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Spatial patterns and temporal trends of heavy metal concentrations in moss and surface soil specimens collected in Norway between 1990 and 2010

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Abstract

Background: The aim of this investigation was to inquire whether the spatial patterns and temporal trends of heavy metal concentrations in moss and soil specimen monitored in two spatial dense networks covering Norway are correlated. To this end, data about concentrations of cadmium, mercury and lead in moss and soil specimens collected were compiled. The data were derived from moss surveys conducted in 1990, 1995, 2000, 2005 and 2010, as well as from soil monitoring campaigns in 1995 and 2005.

Results: The data sets from both moss and soil surveys indicate a decrease of heavy metal concentrations in moss and soil specimen. However, in case of moss samples, the decrease is by far more pronounced and statistically significant. The heavy metal concentrations in moss and soil are correlated significantly with high positive coefficients for Pb, medium for Cd and moderate for Hg. From a set of potentially influencing boundary conditions, the modelled atmospheric deposition showed the highest correlation with the heavy metal concentrations in moss and soil. The spatial patterns of Cd and Pb concentration in moss and soil specimens 1995 and 2005 are similar. Thereby, the spatial differentiation of concentrations in moss is higher than that in soil, while the opposite holds true for the Hg concentration.

Conclusions: Even if the metal concentrations in moss and soil are statistically correlated, they should not be replaced by each other but should be used as complementary monitoring systems.

Keywords: Cadmium; Correlation; Geostatistics; Lead; Mercury; Monitoring

Background

Environmental exposure to pollutants such as heavy metals (HM) can impact structures and functions being relevant for ecosystem integrity and human health [1-6]. To avoid such impacts due to atmospheric HM deposition, the Protocol on Heavy Metals of the Convention on Long-Range Transboundary Air Pollution, adopted in 1998, targets three particularly harmful metals: cadmium (Cd), lead (Pb) and mercury (Hg). Accordingly, Parties have to reduce the respective emissions from industrial sources, combustion and waste incineration below the respective levels in 1990 or an alternative year between 1985 and 1995. As calculated by [7], the European ecosystem area at risk in 2000 of emissions of cadmium, mercury and lead was estimated to amount for about 0.34%, 77% and 42%, respectively. In 2020, these areas are expected to reduce to 0.02%, 74% and 19%, respectively. Thus, the atmospheric deposition of mercury and lead in particular puts large areas of European ecosystems at risk of adverse effects both in 2000 and 2020. The effect-based scenario analysis of emissions of chromium, nickel, copper, zinc, arsenic and selenium indicates that a relatively small ecosystem area in Europe is subject to risk of adverse effects of these metals in 2000. The atmospheric deposition of copper, zinc and selenium is expected to cause risk of adverse effects of 1% at maximum of the European

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ecosystem area in 2020. However, modelled atmospheric deposition of copper, zinc and selenium are significantly underestimated. Nevertheless, none of the metals other than Cd, Hg and Pb achieve high enough concentrations due to atmospheric deposition to cause adverse effects on ecosystems and human health. Thus, the focus on Cd, Hg and Pb as priority metals is regarded as justified [7]. Accordingly, the paper at hand focuses on these three metals.

To validate modelled atmospheric deposition values and risk estimations mentioned above, measurements of atmospheric deposition and complementary estimates from element concentration in mosses are well-established methods [2,5,8-11]. This is due to specific properties: Since soil-inhabiting ectohydric moss species do not have real roots and a weakly developed cuticle, grow slow and show minimal morphological changes during lifetime, element concentrations measured in moss integrates fairly well dry, occult and wet atmospheric deposition. Moss can accumulate large amounts of atmospheric HM deposition due to efficient element capture (high surface-to-volume ratio) and retention as well as resistance to toxic elements [8,10,12-16]. Elements are deposited on moss in aqueous solution, in gaseous form or attached to particles. The bioaccessible HM fraction is the portion of environmentally available metal that interacts at the moss contact surface and is potentially available for adsorption and absorption by the moss. Once adsorbed, HM can be absorbed into and across the biological surface and distributed throughout the organism. The net accumulation of HM in moss that results from exposure to environmentally available HM is called bioaccumulation, including both metal adsorbed to surfaces or absorbed by the organism, expressed on a weight (dry or wet)-adjusted basis [17]. HM accumulate in mosses as layers of particles or entrapment on the surface of the cells, through incorporation into the outer walls of the cells (ion exchange processes), and metabolically controlled passage into the cells. The sorbed metal may be located either in the extracellular region outside of the cytoplasm or bound to the cell wall, and ions have a direct access to the cell wall since mosses do not discriminate HM ions [8].

In Norway, the monitoring of atmospheric HM deposition has been set up since the 1980s and is continued until today at three stations [18]. Due to the limited spatial coverage of the deposition monitoring network in Norway, the spatial and temporal mapping of HM deposition was carried out by means of sampling and analysing moss. First established and implemented in 1970, by means of moss [19] could show a great geographical variety of some HM within Norway, with considerable higher values in the southern part. Therefore, an extensive moss survey with 500 sampling sites distributed all over Norway was carried out in 1977 [20]. In 1985, it was decided to reproduce the moss survey every 5 years with additional surveys in other Nordic countries. Since 1990, further nationwide surveys in at least 21 European countries are carried out every 5 years with an increasing number of HM elements due to improvements in analytical procedures [18,21-24]. Following [25], mapping atmospheric HM deposition from the atmosphere to terrestrial ecosystems by means of mosses can provide a complementary and time-integrated method with a high spatial and temporal resolution.

From the beginning, Norway has incorporated a great number of HM elements compared to concurrent moss surveys in other countries. This paper deals both with spatial patterns and temporal trends of concentrations of Hg, Cd and Pb in moss and soil specimen as well as with potential influencing environmental factors and aimed to investigate whether the spatial patterns and temporal trends of heavy metal concentrations in moss and soil specimen monitored in two spatial dense networks covering Norway are correlated.

Results and discussion

Temporal trend analyses

Table 1 depicts descriptive statistical measures for Cd, Hg and Pb in moss sampled over the period 1990 to 2010, and Table 2 shows the results of the Wilcoxon signed-rank test in terms of the calculated p values. Figures 1, 2 and 3 furthermore show the development of the moss concentrations as box plots. To more clearly illustrate the temporal trend for Cd, Hg and Pb outliers are blinded out of the box plots.

As can be seen from Table 1 and Figures 1, 2 and 3, the highest medians as well as maximum values in moss can be observed in the 1990 survey for all three elements. A clear continuous decrease from 1990 to 2010 can be observed for Pb only reaching from 9.3 μg/g in 1990 to 1.5 μg/g in 2010. Regarding Hg, in 2010, a median concentration of 0.064 μg/g was calculated. This almost reaches the same concentration of Hg in moss as in 1990 and 1995 (0.068 μg/g). The inference statistical comparison of all three elements shows significant differences between the years in all cases except for Cd between 1990 and 1995, 1990 and 2005and 2000 and 2010 as well as for Hg between 1990 and 1995, 1990 and 2010, 1995 and 2010 and 2000 and 2005 (alpha =0.01) (Table 2). As can be seen from Table 1 and Figures 4, 5 and 6, the highest median values in soil can be observed in 1995 for Cd and Pb. There were no data for Hg in 1995. In case of Pb, there was a slight but significant decrease over time reaching from 34.6 μg/g in 1995 to 25.8 μg/g in 2005 (alpha =0.01) (Table 2).

Table 1 Descriptive statistical measures for Cd, Hg and Pb concentrations in moss and in soil

Element	Year	Number	Median	Minimum	Maximum
Cd (μg/g) moss	1990	495	0.126	0.026	3.373
	1995	458	0.128	0.004	1.672
	2000	464	0.087	0.002	2.622
	2005	464	0.089	0.017	2.453
	2010	463	0.081	0.009	1.875
Hg (μg/g) moss	1990	151	0.068	0.014	0.817
	1995	209	0.068	0.002	0.479
	2000	464	0.052	0.022	0.208
	2005	464	0.054	0.019	0.250
	2010	460	0.064	0.025	0.445
Pb (μg/g) moss	1990	495	9.3	1.5	78.9
	1995	458	5.8	0.9	59.4
	2000	464	2.7	0.5	27.7
	2005	464	2.2	0.5	34.3
	2010	463	1.5	0.3	20.8
Cd (μg/g) soil	1995	461	0.45	0.05	6.66
	2005	462	0.40	0.05	5.72
Hg (μg/g) soil	1995	No data			
	2005	462	0.20	0.03	8.86
Pb (μg/g) soil	1995	461	34.56	7.05	798.79
	2005	462	25.75	3.80	1259.80

The descriptive statistical measures for Cd, Hg and Pb concentrations in moss are from 1990 to 2010 and in soil from 1995 and 2005.

