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Spatially valid data of atmospheric deposition of heavy metals and nitrogen derived by moss surveys for pollution risk assessments of ecosystems

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Abstract

For analysing element input into ecosystems and associated risks due to atmospheric deposition, element concentrations in moss provide complementary and time-integrated data at high spatial resolution every five years since 1990. The paper reviews (1) minimum sample sizes needed for reliable, statistical estimation of mean values at four different spatial scales (European and national level as well as landscape-specific level covering Europe and single countries); (2) trends of heavy metal (HM) and nitrogen (N) concentrations in moss in Europe (1990-2010); (3) correlations between concentrations of HM in moss and soil specimens collected across Norway (1990-2010); and (4) canopy drip-induced site-specific variation of N concentration in moss sampled in seven European countries (1990-2013). While the minimum sample sizes on the European and national level were achieved without exception, for some ecological land classes and elements the coverage with sampling sites should be improved. The decline in emission and subsequent atmospheric deposition of HM across Europe has resulted in decreasing HM concentrations in moss between 1990 and 2010. In contrast, hardly any changes were observed for N in moss between 2005, when N was included into the survey for the first time, and 2010. In Norway, both, the moss and the soil survey data sets were correlated, indicating a decrease of HM concentrations in moss and soil. At the site

level, the average N deposition inside of forests was almost three times higher than the average N deposition outside of forests.

Keywords

Bioaccumulation; bioindication; heavy metals; moss; soil; nitrogen

1 Background and objectives

Some of the most significant anthropogenic sources of heavy metals (HM) include metals industry (Al, As, Cr, Cu, Fe, Zn), other manufacturing industries and construction (As, Cd, Cr, Hg, Ni, Pb), electricity and heat production (e.g. Hg, Ni), road transportation (Cu and Sb from brake wear, Pb from petrol, Zn from tires), petroleum refining (Ni, V), and phosphate fertilisers in agricultural areas (Cd) (Harmens et al. 2011 a). N emissions and relateted deposition are due to technical processes and agriculture. Pollutants which were emitted into and transported through the atmosphere finally come down at Earth´s surface as wet (rain, snow), occult (fog, mist, rime) or dry (gases, particles) deposition where they accumulate in biota and sediments of terrestrial and subsequently of aquatic ecosystems.

In Germany, less than 10 % of the HM load of aquatic environments is emitted from industries. More than 80 % of policyclic aromatic hydrocarbons inputs in aquatic systems are derived from atmospheric deposition. About 72 % of the total N load is due to diffuse sources such as agricultural land use (Böhm et al. 2000, Fuchs et al. 2010). Thus, assessing risks for aquatic sediments necessarily needs spatial valid information on atmospheric deposition onto land surfaces of drainage basins (Böhm et al. 2000; Fuchs et al. 2010) where atmospheric deposition can be collected by technical devices such as permanent open (´bulk´) samplers and wet only samplers (Hansen et al. 2013) as well as by biological samplers as for instance moss (Harmens et al. 2015). In contrast to measurements with technical deposition samplers there are only few studies analysing forest tree canopy drip effects on the accumulation of N in moss (Skudnik et al. 2014, 2015) and how this could influence the evaluation of atmospheric deposition patterns in drainage basins with silvicultural land use.

Over the past and future decades atmospheric deposition has received and will retain considerable attention as an environmental problem since acidifying compounds affects soil, limnic systems, aquatic and terrestrial biota (e.g. fish populations, forest trees), reactive N impacts terrestrial and aquatic ecosystems through nutrient enrichment, and HM

