural land use within a 5 km radius	Derived from CORINE Land Cover (CLC 2006)	%	p	p	p	p
Density of forestry land use within a 5 km radius	Derived from CLC 2006	%	p	p	p	p
Density of urban land use within a 5 km radius	Derived from CLC 2006	%	p	p	p	p
Population density	1995, 2000, 2005 or 2010 (respectively)	inhabitants/km <sup>2</sup>	p	p	p	p
Clay content	Proportion of grain size (proxy for soil type)	%	p	p	p	p
HM deposition	Total deposition of Cd, Hg, Pb over three years	µg/m <sup>2</sup>	p	p	p	p
HM concentration in moss	Concentration of Cd, Hg, Pb in moss,	µg/g	r	r	–	p
HM concentration in soil	Concentration of Cd, Hg, Pb in natural surface soil	µg/g	–	p	r	r

**Explanation:** 1–4 = variable sets; r = examined as response variable; p = examined as potential predictors.

models were plotted against theoretical quantiles. Distribution of residuals along a straight line indicates normal distribution of residuals. In all cases, diagnostic plots of the full GLM revealed a better fit than those of the respective linear model. We evaluated the relations of up to ten potential predictor variables (Table 1) with Cd, Pb and Hg concentrations in moss (1995, 2000, 2005, 2010) and natural surface soil (1995, 2005).

Models were optimized using Minimum Adequate Model (MAM). We inspected summary outputs and analysis of deviance type I and II tables derived using the car package (Fox and Weisberg, 2011). Non-significant predictors were stepwise eliminated from a model using a top-down approach. Likelihood ratio tests (R function anova with argument test set to “Chisq”) were used for comparison of the full and reduced models to find the optimum model including only those independent variables which explained best the variance in the data. However, as there were missing values in some predictors, reduced models were often based on a sample size larger than original models. In this case models could not be compared using anova. Regression equations and residuals were extracted from the final model for further analysis. All statistical analysis were implemented in R (R Development Core Team, 2011).

## 2.2. Spatial regression modelling

The following spatio-temporal analysis and modelling of HM concentration in moss and natural surface soil were performed using multivariate regression kriging. This was done by an application of the generalized linear models to available spatial information (regression maps as result), geostatistical analysis and interpolation of the residuals (residual maps as result) and a final summation of both (HM maps).

All geographic information on the predictor variables such as HM deposition, climate, sea proximity, altitude, clay content, population and land use features available with blanket coverage of Norway were firstly combined by means of classical GIS functions (overlay, spatial join). Based on this, generalized linear models were applied to calculate a corresponding number of regression maps, which result from reasonable combinations of HM concentration in moss and natural surface soil samples as dependent variable (Cd,

Hg and Pb) with and without respective HM concentration in moss and natural surface soil samples as predictor variables for the years 1995, 2000, 2005 and 2010.

Secondly the residuals, which represent the unexplained variation after fitting the GLM's, 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 (Schröder et al., 2012). A semi-variogram describes the spatial auto-correlation of point measurements. Meaningful parameters for evaluating the semi-variogram are the so-called nugget, sill and major range (Johnston et al., 2001). 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 with 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 map series of Cd, Hg and Pb concentrations in moss (1995, 2000, 2005 and 2010) and natural surface soil (1995, 2005) respectively with grid size of 5 km × 5 km. Based on these 12.836 grid cells across Norway HM concentration in moss and soil were analyzed for their statistical correlations.

## 3. Results

All analyses with HM concentration in moss or soil as response variable respectively were based on a reasonably large sample size of at least 361 out of 463 sample points. Sample sites within a 2 km radius were assumed as comparable. Some sample sites had to be excluded from the analyses due to missing information with regard to the predictor variables. To avoid multicollinearity, the predictors were analyzed for significant correlations. Multicollinearities were detected in particular concerning the relationship between concentrations of Cd and Pb in moss and soil sample respectively and atmospheric deposition (Table 2).