Table 2 Results of Wilcoxon signed-rank test for Cd, Hg, and Pb concentration in moss and soil

Years	Cd	Hg	Pb
Moss			
1990 to 1995	*0.60*	*0.80*	0.00
1990 to 2000	0.00	0.00	0.00
1990 to 2005	*0.08*	0.00	0.00
1990 to 2010	0.00	*0.65*	0.00
1995 to 2000	0.00	0.00	0.00
1995 to 2005	0.00	0.00	0.00
1995 to 2010	0.00	*0.30*	0.00
2000 to 2005	0.00	*0.09*	0.00
2000 to 2010	*0.52*	0.00	0.00
2005 to 2010	0.00	0.00	0.00
Soil			
1995 to 2005	*0.21*	No data	0.00

The significance level is given by p-values. The italicized values signify $p > 0.01$ (not significant).

Correlations between HM concentrations in moss and soil samples and potential predictors

As can be seen from the results of Spearman correlation analysis (Table 3), significant statistical associations exist between measured HM concentrations in moss and soil (alpha =0.01). Highest coefficients were evident for Pb ($R > 0.8$), followed by Cd ($R > \approx 0.5$). Correlations between Hg concentrations in moss and soil samples ranged between $R \approx 0.3$ and $R \approx 0.4$.

Table 4 depicts the results of Spearman correlation analysis of, on the one hand, measured Cd, Hg and Pb concentrations either in moss and in soil samples and, on the other hand, potential influencing factors such as sea spray effect, elevation, precipitation, land use, population density, soil texture (percentage of clay, silt and sand) and total atmospheric deposition of Cd, Hg and Pb modelled by Environmental Monitoring and Evaluation Programme (EMEP). Regarding the element concentrations in moss (Table 4), the modelled deposition values by far showed the highest significant (alpha =0.01) correlations especially for Pb ($R > \approx 0.7$ for all years) and Cd ($R > \approx 0.6$ for all years). Like in the case of natural surface soil (Table 4), for Hg, the weakest correlations among all three elements were identified, ranging from $R \approx 0.3$ in 2010 and $R \approx 0.5$ in 1990. The same tendency can be observed regarding the statistical association of the metal concentrations in moss and the urban land use percentages within 1- and 5-km radiuses (Table 4): Here, the corresponding coefficients are lower ($R < \approx 0.5$) in all cases. The percentages of agriculture land use ($R_{max} \approx 0.2$ for Pb in 1995) and forest areas ($R_{max} \approx 0.3$ for Cd in 1995) showed generally low and mostly non-significant correlations with the HM concentrations in moss. For agricultural, forested and urban land use, the highest associations were identified within a radius of 5 km. Regarding elevation, mostly low negative ($R < \approx -0.3$) and in six cases non-significant coefficients were computed. Similar holds true for the distance between monitoring sites and the sea: Only for Hg, a weak significant signal for all campaigns except for 2010 was observed.

In a similar way as for the HM concentrations in moss, HM concentrations in soil samples were preferentially correlated with atmospheric HM deposition with R values for Cd > ≈0.5 and for Pb > ≈0.7 (alpha =0.01) (Table 4. Population density was significantly correlated with Pb concentrations (R coefficients > ≈0.4, alpha =0.01) and with Cd concentrations ($R \approx 0.20$); thus, compared to atmospheric deposition values, it is clearly lower. Land use within a 5-km radius around moss and soil sampling sites was most strongly correlated with concentrations of Cd ($R \approx 0.2$ in 2005) and Pb ($R \approx 0.3$).

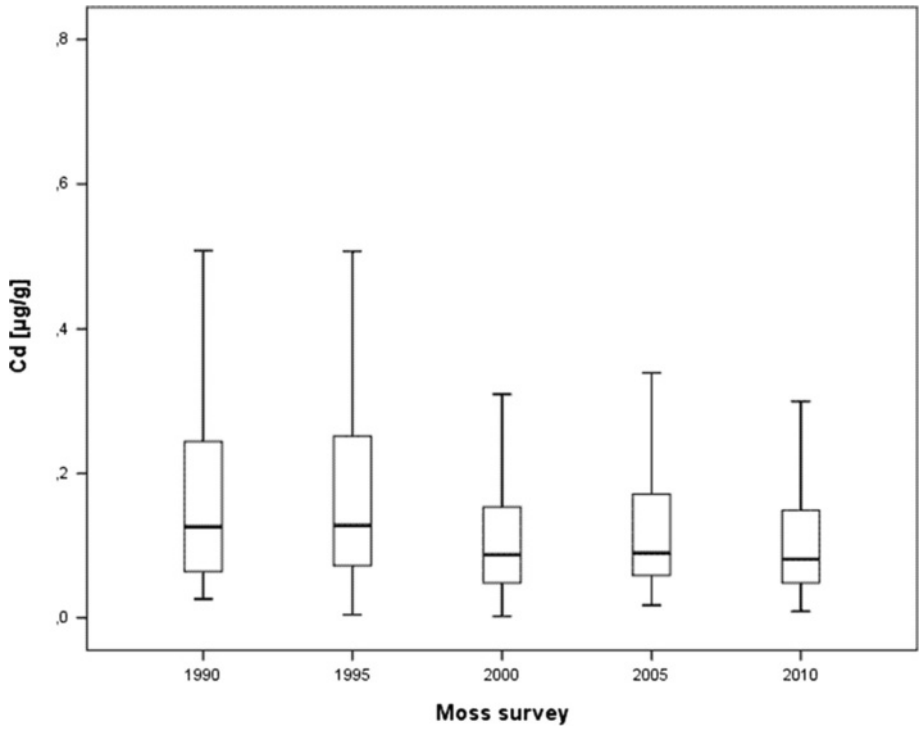


Figure 1 Box plot for Cd in moss, Norway 1990 to 2010 (no outliers depicted).

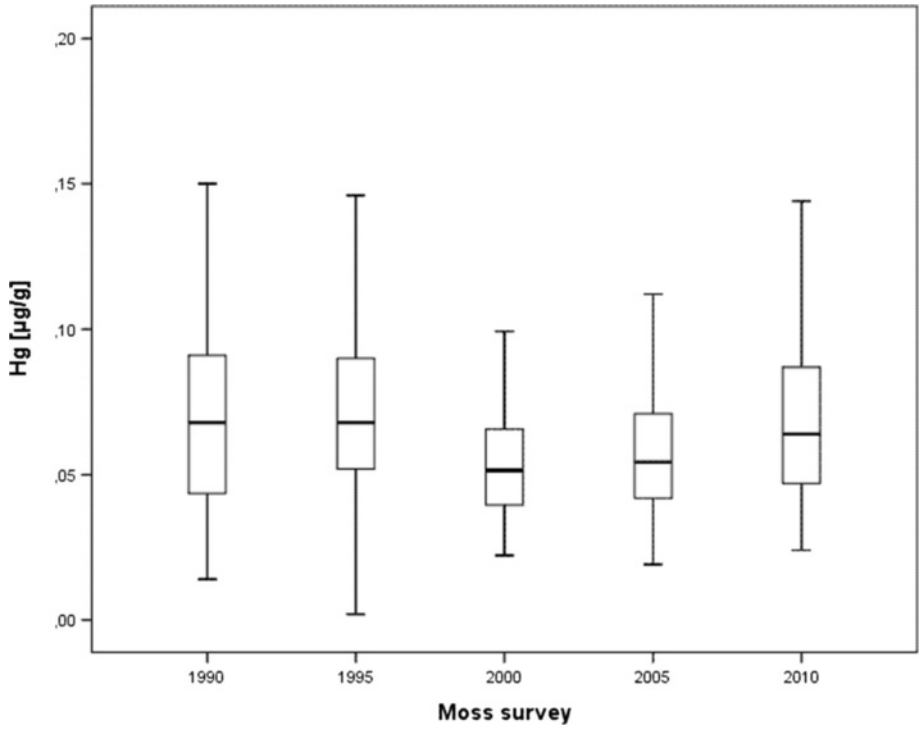


Figure 2 Box plot for Hg in moss, Norway 1990 to 2010 (no outliers depicted).