accumulate in food chains as well as in soils and sediments (de Witt and Wathne 2015; EEA 2014; Garmo et al. 2014; WGE 2013). The latter can serve as an important HM source for aquatic ecosystems (EU 2002). Therefore, the Convention on Long-Range Transboundary Air Pollution (CLRTAP) was implemented in 1979 to reduce air pollutant emissions in Europe and North America and thereby improve the environmental status of terrestrial and aquatic ecosystems. Under the CLTRAP, six International Cooperative Programmes (ICP) were launched to assess the impact of atmospheric pollution on ecosystems and the effects of emission control, amongst them: *ICP Integrated Monitoring* (2 sites in NE- and SE-Germany, Bringmark et al. 2013; Dirnböck et al. 2014), ICP *Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests)* (66 sites in Germany according to Seidling, Email 2015.02.25; Michel and Seidling 2015), *ICP Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation)* (700-1030 moss survey sites in Germany, section 2.1.1) and the ICP *Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP Waters)* (35 sites in Germany, Garmo et al. 2014). The latter aims at monitoring effects of N and HM (Cd, Hg, Pb) atmospheric deposition on water chemistry, on presences / absence of aquatic biota and on concentrations in biota and in sediments (Garmo et al 2014; Holen et al. 2013). The objective of the *ICP Integrated Monitoring* is to investigate the state of ecosystems or catchments regarding the spatial variation and impact of air pollutants such as N and HM including effects on biota. Thereby, biomonitoring approaches such as the use of moss as natural deposition sampler are included connecting the *ICP Integrated Monitoring* with the *ICP Vegetation* (Meyer et al. 2015 b).

Atmospheric deposition is often used as input parameter for modelling fluxes of N and HM into surface waters (Fuchs et al. 2010) and can be determined by numeric models such as LOTOS-EUROS (Builtjes et al. 2014; Mues et al. 2014; Schaap et al. 2008) and EMEP (Simpson et al. 2014 a, 2014 b) using emission and meteorological data and validated by chemical analyses of deposition collected with technical devices such as bulk and wet only samplers (Adriaenssens et al. 2013; Hansen et al. 2013) or by biomonitors such as mosses (Harmens et al. 2013 a, 2014, 2015). Due to specific advantages and disadvantages afore mentioned approaches should be applied complementarily. Technical sampling enables high time resolution, however only a sparse spatial coverage (Tørseth et al. 2012). Benefits using the moss technique are that metals accumulate in moss, leading to much higher concentrations than in air, rain and snow and, thus, reducing problems of contamination during sampling and analysis (Harmens et al. 2015). Additionally, the moss survey covers large areas of Europe and many elements and enables spatially valid estimates of the exposure of drainage basins to atmospheric deposition. Therefore, this article concentrates on the moss technique.

To map atmospheric deposition and to validate and spatially differentiate measured and modelled deposition values, the use of estimates from element concentrations in moss is well established (Harmens et al. 2012; Nickel et al. 2015 a, 2015 b;

Schröder et al. 2012). Since 1990, the moss technique was used for HM surveys encompassing up to 7000 sites across Europe every 5 years (Harmens et al. 2015). By far the most sampling sites are located in forested areas which are of great importance for the quantity and quality of water and sediments in drainage basins. The latest moss survey was conducted in 2010. Germany participated in the surveys 1990-2005. Since 2005, N and since 2010 persistent organic pollutants (POP) complemented the chemical analyses of HM in moss (Harmens et al. 2013 a, 2014, 2015). The European moss survey provides complementary and time-integrated data at a high spatial resolution which are used to identify areas at risk of high of atmospheric deposition and assess temporal trends. Thus, the moss data could be used as an additional source to estimate the atmospheric input of pollutants into sediments of catchment basins and aquatic ecosystems and, thus, contribute to the topics *Inputs of pollutants and risk assessment in context with the Water Framework Directive* of the International Conference Contaminated Sediments 2015. In this context, the paper at hand introduces the European moss survey as a suitable data base for quantifying the contamination of terrestrial and aquatic sediments due to atmospheric deposition – directly through atmospheric deposition onto water surfaces and indirectly through run off from terrestrial surfaces of drainage areas exposed to deposition (Downs et al. 1998; Schwesig and Matzner 2001). To this end, investigations at different spatial scales relevant for risk assessments of catchments were conducted dealing with the following questions:

1. Are there enough sample sites for reliable statistics for Europe as a whole, single countries and ecologically defined land classes covering Europe (methods Sections 2.2.1, results: Section 3.2)?

2. What are the trends of HM and N atmospheric deposition from 1990-2010 (HM) and 2005-2010 (N), respectively (methods Sections 2.1.1 and 2.2.2, results: Section 3.3)?

3. Are HM concentrations in moss correlated with HM concentrations in soil and, thus, due to leaching of HM from soil, indicate a potential risk for aquatic ecosystems and their sediments (investigation at *national level by example of Norway*; methods Sections 2.1.2 and 2.2.3, results Section 3.4)?