### 3.1. Lead (Pb)

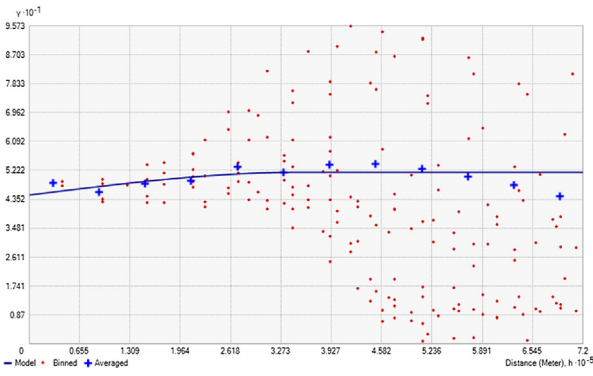
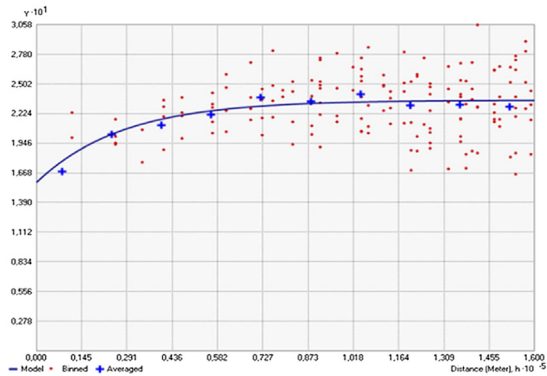
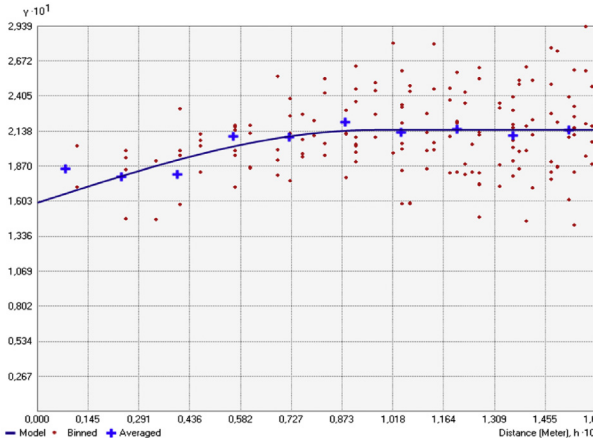
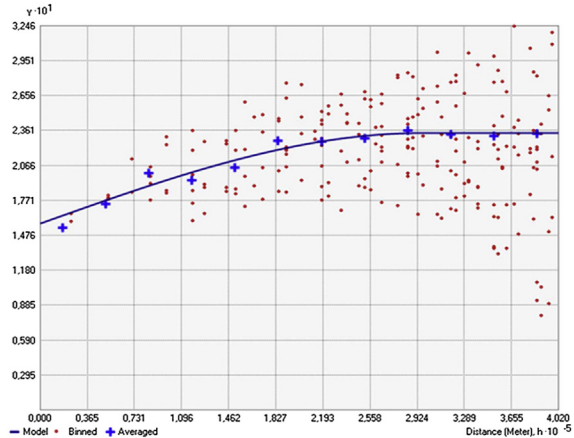
After model optimization the main factors influencing the concentration of Pb in moss in all four sample years were density of

**Table 2**

Spearman's rank correlation coefficients of relationships between HM deposition across Norway and concentration in moss and natural surface soil respectively.

Heavy metal (HM)	HM deposition vs. concentration in moss	HM deposition vs. concentration in soil
Cadmium (Cd)	0.58	0.50
Mercury (Hg)	0.30	0.18
Lead (Pb)	0.70	0.67

**Table 3**  
Semi-variograms of residuals of modelled Pb concentration in moss in 1995, 2000, 2005 and 2010 without respective concentration in natural surface soil as predictor variable.

1995	2000
 <p>Method: Ordinary Kriging</p> <p>Lag size 60 km Nugget/sill ratio 87% Range 350 km Mean error -0.0819 Model type Spherical</p>	 <p>Method: Ordinary Kriging</p> <p>Lag size 16 km Nugget/sill ratio 70% Range 90 km Mean error -0.00062 Model type Spherical</p>
2005	2010
 <p>Method: Ordinary Kriging</p> <p>Lag size 20 km Nugget/sill ratio 76% Range 90 km Mean error -0.00048 Model type Spherical</p>	 <p>Method: Ordinary Kriging</p> <p>Lag size 33.5 km Nugget/sill ratio 65% Range 290 km Mean error -0.00062 Model type Spherical</p>

forestry and urban land use in a 5 km radius around the sample site and atmospheric deposition of Pb over a three year period. The 1995 and 2005 samplings additionally revealed a significant correlation of agricultural land use in a 5 km radius. In 2010 the samplings indicate an effect of sea distance. Elevation was found to be an important factor in 2000, 2005 and 2010. Clay content in soil was a relevant factor in 1995. Pb concentration decreased slightly with increasing elevation. Lower densities of forest, urban or agricultural land cover lead to decreased Pb concentration in moss. Increasing atmospheric deposition of Pb over a three year

timeframe entailed an increase in Pb concentration in moss. The Pb concentration in moss and clay content showed an inverse correlation.