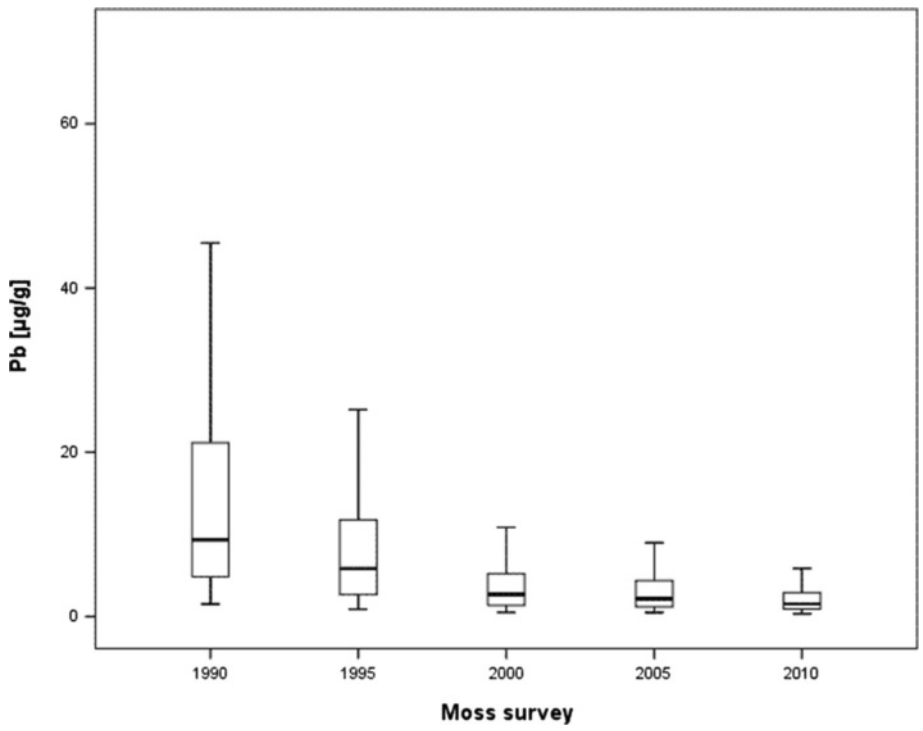


Figure 3 Box plot for Pb in moss, Norway 1990 to 2010 (no outliers depicted).

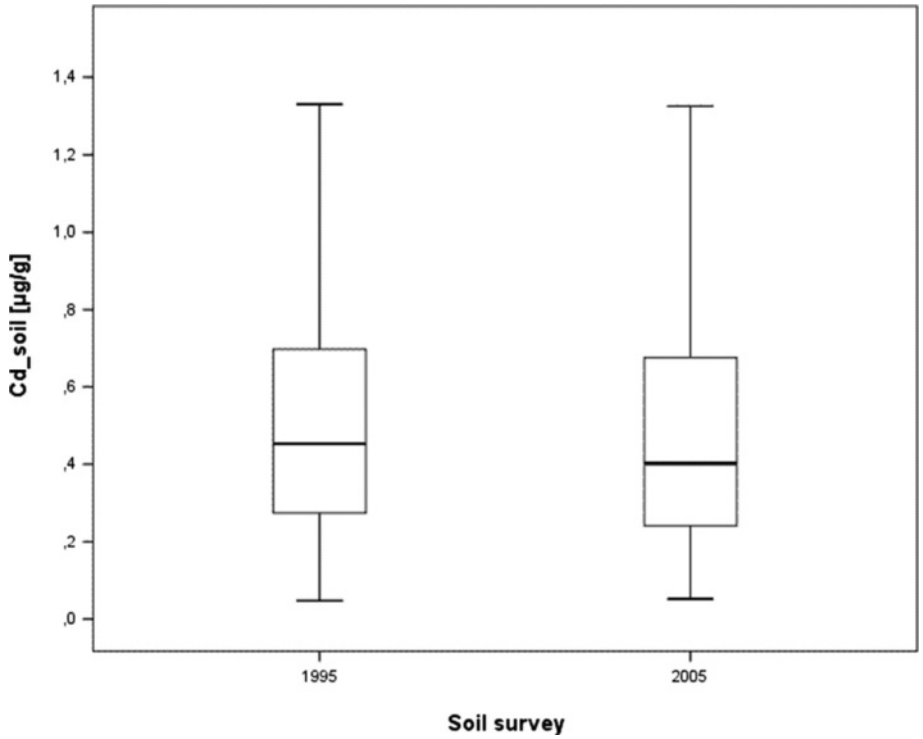


Figure 4 Box plot for Cd in soil, Norway 1995 and 2005 (no outliers depicted).

Figure 5 Box plot for Hg in soil, Norway 2005 (no outliers depicted, no data for 1995).

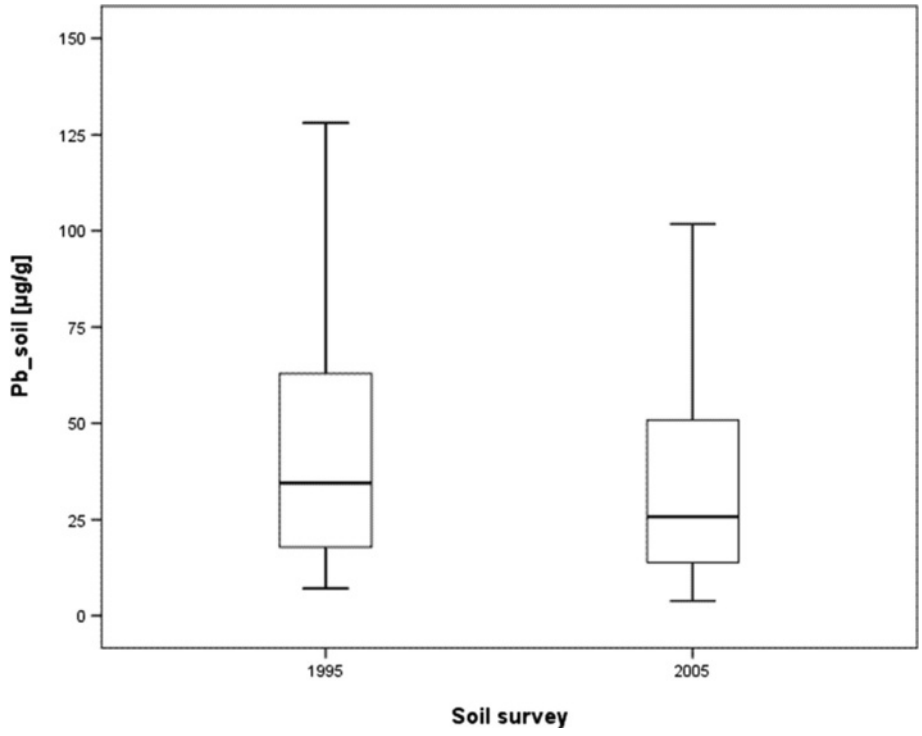


Figure 6 Box plot for Pb in soil Norway 1995 and 2005 (no outliers depicted).

Table 3 Spearman correlations between measured Cd, Hg and Pb concentrations in moss and soil samples, Norway

	Number	Cd	Pb	Hg
Moss 1990 - soil 1995	211	*0.59*	*0.87*	
Moss 1995 - soil 1995	456	*0.65*	*0.84*	
Moss 2000 - soil 1995	463	*0.57*	*0.78*	
Moss 2000 - soil 2005	219	*0.50*	*0.73*	*0.29*
Moss 2005 - soil 2005	364	*0.56*	*0.76*	*0.36*
Moss 2010 - soil 2005	462	*0.56*	*0.72*	0.11

The correlations between the measured HM concentrations in moss samples collected in 1990 with the measured HM concentrations in soil specimen sampled in 1995 included only those soil sampling sites with a spatial distance of 2 km at maximum. The sampling sites for moss and soil were identical in 1995 as well as in 2005. The italicized values denote p <0.01.

Geostatistical analysis and mapping

Figures 7, 8, 9, 10, 11 and 12 illustrate the results of variogram analyses, cross-validation and mapping via Lognormal Universal Kriging for Cd, Hg and Pb concentrations in moss and soil specimens sampled in 1995 and 2005. Respective results for Cd, Hg and Pb concentrations in moss collected in 1990, 2000 and 2010 are illustrated in Additional file 1: Figure S1 A, B and C. Regarding the element concentrations in moss, in nearly all cases, the modelled variograms show clear spatial autocorrelation patterns with nugget-to-sill ratios lying between 11% (for Hg in 1990) to 55% (for Hg in 2005). Regarding the HM concentrations in the soil samples, the nugget-to-sill ratio ranged between 37% (for Cd in 1995) and 72% (for Pb in 2005). For HM concentration in the moss samples, the cross-validation yielded mean error (ME) close to 0, indicating the semi-variogram models and the following surface estimation via Kriging to be unbiased. This is also the case for Cd and Hg concentrations in soil samples, but not for Pb. Moreover, the median percental errors (MPEs) reach from 18% (Hg in 1995) to 36.4% (Cd in 1990), indicating a fair quality of estimation. For HM concentrations in soil specimen, MPEs reaching from 22% (Hg in 2005) to 38.3% (Cd in 2005) were calculated.