4. Do N concentrations in moss samples reflect *site*-specific variance due to the filter effect of vegetation canopies (methods Sections 2.1.3 and 2.2.4, results Section 3.5)?

2 Materials and Methods

2.1 Sampling and chemical analyses

2.1.1 Trends of HM (1990-2010) and N (2005-2010) concentrations in moss collected across Europe

The trend analysis detailed in sections 2.2.2 and 3.3 was based on moss specimens collected between 1990 and 2010 across Europe. Based on experience with Norwegian moss surveys in 1977 and 1985 relying on around 460 sampling sites (Steinnes et al. 2011), since 1990 the European moss survey has been providing data on HM and since 2005 on N concentrations in naturally growing moss following a harmonized methodology for sampling, chemical analyses and quality control ensuring spatial and temporal comparability. The latest manual was updated for the 2015 survey (ICP Vegetation 2014). The concentration of HM (expressed as mg kg^{-1} dry weight at 40° C) and N (in [%] or [mg g^{-1}] of dry weight at 40° C) were determined by several analytical techniques such as Inductively Coupled Plasma Optical Emission Spectrometry (sometimes referred to as an ICP-Atomic Emission Spectrometry), ICP Mass Spectrometry or Neutron Activation Analysis (Barandovski 2015; Harmens et al. 2013 c; Špirić et al. 2012, 2013, 2014 a, 2014 b). Quality control exercises are based on moss reference material M2, containing elevated concentrations for most metals, and M3, containing background concentrations for most metals (Steinnes et al. 1997). Recommended values for the N concentration in M2 and M3 were established in the 2005 European moss survey. In addition, some laboratories used other certified reference material for quality assurance (Harmens et al. 2010, 2011 b, 2013c, 2014, 2015; Kluge et al. 2013; Meyer et al. 2015 a, 2015 b; Schröder et al. 2009).

The European moss survey provides data on concentrations of at least ten HM (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, Zn) in naturally growing mosses, and since 2005 also for Al, Sb and for N. By far more metal elements are determined in some countries such as Albania and Macedonia (Barandovski et al. 2015; Qarri et al. 2013). In 2010, a pilot study was conducted on the application of mosses as biomonitors of selected POPs (Harmens et al. 2013a, 2013 b). The HM data reported from the European surveys 1990 and 1995 were based on moss specimens collected at 4661 (Germany 592, Norway 458) and 7311 (Norway 458) sites, respectively. In the 2000 / 2001 survey moss specimens were sampled at almost 7000 (Norway 464) sites in 29 European countries (Harmens et al. 2004). In 2005 / 2006 the HM concentrations were derived from moss specimen sampled at more than 7000 sites (Norway 464) in 32 European countries and the N concentrations from moss collected at 3200 sites (Norway without N measurements) (Harmens et al. 2006). 25 European countries reported on HM concentrations in moss sampled at over 4500 sites and on N concentrations in moss specimens sampled at roughly 2400 sites in 15 countries 2010 / 2011 (Norway 464). Germany did not participate in this survey “leaving a big gap in the data for central Europe” (Harmens et al. 2015).

In 2010, *Pleurozium schreberi* was the moss species most frequently sampled across Europe (ca. 42 %), followed by *Hylocomium splendens* (23.5 % and 15.3 % for HM and N, respectively), *Hypnum cupressiforme* (19.6 % and 26.9 %, respectively), *Pseudoscleropodium purum* (7.7 % and 7.5 %, respectively) and other species (7.1 % and 8.7 %, respectively).

For quality assurance purposes moss reference material (Steinnes et al. 1997) was used. Where necessary, correction factors were applied to outliers, and in some cases severe outliers were excluded from further data processing (Harmens et al. 2015; Meyer et al. 2015 b). In all survey years, the reported data were checked for anomalies and the format harmonized before maps were produced. The maps display the spatial pattern of HM and N concentrations across Europe on a 50 km by 50 km grid enabling a direct comparison with the atmospheric total HM and N deposition modelled by EMEP. Additional computations allowed for mapping element concentrations in moss with a significant higher spatial resolution (Schröder et al. 2012, 2013, 2014).