Based on these four optimized statistical models a respective number of regression maps were calculated by applying the GLM's on geographic information on predictors available with blanket coverage of Norway. Secondly the modelled data were spatially fitted to the measurements by integrating the residuals into the regression maps (chapter 2). Table 3 contains the semi-variograms of Pb concentration in moss for all four sample years. It becomes

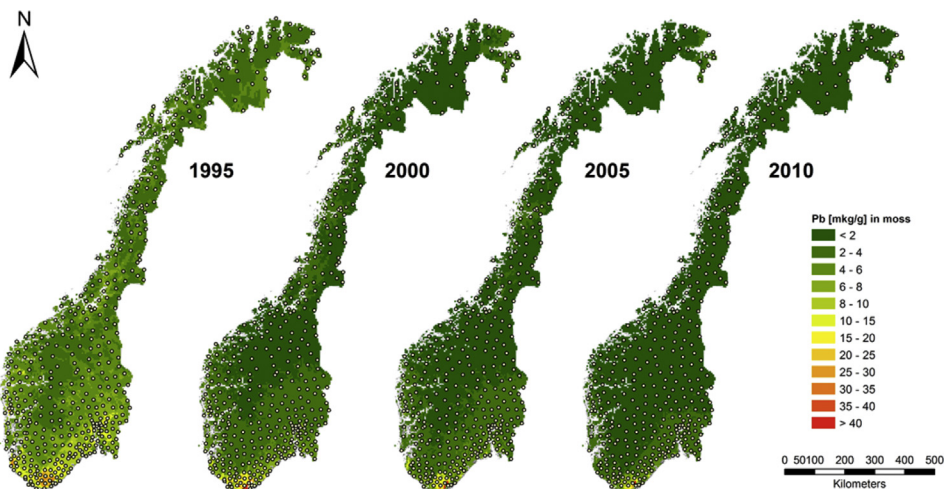


Fig. 1. Temporal trend of Pb concentration in moss (1995–2010) modelled without respective concentration in natural surface soil as predictor variable.

clear, that in every case the residual values ( $\gamma$ ) increase with the distance ( $h$ ). But, regarding the nugget/sill ratios of Pb residuals a positive auto-correlation could only be ascertained in 2000, 2005 and 2010. Accordingly the sample sites for these years represent a continuous surface, so that the modelled semi-variance could be applied with kriging interpolation within the calculated major range (Table 3) around the sample sites.

In contrast the prevailing negative auto-correlation of Pb residuals in 1995 suggests that the GLM's alone explain best the given variance. Derived from the time-discrete map series depicted in Fig. 1 the median value of modeled Pb concentration in moss across Norway decreased from 4.23  $\mu\text{g/g}$  in 1995 to 1.96  $\mu\text{g/g}$  in 2000, 1.64  $\mu\text{g/g}$  in 2005, and 1.15  $\mu\text{g/g}$  in 2010 (Table 4).

The core areas with Pb concentration above the median of 1.15  $\mu\text{g/g}$  in 2010 are located in the counties of Hinnøya, Nordland, Sogn og Fjordane, Hordaland, Rogaland, Sørlandet, Telemark, Buskerud, Vestfold, Østfold, Oslo, Akershus, in the South of Hedmark and Oppland respectively and in the eastern Part of the Finnmark county. The highest Pb concentrations ( $>2.26 \mu\text{g/g}$  in 2010 = 90th percentile) are observed in the southernmost part of Norway: Rogaland, Agder, Telemark, Vestfold, Østfold, Akershus, Oslo (Fig. 1).

With respect to the concentration of Pb in natural surface soil the density of urban land use in a 5 km radius around the sample site and deposition of Pb over a three-year period are the key factors in both sampling years (1995, 2005). In 1995 population density also appears as an important factor. There was no correlation of elevation, precipitation, clay content, or distance to the ocean with Pb concentration in natural surface soil. Lower densities of urban land cover and population correspond to lower Pb concentration in natural surface soil. Increasing deposition of Pb over a three-year timeframe causes an increase in Pb concentration in natural surface soil.

The residuals of HM concentration in natural surface soil reveal a positive spatial auto-correlation in 1995. By contrast, the residual analysis of the data for 2005 suggests, that the GLM's alone explain

best the given variance. In the period of 1995–2005 the modelled Pb concentration in natural surface soil decreases from 24.75  $\mu\text{g/g}$  to 21.43  $\mu\text{g/g}$  (Fig. 2, Table 4). In contrast to that slightly declining trend, there were still 20.5% of the country's land area with partly significant increases in Pb concentration in natural surface soil. The main counties with Pb concentration above the median value in 2005 are Hordaland, Rogaland, Sørlandet, Telemark, Vestfold, Østfold, Oslo, Buskerud, Akershus, the South of Hedmark and Oppland respectively, Nordland and several parts of the Finnmark. Core areas with Pb concentration  $>59.93 \mu\text{g/g}$  (= 90th percentile) were observed in the counties of Rogaland, Agder, Sørlandet, Telemark, Vestfold, Østfold, Akershus, and Oslo.