The Kriging maps (Figures 7, 8, 9, 10, 11 and 12, Additional file 1: Figure S1 A, B and C) depict the spatial patterns of the metal concentration in moss for the surveys 1990, 1995, 2000, 2005 and 2010, showing lower metal loads in 2010 than in 1990. For Cd, the highest values are found in the southern part of Norway near the North Sea and Skagerrak coast. In addition, there is a distinct hot spot in the area east of Bergen, related to emissions from the Odda zinc smelter. Pb shows a pattern in Norway similar to that of Cd but without distinct hot spots indicating contributions from local point sources. In 2000, Hg reveals spatial patterns that are very similar to those of Cd and Pb. In 2010, some enrichment is, e.g. depicted in the southern part of Norway around Kristiansand.

The spatial patterns of Cd and Pb concentrations in surface soil are roughly similar to those in moss. With higher values near the North Sea and Skagerrak coast, the maps depicting the spatial patterns of Cd and Pb concentrations in soil samples are spatially less differentiated than those for respective HM concentration in moss samples. Contrary to that is the high spatial differentiation of Hg concentrations in soil sampled in 2005. The maps spatially illustrate that the decrease of HM concentrations is more pronounced in moss than in soil. Soil responds more slowly to decreasing atmospheric HM deposition than moss. This is due to the higher complexity of the regulatory processes acting in soils compared to those in moss. As the spatial extent or the structural und functional complexity of an ecological system increases, so does the temporal extent over which the system's dynamics can be observed [26-29].

Table 5 contains the Spearman correlation coefficients between the *measured* Cd, Hg and Pb concentration in moss and the respective Kriging *estimated* concentrations in soil and between the *measured* Cd, Hg and Pb concentration in soil and the respective Kriging *estimated* concentration in mosses (1995 and 2005). Significant statistical associations between HM concentration in moss and soil are evident (alpha = 0.01): The highest coefficients are shown for Pb ($R > \approx 0.8$), followed by Cd (R >0.6 with a maximum of $R \approx 0.78$). Hg shows only moderate correlation patterns. Compared to the results listed in Table 4, the correlation coefficients show the same tendency and are slightly higher.

In previous publications from the authors dealing with data from the nationwide surveys [30,31], the distinctly higher contents of Pb and Cd in the south of the country than elsewhere and the apparent similarity with the geographical distribution in moss samples have led to the conclusion that long-range atmospheric transport from elsewhere in Europe may be the main reason for the observed geographical distributions of these elements in the natural surface soils. The strong statistical asso
ciations demonstrated here strongly support this view. In the case of Hg, more uniform distribution over the country may indicate significant contribution from the hemispheric pool of Hg^0, which is assumed to be quite uniformly distributed over the entire northern hemisphere [32].

Conclusions

The results of this study show that there are significant correlations between HM concentrations in moss and soil collected in Norway during 1990 to 2010 (Table 3). Variogram analysis proved the HM concentrations in moss and soil to be spatially auto-correlated with nugget-to-sill

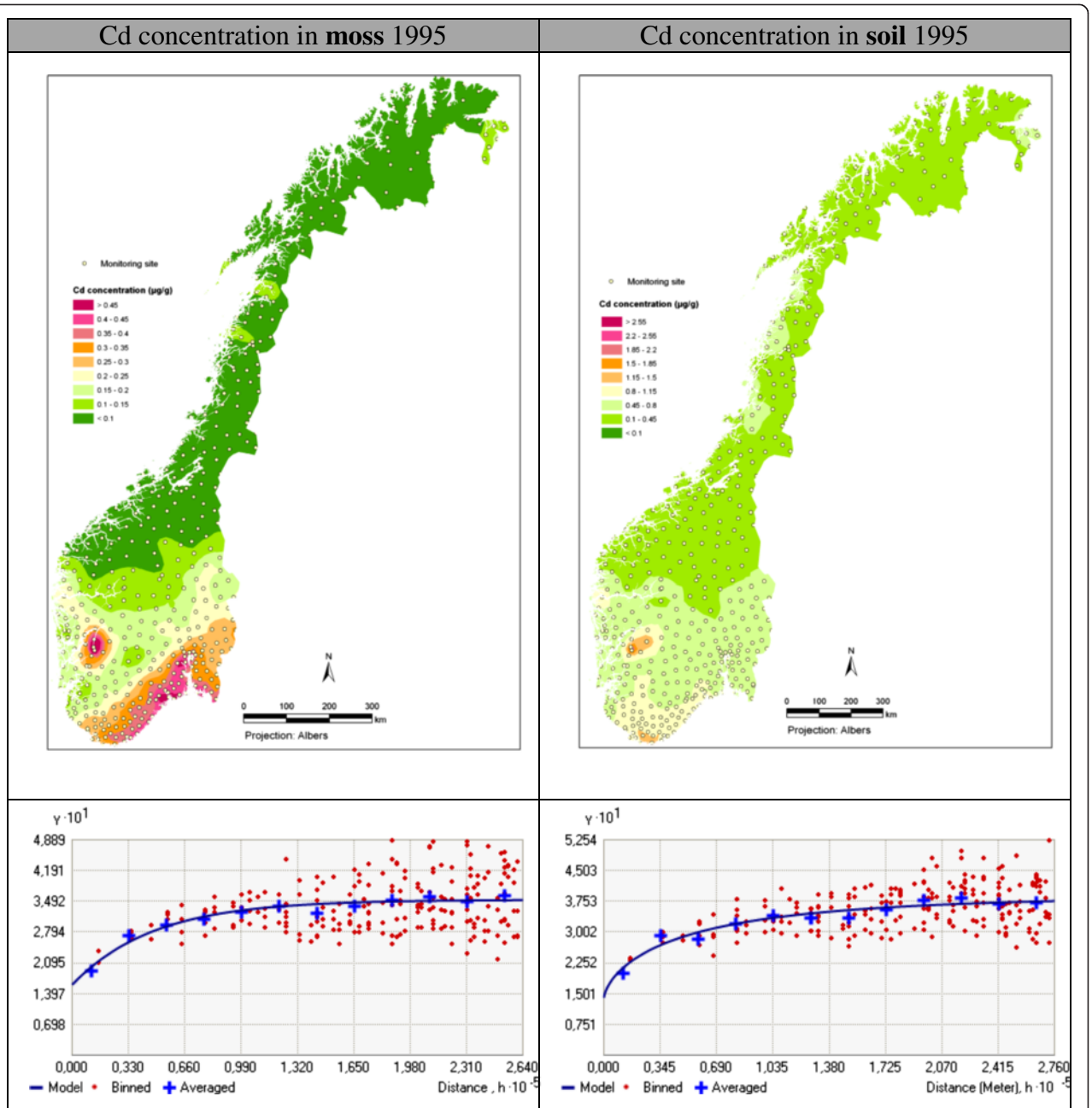
Table 4 Spearman correlations between Cd, Hg, and Pb concentrations in moss and soil and environmental predictors