2.1.2 Correlation of HM concentrations in moss and soil sampled across Norway 1990-2010

The data base for correlation analyses (sections 2.2.3, 3.4) were moss and soil samples collected across Norway mainland. The moss data were derived from specimens collected in 1990, 1995, 2000, 2005 and 2010 at 458 to 464 sites distributed across the mainland of Norway according to the harmonized European protocol (section 2.1.1; Steinnes et al. 2011, 2013). At nearly the same sites, samples of natural organic surface soils were collected in 1995 and 2005 according to a procedure described by Nygård et al. (2012).

2.1.3 Variation of N concentrations in moss at site level due to canopy drip effects

Up to now, only few studies on canopy effects on N concentration in moss were published (Skudnik et al. 2014, 2015). This investigation of canopy drip effects on N concentrations in moss (sections 2.2.4, 3.5) relies on two data bases, one published by Kluge et al. (2013) and Meyer et al. (2015 a) and the other by Harmens et al. (2014), which were compiled and assessed statistically by Meyer et al. (2015 b).

Since spatial dense deposition monitoring with technical samplers such as bulk and wet-only samplers is rare (Tørseth et al. 2012) but feasible with the moss technique, we systematically examined whether the filter effect of forest stands for atmospheric N deposition as already confirmed by technical deposition samplers for single sites could be corroborated by use of moss and, thus, applied for surveys covering areas of large spatial extend. To this end, in addition to the measurement of N concentration in mosses sampled at 720 sites across Germany in 2005 (Section 2.1.1) a systematic investigation of canopy drip-related variation of N concentration in moss was conducted (Kluge et al. 2013; Meyer et al. 2015 a, 2015 b). The moss specimens were sampled in 2012 and 2013 across North-western Germany beneath tree canopies (in

the following referred to as “throughfall sites”, n = 30) and at adjacent (i.e. 2 km distance at maximum) places outside of peripheral tree canopies (“open sites”, n = 26) which in the following are referred to as ‘DE-NI_12 / 13’). These measurements were joined with respective data derived from a study dealing with the statistical relation between site-specific N concentrations in mosses and measured atmospheric N deposition across Europe sampled in Austria (AT), Switzerland (CH), Germany (DE), Spain (ES), Finland (FI), France (FR), and Slovenia (SI) between 1998 and 2012 (Harmens et al. 2014). *Pleurozium schreberi* was collected most frequently (n = 136; 48 %) followed by *Pseudoscleropodium purum* (n = 69; 24 %), *Hypnum cupressiforme* (n = 58; 20%), *Hylocomium splendens* (n = 10; 4 %), *Thuidium tamariscinum* (n = 9; 3 %) and *Abietinella abietina* (n = 2; 1 %). In accordance with the investigation purposes, moss samples were collected either outside of the peripheral tree canopy (“open sites”) as holds true for AT, CH, DE, FI, and SI (n = 147) or inside (in the following referred to as “throughfall sites”) in DE, ES, and FR (n = 137).

Sampling, preparation and chemical analyses were conducted according to the guidelines of the European moss survey (Section 2.1.1) and described by Harmens et al. (2013 c, 2014) and Meyer et al. (2015 a, 2015 b). Accordingly, for quality control purposes, moss reference materials M2 and M3 (Steinnes et al. 1997) were used in all participating countries except for DE (1998-2010) using reference materials according to DIN standards (DIN EN ISO 17025). For ‘DE-Ni_12 / 13’, certified reference material reviewed by inter-laboratory tests was used for quality assurance (Meyer et al. 2015 a, 2015 b).

2.2 Statistics

2.2.1 Calculation of minimum number of sampling sites needed for reliable statistics

Measurement values should be meaningful not only for single observed points in space and time but should rather allow for spatial and temporal generalizations so that the number of samples required should be based on a specified confidence interval of the mean of the variable considered (Nelson and Ward 1981). Therefore, the minimum number of sampling sites (MSS) needed for reliable statistics were calculated for concentrations of Al, As, Cd, Cr, Cu, Fe, Hg, N, Ni, Pb, S, Sb, V, and Zn in moss collected in 2010. The minimum number was computed for (a) Europe in terms of the sum of the territories of countries which participated in both moss surveys; (b) each of the participating countries; (c) each of the 40 Ecological Land Classes of Europe (ELCE 40) covering the whole Europe and (d) for each ELCE unit within the participating countries covered by the survey network. This spatial differentiation is of importance since the landscape specific differentiation (c) is not fixed to administrative boundaries. However, while some of the participating countries might comply with the MSS for a

certain element the MSS potentially could not be reached when considering the MSS of specific landscapes within the respective country (d).