Based on a grid with a resolution of 5 km by 5 km across Norway the calculated Pb concentrations in moss and natural surface soil correlated significantly with a spearman's rank coefficient of  $r(s) = 0.65$  (1995) and  $0.76$  (2005) respectively ( $p < 0.05$ ). This may be classified as a strong association (Brosius, 2013). The temporal decrease of the Pb concentration in moss is generally more

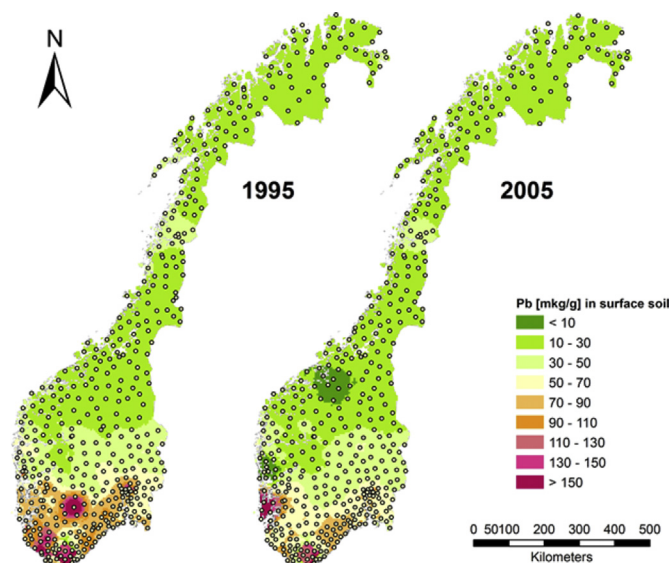


Fig. 2. Temporal trend (1995–2005) of Pb concentration in natural surface soil modelled without respective concentration in moss as predictor variable.

Table 4  
Percentiles of modelled Pb concentration in moss and natural surface soil.

Year	Pb in moss [ $\mu\text{g/g}$ ]				Pb in soil [ $\mu\text{g/g}$ ]	
	1995	2000	2005	2010	1995	2005
50th p	4.23	1.96	1.64	1.15	24.75	21.43
90th p	7.01	4.03	3.43	2.26	78.14	59.93

**Table 5**  
Percentiles of modelled Cd concentration in moss and natural surface soil.

Year	Cd in moss [µg/g]				Cd in soil [µg/g]	
	1995	2000	2005	2010	1995	2005
50th p	0.08	0.07	0.07	0.07	0.41	0.45
90th p	0.15	0.13	0.09	0.12	0.79	0.79

pronounced than in the case of respective HM concentration in natural surface soil.

Two apparent “hot spots” in Fig. 2 are caused by anomalously high values at one single site: In 1995 in Telemark county (799 ppm) and in 2005 in Rogaland county (1259 ppm). At ten surrounding sites the Pb levels were  $48 \pm 15$  ppm and  $68 \pm 42$  ppm, respectively. Presumably these single high values are due to either local Pb contamination, e.g. from leaded ammunition used by hunters.

3.2. Cadmium (Cd)

A similar pattern to that observed for Pb was found regarding Cd concentration in moss, which increased with increasing forestry, agricultural and urban land use in all four sampling years. There was no correlation between elevation and Cd concentration in the moss. Decreased precipitation had a positive effect on Cd bioaccumulation in moss (1995, 2000 and 2005). Again the total deposition of Cd over a three year period was significantly associated with its concentration in moss. With increasing total deposition, the deposition in moss increased. The association between clay content and Cd concentration in moss is characterized by a negative correlation.

In view of negative spatial auto-correlations in 1995, 2000 and 2010, each of the maps (incl. 2005) was calculated without residual kriging. As can be seen in Table 5 the median of Cd concentration in moss amounts to 0.08 µg/g in 1995, 0.07 µg/g in 2000, 0.07 µg/g in 2005 and 0.07 µg/g in 2010, i.e. the model calculations do not exhibit any significant trend.

HM accumulation in moss with values > 0.07 µg/g in 2010 (= 50th percentile) are located in Sogn og Fjordane, Hordaland, Rogaland, Sørlandet, Telemark, Vestfold, Østfold, Oslo, Buskerud, Akershus and in the South of Hedmark and Oppland respectively (Fig. 3). Centers with values >0.12 µg/g (= 90th percentile) have

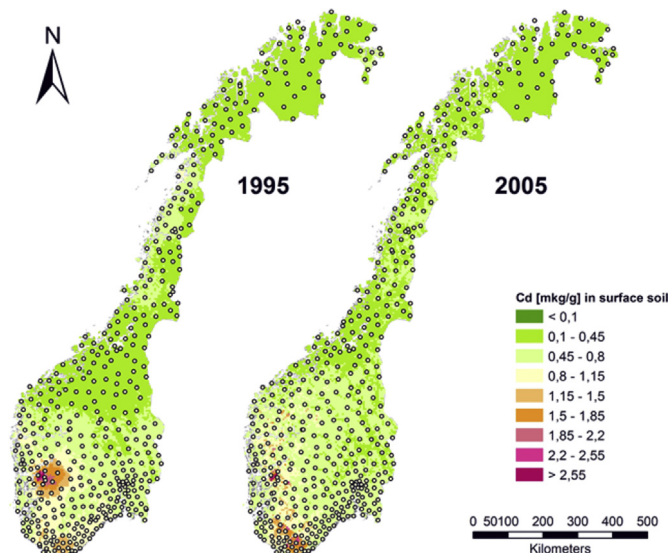


Fig. 4. Temporal trend (1995–2005) of Cd concentration in natural surface soil modelled without respective concentration in moss as predictor variable.

been detected in Sørlandet, Telemark, Vestfold, Østfold, Akershus, Oslo and the east of Finnmark county in the year of 2010.