Descriptor	1990			1995			2000			2005			2010		
	Cd	Hg	Pb	Cd	Hg	Pb	Cd	Hg	Pb	Cd	Hg	Pb	Cd	Hg	Pb
Moss															
Distance to sea (km)	0.11	*−0.29*	0.01	0.09	*−0.22*	−0.05	−0.03	*−0.29*	−0.11	0.06	*−0.24*	−0.07	0.00	−0.08	*−0.15*
Elevation (m)	−0.01	*−0.30*	−0.09	−0.05	−0.14	*−0.14*	*−0.15*	*−0.31*	*−0.19*	−0.04	*−0.22*	*−0.15*	−0.12	*−0.13*	*−0.22*
Precipitation (mm)	0.10	*0.22*	*0.25*	0.11	0.10	*0.22*	0.07	0.06	*0.23*	0.10	*0.17*	*0.19*	0.10	*0.14*	*0.21*
Ratios agricultural land use 1 km (%)	0.04	0.05	0.07	0.08	0.08	0.12	0.09	0.11	0.11	0.06	*0.21*	0.12	0.09	0.12	*0.13*
Ratios agricultural land use 5 km (%)	*0.14*	0.14	*0.22*	*0.17*	*0.20*	*0.23*	*0.15*	0.12	*0.17*	*0.14*	*0.20*	*0.18*	*0.15*	0.09	*0.18*
Ratios forestal land use 1 km (%)	0.11	−0.13	*0.13*	*0.18*	−0.12	0.10	0.11	−0.06	0.07	*0.15*	−0.07	0.07	0.10	0.04	0.06
Ratios forestal land use 5 km (%)	*0.27*	−0.09	*0.28*	*0.33*	−0.08	*0.27*	*0.25*	0.01	*0.22*	*0.28*	−0.01	*0.22*	*0.25*	0.09	*0.21*
Ratios urban land use 1 km (%)	*0.21*	0.19	*0.24*	*0.20*	0.12	*0.25*	*0.19*	*0.16*	*0.22*	*0.13*	0.02	*0.19*	0.11	0.05	*0.14*
Ratios urban land use 5 km (%)	*0.27*	*0.25*	*0.35*	*0.27*	*0.21*	*0.36*	*0.28*	*0.14*	*0.31*	*0.34*	0.06	*0.35*	*0.32*	0.12	*0.34*
Population density (residents/km^2)	*0.35*	*0.39*	*0.46*	*0.34*	*0.42*	*0.48*	*0.34*	*0.31*	*0.44*	*0.36*	*0.31*	*0.44*	*0.41*	*0.17*	*0.45*
Percentage clay in soil (%)	0.12	−0.08	0.05	0.12	−0.04	0.06	0.09	−0.08	0.03	*0.19*	−0.02	0.10	*0.15*	0.00	0.10
Percentage silt in soil (%)	*−0.15*	0.07	−0.07	*−0.15*	0.03	−0.09	−0.08	0.02	−0.07	−0.12	0.01	−0.03	−0.10	−0.08	−0.05
Percentage sand in soil (%)	*0.15*	−0.07	0.07	*0.15*	−0.03	0.09	0.08	−0.02	0.07	0.12	−0.01	0.04	0.10	0.08	0.05
Total deposition Cd - 3-year sum (mg/m^2/year)[a]	*0.62*			*0.68*			*0.63*			*0.61*			*0.73*		
Total deposition Hg - 3-year sum (mg/m^2/year)[a]		*0.46*			*0.43*			*0.33*			*0.33*			*0.26*	
Total deposition Pb - 3-year sum (mg/m^2/year)[a]			*0.81*			*0.82*			*0.78*			*0.69*			*0.72*
Soil															
Distance to sea (km)				−0.02		−0.01				0.00	−0.08	0.03			
Elevation (m)				0.02		−0.06				0.07	*−0.13*	0.00			
Precipitation (mm)				*0.18*		*0.27*				*0.18*	−0.03	*0.19*			
Ratios agricultural land use 1 km (%)				−0.04		0.07				0.00	*0.11*	0.05			
Ratios agricultural land use 5 km (%)				−0.03		*0.17*				0.01	*0.14*	*0.10*			
Ratios forestal land use 1 km (%)				0.03		*0.10*				0.07	0.02	0.08			
Ratios forestal land use 5 km (%)				0.07		*0.21*				*0.14*	*0.13*	*0.20*			
Ratios urban land use 1 km (%)				*0.12*		*0.21*				0.02	0.08	0.08			
Ratios urban land use 5 km (%)				*0.13*		*0.29*				*0.20*	*0.20*	*0.29*			
Population density (inhabitants/km^2)				*0.23*		*0.45*				*0.25*	*0.28*	*0.40*			
Percentage clay in soil (%)				−0.07		0.00				0.05	*0.10*	0.07			
Percentage silt in soil (%)				−0.02		−0.05				0.06	−0.03	−0.03			
Percentage sand in soil (%)				0.01		0.01				0.03	0.02	0.02			

Table 4 Spearman correlations between Cd, Hg, and Pb concentrations in moss and soil and environmental predictors *(Continued)*

Total deposition Cd - 3-year sum (mg/m^2/year)[a]	*0.60*			*0.51*		
Total deposition Hg - 3-year sum (mg/m^2/year)[a]					*0.16*	
Total deposition Pb - 3-year sum (mg/m^2/year)[a]		*0.81*				*0.68*

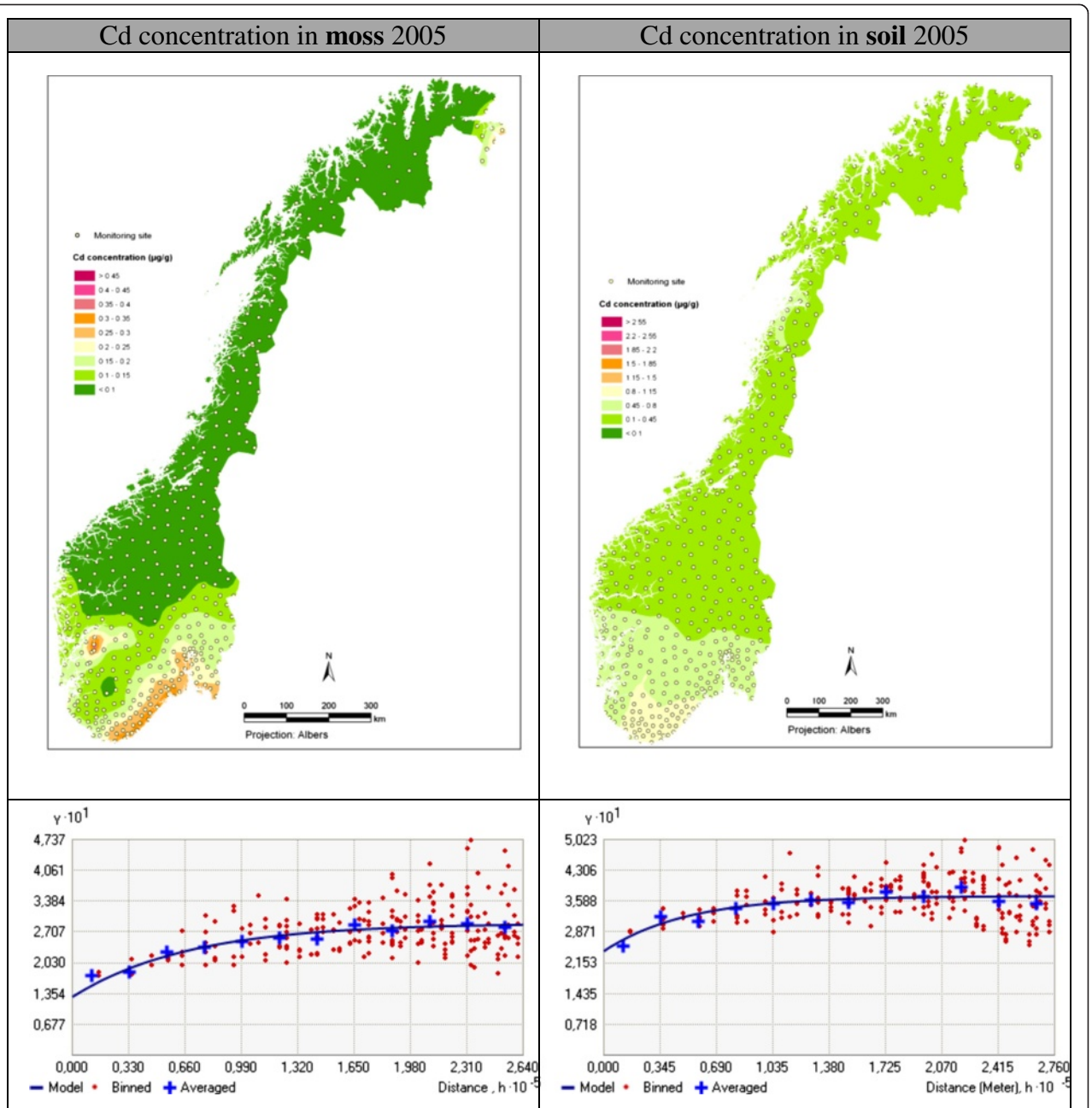
[a]With exception to 1990 where only modelled data from 1990 was available. Italicized values signify p <0.01.



Method: Universal Lognormal Kriging 2nd order		Method: Universal Lognormal Kriging 2nd order	
Nugget/Sill Ratio	45 %	***Nugget/Sill Ratio***	37 %
Range	22 km	***Range***	23 km
Mean Error	0.00341	***Mean Error***	-0.0137
Median Percental Error	31.4 %	***Median Percental Error***	36.0 %
Model Type	Exponential	***Model Type***	Stable

Figure 7 Geostatistical analysis and mapping of Cd in moss and soil 1995.

ratios between 11% (for Hg in 1990) to 55% (for Hg in 2005) in moss and between 37% (for Cd in 1995) and 72% (for Pb in 2005) in natural surface soil. In all cases, the MEs are close to 0, indicating that the semi-variogram models and the following Kriging estimation to be unbiased. The MPEs reach from 18% (Hg in 1995) to 36.4%

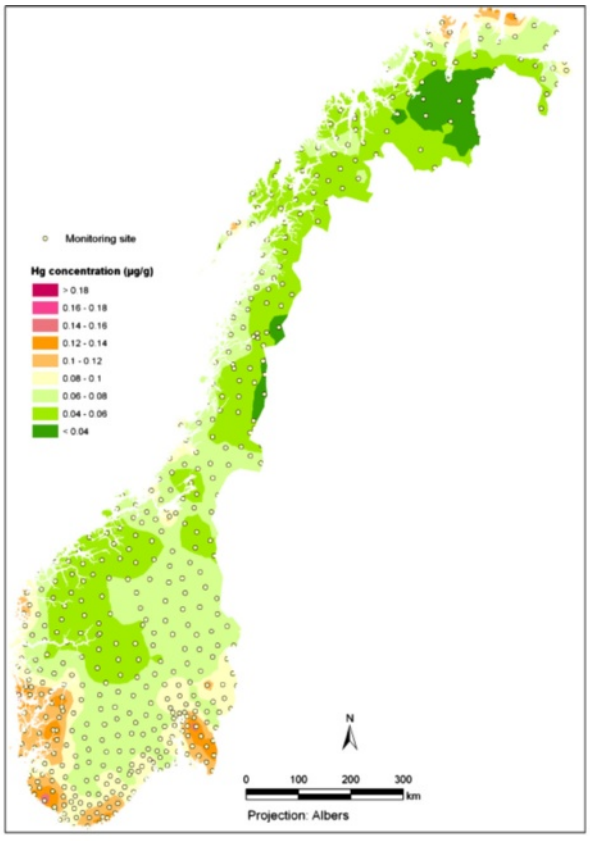


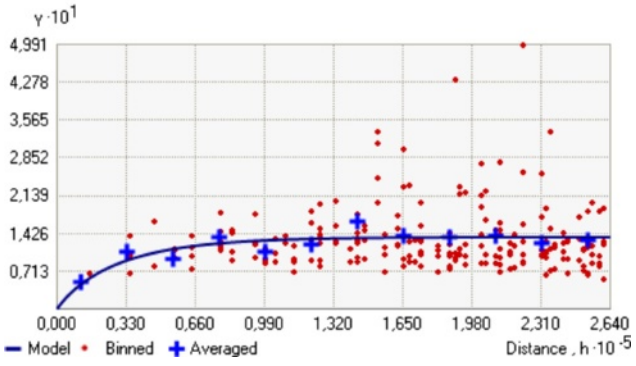
Method: Universal Lognormal Kriging 2nd order		Method: Universal Lognormal Kriging 2nd order	
Nugget/Sill Ratio	44 %	***Nugget/Sill Ratio***	65 %
Range	22 km	***Range***	23 km
Mean Error	-0.00260	***Mean Error***	-0.00260
Median Percental Error	26.2 %	***Median Percental Error***	38.3 %
Model Type	Exponential	***Model Type***	Exponential

Figure 8 Geostatistical analysis and mapping of Cd in moss and soil 2005.

(Cd in 1990) in moss and from 22% (Hg in 2005) to 38.3% (Cd in 2005) in soil, indicating a fair quality of estimation. These results enabled geostatistical surface estimations (Figures 7, 8, 9, 10, 11 and 12, Additional file 1: Figure S1 A to C). Geostatistical surface estimation allowed to spatially link the HM concentration values with surface

Hg concentration in **moss** 1995

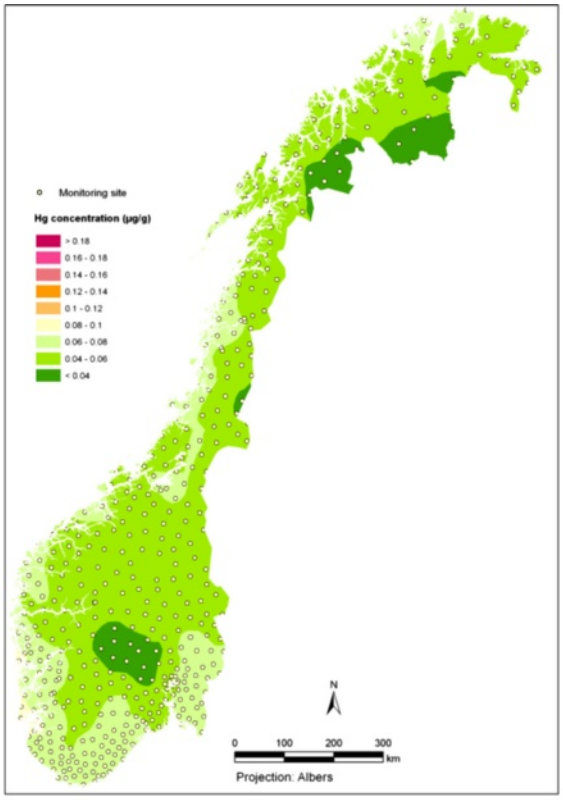
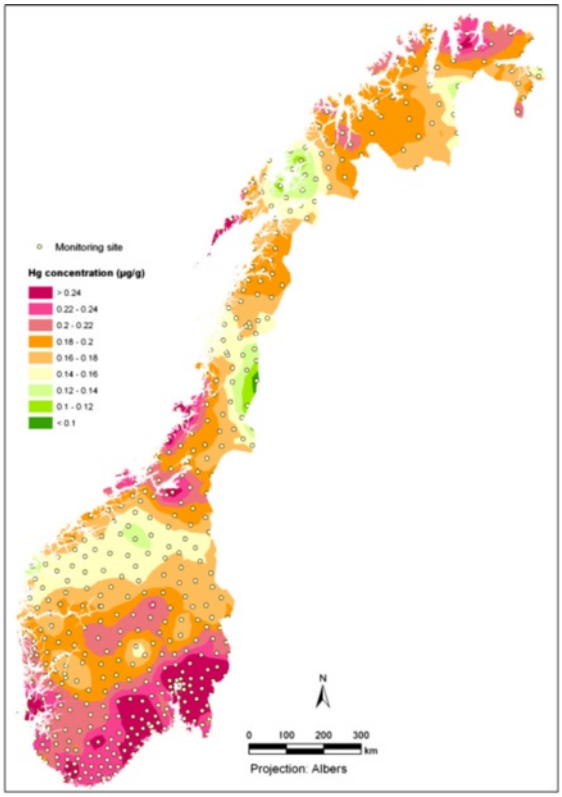
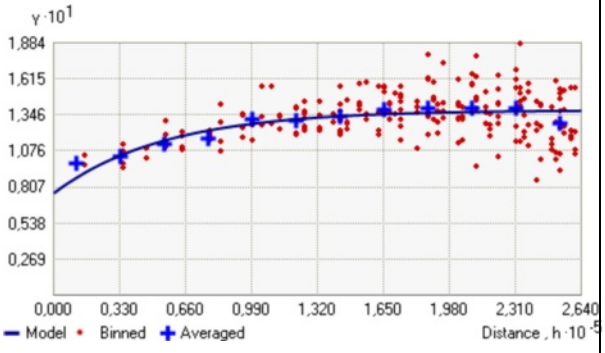
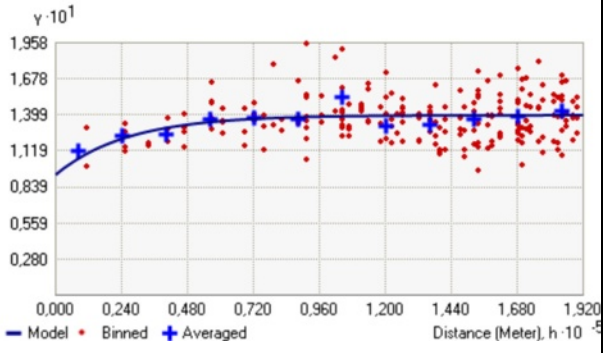




Method: Universal Lognormal Kriging 2nd order

Nugget/Sill Ratio	0 %
Range	22 km
Mean Error	-0.00063
Median Percental Error	17.9 %
Model Type	Stable