Regarding Cd concentration in natural surface soil we found a positive correlation with elevation in both sample years. Neither population density, density of forestry/agricultural land use, distance to the sea nor annual precipitation had a significant impact on the Cd concentration in natural surface soil. In 1995 decreased clay content had a positive correlation with Cd accumulation in natural surface soil. In 2005 a positive relationship was apparent between density of urban land use and Cd concentration in natural surface soil. Again the total deposition of Cd over a three year period had a significant influence on its concentration in natural surface soil.

Comparing both regression models with/without respective concentration in moss as independent variables, the Root Mean Square Errors amounts to 0.49 and 0.54 in 2005. To avoid multicollinearity as mentioned above we use the model, which do not take into account the concentration in moss as predictor. The median of the modelled Cd content in natural surface soil throughout

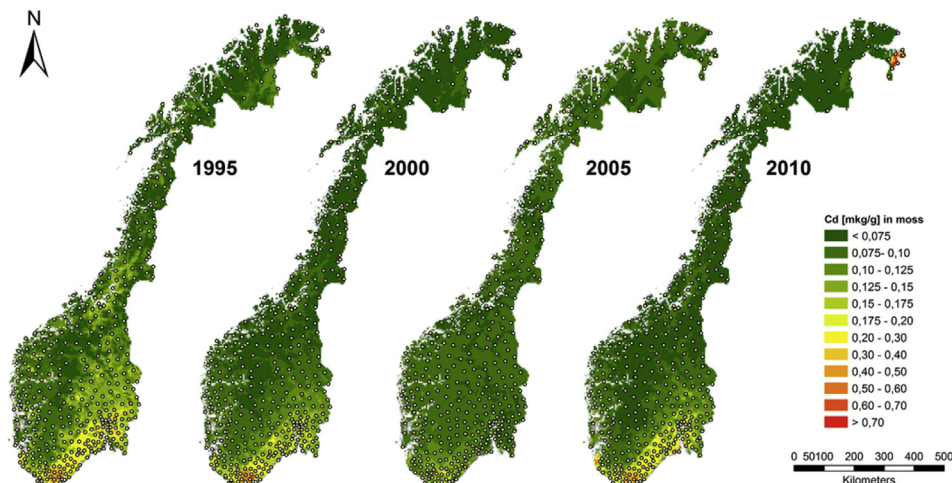
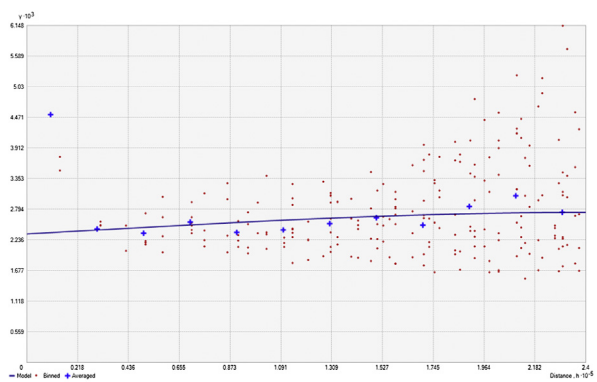
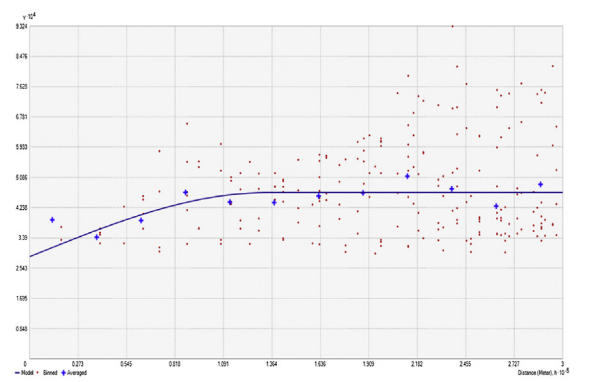
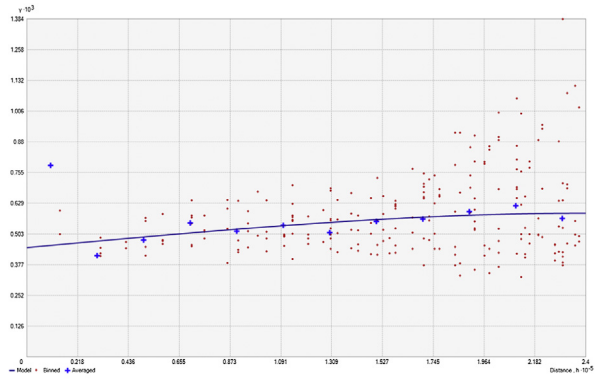
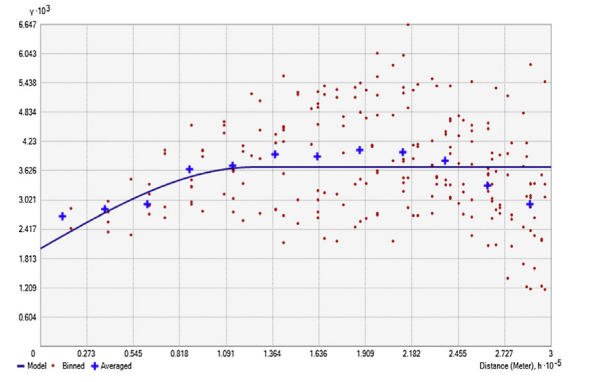