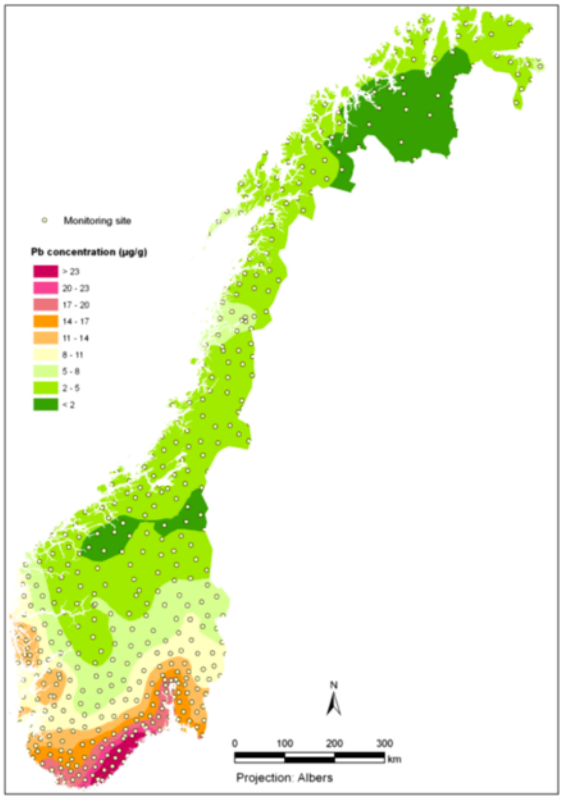
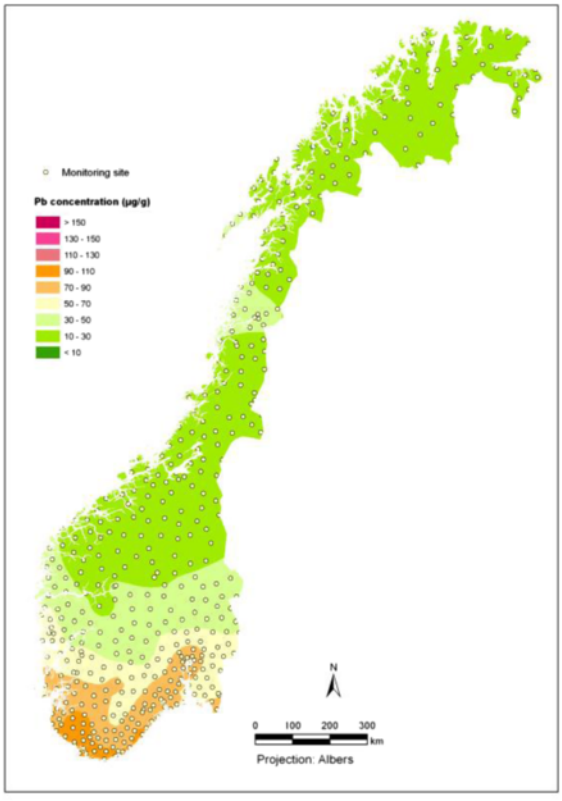
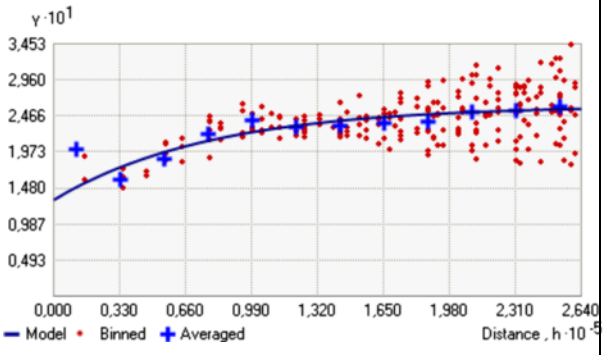
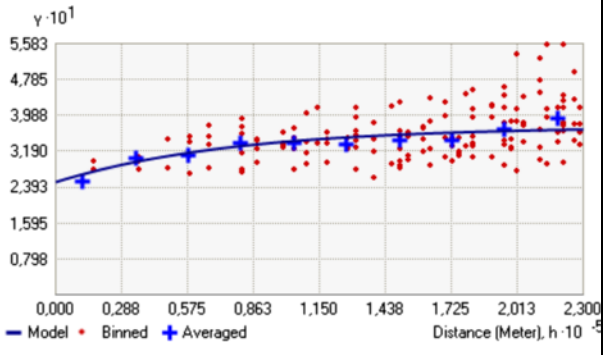
Figure 9 Geostatistical analysis and mapping of Hg in moss and soil 1995. Data of Hg concentration in soil 1995 was not available.

Hg concentration in **moss** 2005	Hg concentration in **soil** 2005
	
	
Method: Universal Lognormal Kriging 2nd order	Method: Universal Lognormal Kriging 2nd order

Nugget/Sill Ratio	55 %	***Nugget/Sill Ratio***	67 %
Range	22 km	***Range***	16 km
Mean Error	-0.00003	***Mean Error***	0.00016
Median Percental Error	21.3 %	***Median Percental Error***	22.0 %
Model Type	Exponential	***Model Type***	Exponential

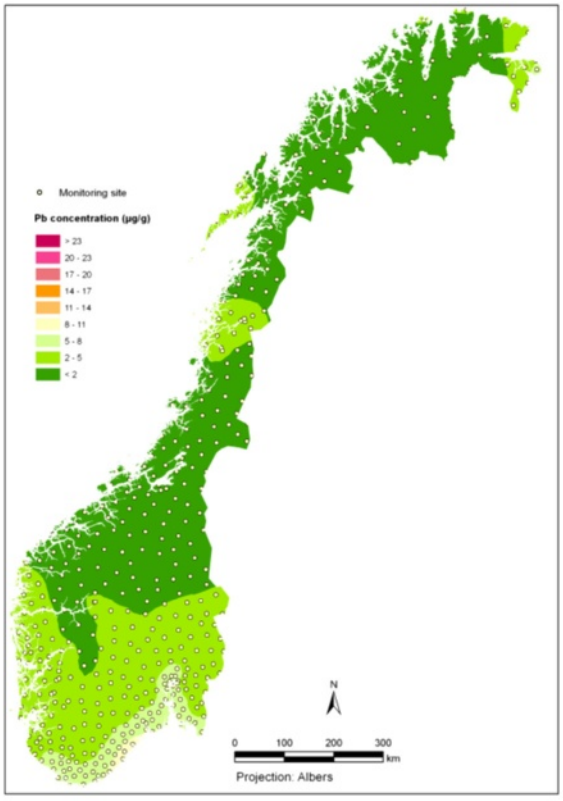
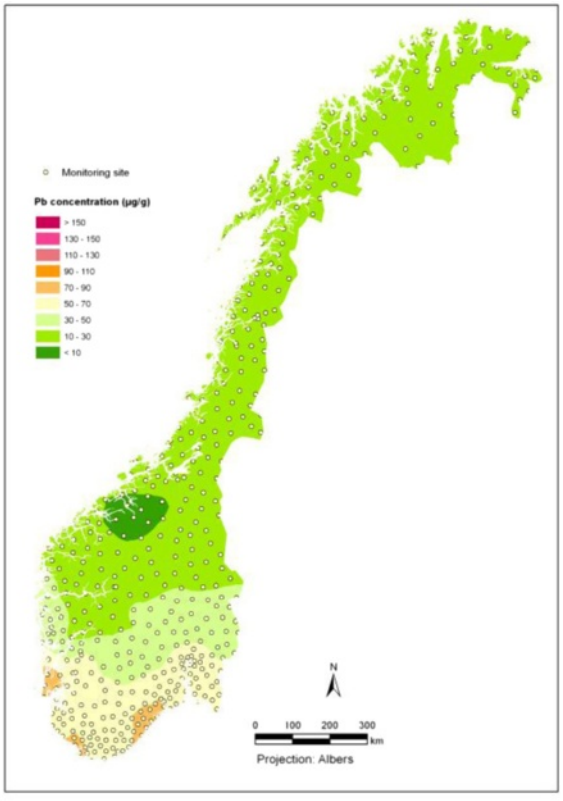
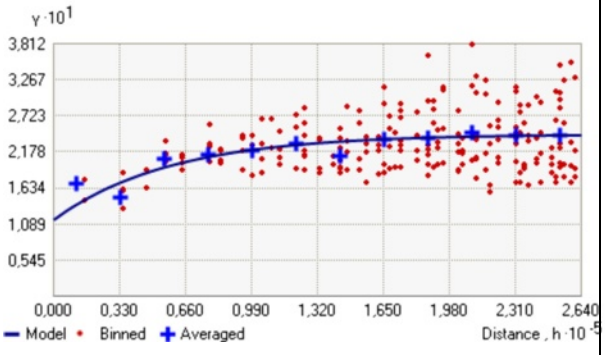
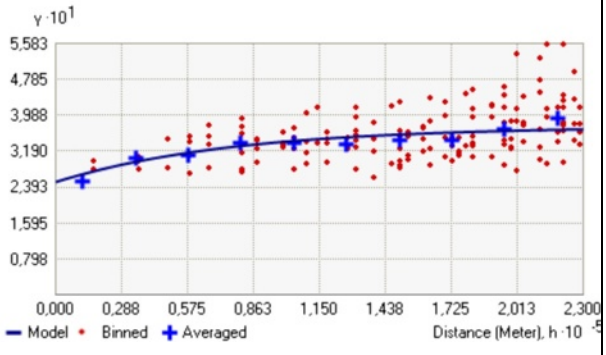
Figure 10 Geostatistical analysis and mapping of Hg in moss and soil 2005.

data on potential influencing factors. By this, pronounced correlations between Cd, Hg and Pb concentration in moss and soil and influence factors could be established. Following the hypothesis that ecosystems are complex indicators for combinations of causal factors [3], future research is needed to analyse relations between landscape-

Pb concentration in **moss** 1995	Pb concentration in **soil** 1995
	
	
Method: Universal Lognormal Kriging 2nd order	Method: Universal Lognormal Kriging 2nd order

Nugget/Sill Ratio	51 %	***Nugget/Sill Ratio***	67 %
Range	22 km	***Range***	23 km
Mean Error	0.002847	***Mean Error***	-1.85477
Median Percental Error	27.7 %	***Median Percental Error***	35.4 %
Model Type	Exponential	***Model Type***	Exponential

Figure 11 Geostatistical analysis and mapping of Pb in moss and soil 1995.

Pb concentration in **moss** 2005	Pb concentration in **soil** 2005
	
	
Method: Universal Lognormal Kriging 2nd order	Method: Universal Lognormal Kriging 2nd order

Nugget/Sill Ratio	47 %	***Nugget/Sill Ratio***	67 %
Range	22 km	***Range***	23 km
Mean Error	-0.06968	***Mean Error***	-1.85477
Median Percental Error	25.3 %	***Median Percental Error***	35.4 %
Model Type	Exponential	***Model Type***	Exponential

Figure 12 Geostatistical analysis and mapping of Pb in moss and soil 2005.

Table 5 Spearman correlations between measured and geostatistically estimated HM concentrations both in moss and soil

	Number	Cd	Hg	Pb
Moss data and estimated soil data				
Moss 1995 - soil 1995	458	*0.78*		*0.88*
Moss 2005 - soil 2005	464	*0.74*	*0.39*	*0.81*
Soil data and estimated moss data				
Soil 1995 - moss 1995	464	*0.65*		*0.86*
Moss 2005 - soil 2005	464	*0.65*		*0.86*

Values in italics signify $p < 0.01$.

specific factors and the concentrations of a broader range of metals in moss and soil samples.

Methods

Moss sampling and chemical analyses

Samples of the feather moss *Hylocomium splendens* (Hedw.) Schimp were collected at around 500 sites distributed over the mainland of Norway and the associated archipelago during the summer of 1977, 1985, 1990, 1995, 2000, 2005 and 2010. Starting in 1995, a fixed network of 464 sites was employed. Samples were dried at room temperature and the last 3 years' growth was selected for determination of trace elements. In 1977 and 1985, the analyses were carried out by instrumental neutron activation analysis for 24 elements and atomic absorption spectrometry for Cu, Zn, Cd and Pb [33]. In 1990 and later years, to which the study at hand relates, inductively coupled plasma mass spectrometry (ICP-MS) was used for all elements, except for Hg which was determined by atomic fluorescence spectrometry. In the 2010 survey, as much as 52 elements were reported [18]. Prior to the ICP-MS analysis, the moss samples were decomposed in a mixture of concentrated nitric acid and hydrogen peroxide and analysed after appropriate dilution. For quality control, three moss reference samples [34] were employed.

Soil sampling and chemical analyses

Surface soil specimens were collected in 1995 and 2005 according to a procedure described by [31]. At most sites, podzols with a well-developed humic surface horizon were sampled. The material collected from the humus layer at 0- to 3-cm depth after removal of litter was analysed by ICP-MS in a similar way as for the moss samples. No data for Hg were obtained in the 1995 soil survey.

Temporal trend analyses

Basic descriptive statistical measures (number of sites, minimum, maximum, median) for the Cd, Hg and Pb concentrations in moss were calculated from the moss data collected in 1990, 1995, 2000, 2005 and 2010 as well as from the soil values in 1995 and 2005. In order to depict temporal trends, box plots were derived by use of IBM SPSS Statistics Version 21. To investigate whether significant differences between the data from different monitoring campaigns exist, Wilcoxon signed-rank test were applied.

Correlation analyses of measured HM concentrations

The statistical dependences between the Cd, Hg and Pb concentrations in moss and soil were computed by means of correlation analyses according to [35]. Since soil data were available only for the years 1995 and 2005, HM concentrations in mosses collected from 1990, 1995 and 2000 were compared to the HM concentrations in soil specimen from 1995, whereas the HM concentrations in moss sampled in 2000, 2005 and 2010 were compared to the HM concentrations in soil samples from 2005. The correlations between the measured HM concentrations in moss samples collected in 1990 with the measured HM concentrations in soil specimen sampled in 1995 included only those soil sampling sites which were situated no more than 2 km away from the moss collection sites. The sampling sites for moss and soil were identical in 1995 as well as in 2005. The correlation analyses based on measured HM concentrations in moss and soil samples complement the correlation analyses relying on geostatistically estimated HM concentrations explained in 'Correlation analyses of measured and geostatistically estimated HM concentrations' section below.

Integration of surface data on potential predictors

Geodata on potential influencing factors were intersected with the moss and soil data in order to explain spatial and temporal variations of Cd, Hg and Pb concentrations in moss and in soil: elevation (GLOBE [36] 1 km × 1 km), precipitation ([37] 20 km × 20 km) and soil texture, i.e. sand, clay and silt content in the upper soil ([38] 1 km × 1 km). The sea spray effect was accounted for in terms of the distance of each moss and soil sampling site to the Norwegian Sea calculated within ArcGIS 10.0. To include land use patterns into the analysis percentages of forests as well as urban and agricultural areas around 1 and 5 km, the moss and soil sampling sites were derived from the Corine Land Cover maps 2000 and 2006 [39] and intersected with the HM concentration values measured in moss and soil specimen. Land use indices derived from the land cover maps 2000 were thereby assigned to the moss data from 1990, 1995 and 2000; those derived from the corresponding map 2006 were assigned to moss data from 2005 and 2010. Furthermore, grid data in a 2.5 arc minute resolution on estimated population densities for the years 1990, 1995, 2000, 2005, 2010 and 2015 were downloaded

from the *Gridded Population of the World* (GPW, version 3 [39,40]) and included in the analysis.

Finally, the HM concentrations in moss and soil samples were intersected with maps on modelled total deposition of Cd, Hg and Pb provided by the MSC-E (Meteorological Synthesizing Centre-East) of the EMEP. Within EMEP, the deposition values are modelled for 50 km × 50 km by use of the MSCE-HM atmospheric transport model [41-43]. For the metal concentrations in moss, the median for each of the EMEP raster cells was used for the correlation analysis. With exception of 1990, the 3-year sum of the modelled deposition values, preceding the time of the sampling of the moss specimen, were calculated and assigned to each EMEP cell since the analysed moss shoots represent the recent 3 years of growth. For 1990 moss values, only modelled deposition data from that same year was available.

Variogram analysis and Kriging estimation

To investigate spatial patterns and temporal trends of the measured Cd, Hg and Pb concentrations in moss (1990, 1995, 2000, 2005 and 2010) and in soil (1995, 2005) and to relate them spatially, geostatistics were applied. To this end, variogram analysis and Kriging procedures were carried through by use of the ArcGIS 10.1 extension *Geostatistical Analyst*. The average nearest neighbour distance was calculated for each year of the abovementioned sampling campaigns and used as a starting point to set the lag distances, amounting for about 22 km in each case. Since all element concentrations showed highly right-skewed data distributions and clear spatial drifts, Lognormal Universal Kriging was applied to calculate surface maps for Cd, Hg and Pb concentration in Norwegian moss and soil samples in a spatial resolution of 5 km × 5 km. Within a four-sector searching window, the ten sites nearest to each raster cell were used to perform the surface estimations in each case. To assess the quality of estimation, the ME and the MPE were calculated from the results of cross-validation.

Correlation analyses of measured and geostatistically estimated HM concentrations

Next to mapping spatiotemporal trends, the surface maps calculated by use of the Kriging estimation were used to analyse the statistical dependencies between both the measured Cd, Hg and Pb concentration in moss and the spatially estimated soil data, and the measured Cd, Hg and Pb concentration in soil and the spatially estimated moss data in 1995 and 2005. This procedure complements the correlation analyses based on the measured HM concentrations explained in the 'Correlation analyses of measured HM concentrations' section.

Additional file

Additional file 1: Supplementary figures. This file contains figures on the geostatistical analysis of Cd, Hg and Pb in moss in 1990, 2000 and 2010.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

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

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