Fig. 3. Temporal trend of Cd concentration in moss (1995–2010) modelled without respective concentration in surface soil as predictor variable.

**Table 6**

Semi-variograms of residuals of modelled Hg concentration in moss in 1995, 2000, 2005 and 2010 without respective concentration in natural surface soil as predictor variable.

1995	2000
 <p>Method: Ordinary Kriging</p> <p>Lag size 20 km Nugget/sill ratio 86% Range 240 km Mean error -0.000682 Model type Spherical</p>	 <p>Method: Ordinary Kriging</p> <p>Lag size 25 km Nugget/sill ratio 61% Range 135 km Mean error -0.000197 Model type Spherical</p>
2005	2010
 <p>Method: Ordinary Kriging</p> <p>Lag size 20 km Nugget/sill ratio 76% Range 240 km Mean error -0.0000081 Model type Spherical</p>	 <p>Method: Ordinary Kriging</p> <p>Lag size 23 km Nugget/sill ratio 55% Range 125 km Mean error -0.000069 Model type Spherical</p>

Norway goes up slightly from 0.41 µg/g in 1995 up to 0.45 µg/g in 2005 without any distinct changes in the 90th percentile (Table 5).

As depicted in Fig. 4 the core areas with concentrations above the 50th percentile in 2005 are located in almost every county of Norway except Møre og Romsdal, Sør Trøndelag, Hinnøya, Troms and Finnmark. The generally highest Cd concentrations in surface soil (>0.79 µg/g = 90th percentile) in 2005 were observed in the southernmost regions of Norway and the greater Oslo region. An apparent anomaly in Hordaland county is related to contamination from the Odda zinc smelter. The spatial estimates of Cd concentration in moss and natural surface soil correlated significantly with Spearman's rank coefficient of  $r(s) = 0.49$  in 1995 and  $r(s) = 0.67$  in

2005. These relationships can be characterized as medium and strong respectively.

### 3.3. Mercury (Hg)

Concerning the accumulation patterns of Hg in moss a decrease with increasing elevation is observed in all four sampling years, and an increase with increasing deposition of Hg. The model examining data from 2000 additionally revealed a decrease of Hg concentration in moss with increasing annual precipitation and forestry land use. The model for the 2005 sampling showed a positive correlation of population density with Hg concentration.

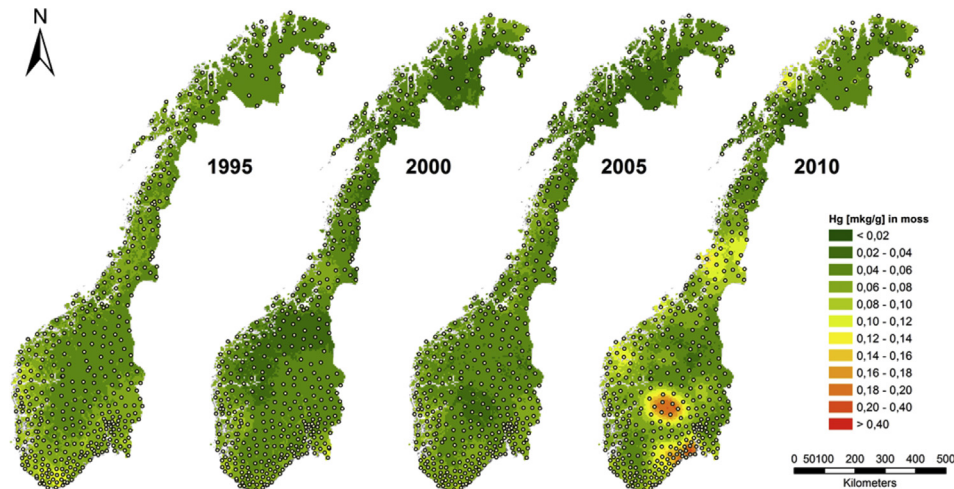


Fig. 5. Temporal trend of Hg concentration in moss (1995–2010) modelled without respective concentration in natural surface soil as predictor variable.

Relevant factors for the accumulation of Hg in natural surface soil are forestry, agricultural and urban land use, and also total atmospheric deposition with positive correlations in the sample year 2005. Elevation and population density appear to show no correlation. Additionally we found a decrease of Hg concentration in natural surface soil with increasing annual precipitation and distance from the ocean. The alternative exploration with respective concentration in moss as predictor variable (Table 1) revealed a positive impact on concentration in natural surface soil. In this case the correlation of sea distance and Hg deposition is not statistically significant.

With regard to the HM concentration in moss positive spatial auto-correlation was found in the residuals in 2000, 2005 and 2010 (Table 6), so a respective number of residual maps were calculated by use of kriging interpolation. The semi-variograms reveal nugget/sill-ratios between 55% and 76%. In 1995 the nugget/sill-ratio of 86% indicates, that the GLM's alone explain best the given variance. In a similar way the HM concentration in natural surface soil in 2005 did not show any significant spatial auto-correlation.

Fig. 5 illustrates a heterogeneous spatio-temporal distribution of Hg in moss. The median of the concentration in moss amounts to 0.06  $\mu\text{g/g}$  (1995, 2000, 2010) and 0.05  $\mu\text{g/g}$  (2005), i.e. any significant trend could not be detected (Table 7). The 90th percentile of 0.10  $\mu\text{g/g}$  in 2010 indicates slightly higher levels of Hg deposition in 2010 than before.

Based on the underlying data of Fig. 6 the median value of Hg concentration in natural surface soil throughout Norway have been calculated to 0.18  $\mu\text{g/g}$  in 2005. Regarding the 50th and 90th percentiles in Table 7 and the Root Mean Square Errors with  $\text{RSME} = 0.11$  both modellings without and with respective Hg concentration in moss as predictor variable appear with no significant difference. Inequalities regarding the distributions were also checked for statistical significance by means of Mann–Whitney–U-Test. According to this both populations in contrast appear to be different ( $p = 0.05$ ). The core areas with Hg

concentration above 0.21  $\mu\text{g/g}$  (= 90th percentile) are located in the South of Norway in the counties of Sørlandet, Telemark, Buskerud, Vestfold, Østfold, Akershus and Oslo.

The statistical relationship between Hg concentration in moss and natural surface soil respectively has to be classified as weak (Brosius, 2013) with a low rank coefficient of  $r(s) = 0.18$ .

#### 4. Conclusions

The integrated use of multivariate generalized linear models and kriging interpolation enables to extend established methods of modelling and mapping spatial patterns and temporal trends of HM accumulation in the environment. The multivariate regression-kriging approach enables to, both, investigate the statistical relevance of a comprehensive set of potentially influencing variables such as elevation, precipitation, density of urban, agricultural and forestry land use atmospheric deposition, and map the spatial pattern of the respective target variable.

Using the example of Norway it was confirmed, that full and optimized generalized linear models can reveal a better fit than those of the respective linear models. This is because GLM's do not assume normal error distribution of HM concentration as response variable. Based on the presented spatial regression modelling approach HM maps with a high spatial resolution can be calculated.

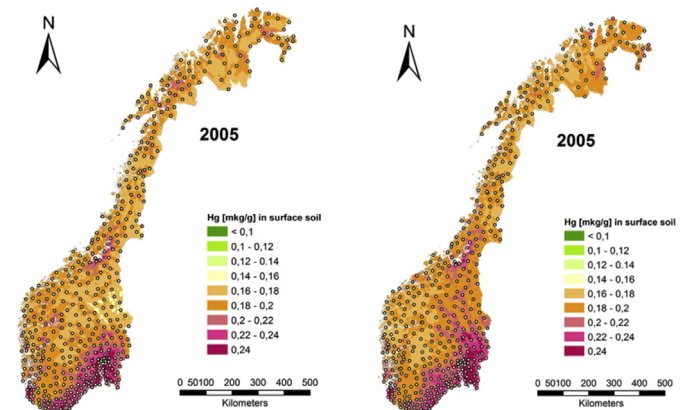


Fig. 6. Hg concentration in natural surface soil (2005) modelled without (left) and with respective concentration in moss (right) as predictor variable.

Table 7  
Percentiles of modelled Hg concentration in moss and natural surface soil.

Year	Hg in moss [ $\mu\text{g/g}$ ]				Hg in soil [ $\mu\text{g/g}$ ]	
	1995	2000	2005	2010	1995	2005
50th p	0.06	0.06	0.05	0.06	No Data	0.18
90th p	0.08	0.07	0.07	0.10	No Data	0.21



The spatial patterns of Pb and Cd concentrations in moss and natural surface soil are similar. The spatial distributions of the HM concentrations in moss and natural surface soil are significantly correlated with high coefficients for Pb and medium for Cd. The response times of Pb concentration in moss appear to be generally shorter, i.e. the biomonitor enables faster evaluation and decision-making in comparison to HM concentration in natural surface soil. By contrast, the association between Hg concentration in moss and natural surface soil appears to be rather moderate.

From 1995 to 2010 the moss and the natural surface soil survey data sets indicate a decrease of Pb concentrations in moss and natural surface soil. In contrast to investigations, which are limited to the monitoring sample sites (Steinnes et al., 2011; Kluge et al., 2014), the modelled Cd and Hg concentrations do not exhibit any significant trend.

#### Authors' contributions

ES and HU supplied the data. WS headed the investigation and the computations executed by AH, RP and SN. All authors participated in writing the article and read and approved the final manuscript.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2014.09.059>.

#### References

- Brosius, F., 2013. SPSS 21. Mitp/bhv, Heidelberg, pp. 1–1054.
- Dalgaard, P., 2002. Introductory Statistics with R. Statistics and Computing. Springer, Heidelberg, pp. 1–363.
- Fox, J., Weisberg, S., 2011. An {R} Companion to Applied Regression, second ed. Sage Publications, London, pp. 1–449.
- Harmens, H., Buse, A., Büker, P., Norris, D., Mills, G., Williams, B., Reynolds, B., Ashenden, T.W., Rühling, A., Steinnes, E., 2004. Heavy metal concentrations in European mosses: 2000/2001 survey. *J. Atmos. Chem.* 49, 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.A., Koerber, G.R., Buse, A., Steinnes, E., Pissapanen, J., Alber, L., et al., 2010. Mosses as biomonitors of atmospheric heavy metal deposition: spatial patterns and temporal trends in Europe. *Environ. Pollut.* 158, 144–156.
- Hengl, T., Heuvelink, G.B.M., Stein, A., 2004. A generic framework for spatial prediction of soil variables based on regression-kriging. *Geoderma* 120 (1–2), 75–93.
- ICP Vegetation, 2010. Heavy Metals in European Mosses: 2010 Survey. Monitoring Manual, International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops. ICP Coordination Centre, CEH Bangor, pp. 1–16.
- Johnston, K., Ver Hoef, J.M., Krivoruchko, K., Lucas, N., 2001. Using ArcGIS Geostatistical Analyst. Redlands, pp. 1–300.
- Kluge, M., Pesch, R., Schröder, W., Steinnes, E., Uggerud, H.T., 2014. Spatial patterns and temporal trends of heavy metal concentrations in moss and soil specimen collected in Norway between 1990 and 2010. *Environ. Sci. Eur.* (submitted for publication). Manuscript Id: 8813383301302047.
- Madsen, H., Thyregod, P., 2011. Introduction to General and Generalized Linear Models. Chapman & Hall/CRC.
- Nelder, J., Wedderburn, R., 1972. Generalized linear models. *J. R. Stat. Soc. Ser. A* 135 (3), 370–384.
- Nygård, T., Steinnes, E., Røyset, O., 2012. Distribution of 32 elements inorganic surface soils: contributions from atmospheric transport of pollutants and natural sources. *Water Air Soil Pollut.* 223, 699–713.
- 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* 67 (3–4), 215–226.
- R Development Core Team, 2011. R: a Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna.
- Schröder, W., Holy, M., Pesch, R., Zechmeister, H., Harmens, H., Ilyin, I., 2011. Mapping atmospheric depositions of cadmium and lead in Germany based on EMEP deposition data and the European Moss Survey 2005. *Environ. Sci. Eur.* 23 (19), 1–14.
- Schröder, W., Pesch, R., Harmens, H., Fagerli, H., Ilyin, I., 2012. Does spatial-autocorrelation call for a revision of latest heavy metal and nitrogen deposition maps? *Environ. Sci. Eur.* 24 (20), 1–8.
- Steinnes, E., Berg, T., Uggerud, H.T., 2011. Three decades of atmospheric metal deposition in Norway as evident from analysis of moss samples. *Sci. Total Environ.* 412–413, 351–358.
- Tørseth, K., Aas, W., Breivik, K., Fjæraa, A.M., Fiebig, M., Hjellbrekke, A.G., Lund Myhre, C., Solberg, S., Yttri, K.E., 2012. Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972 and 2009. *Atmos. Chem. Phys.* 12, 5447–5481.
- UCLA – Statistical Consulting Group, 2011. FAQ: What are Pseudo R-Squareds?.
- Zuur, A.F., Iena, E.N., Walker, N., Saveliev, A.A., Smith, G.M., 2009. Mixed Effects Models and Extensions in Ecology with R. Statistics for Biology and Health. Springer, Heidelberg, pp. 1–574.