For calculating the minimum sample number needed to adequately cover the ecoregions of Europe the data on HM and N concentrations in moss collected 2010 (HM, N) were linked to a map of ecological land classes across Europe. This map was calculated by means of Classification and Regression Trees (CART; Breimann et al. 1984) from 48 digital maps each depicting the spatial pattern of one of 48 ecologically relevant characteristics of landscapes / drainage basins covering climate, altitude, soil, and potential natural vegetation in Europe. ELCE subdivides Europe into spatial units mapped on grids of about 20 km by 20 km (Schröder et al. 2014) (Figure S1 and Table S1).

As the majority of moss data were not normally distributed, a different treatment of these data was necessary to calculate the MSS values: For those moss data, that were not normally distributed concerning the respective spatial scale, logarithmic transformation – in fact, natural logarithm of base e – to approximate normal distribution and MSS-formula (2) were applied instead of the MSS-formula (1). For normally distributed moss data, MSS values were calculated by means of the original MSS-formula (1).

(1) MSS-formula of the moss-manual (ICP 2014)

$$MSS = \left(\frac{1.96 * Stdev}{tol * Mean}\right)^2$$

(2) MSS-formula according to Wosniok (2015)

$$MSS = -\frac{B}{4A} + \sqrt{\left(\frac{B}{4A}\right)^2 - \frac{Stdev_{log}^2}{A}}$$

with:

$$A = \left(\frac{1}{1.96}\left\{\ln[Mean * (1 + tol)] - Mean_{log} - \frac{Stdev_{log}^2}{2}\right\}\right)^2$$

$$B = -2A - 2 * Stdev_{log}^2 - Stdev_{log}^4$$

$$Mean_{log} = \ln(Mean) - \frac{Stdev_{log}^2}{2}$$

$$Stdev_{log} = \sqrt{\ln\left(1 + \frac{Stdev^2}{Mean^2}\right)}$$

Stdev = Standard deviation of measured element concentration in mosses

1.96 = Z-value, indicating significance level of 0.05

tol = Error tolerance, here: 0.2 (= 20 %)

Mean = Mean value of measured element concentration in mosses

The idea of determining the minimum number of sampling sites is, to ensure a maximal distance of 'tol * Mean' between empirical and true mean at a significance level of 0.05. MSS-formula (2) is based on the 'Cox method' (mentioned as 'personal communucation' in Land 1971 as cited in Olsson 2005) for calculating confidence intervals for the mean of a log-normal distribution. For calculating MMS, the Cox equation was resolved by Wosniok (2015).

2.2.2 Trends of HM (1990-2010) and N (2005-2010) concentrations in moss collected across Europe

Statistical analyses of temporal trends derived from data collected in 1990, 1995, 2005 and 2010 across Europe were performed as described by Harmens et al. (2010). Accordingly, for each metal, data were only included for those countries that had determined the element concentrations for at least four out of the five survey years. However, for Hg some countries were also included that had reported data for three out of the last four survey years. Regarding Al, Sb and N, the development was determined between 2005 and 2010. For HM, a general linear model with the geometric mean as the response and country and year as factors was then run. Tukey tests applied for pairwise element-specific comparisons between years (Harmens et al. 2015).

2.2.3 Correlation of HM concentrations in moss and soil collected across Norway 1990-2010

Descriptive and correlation statistics, and testing for significant differences between surveys

Basic descriptive statistical measures (number of sites, minimum, maximum, median) for the concentrations of As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Ti, Sb, V, and Zn in moss were calculated for specimens collected in 1990, 1995, 2000, 2005, and 2010 as well as for natural surface soil sampled in 1995 and 2005. Wilcoxon signed rank test were applied to investigate whether significant differences between the data from different monitoring campaigns exist.

Correlations between the Cd, Hg and Pb concentrations in moss and soil were computed according to Spearman (1904) (r_s). 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 were complemented by correlation analyses including geostatistically estimated HM concentrations which were computed to estimate potential bias due to surface estimation and by analyses of correlations between measured HM concentrations and potential predictors for element concentrations in moss and soil.

Identification and ranking potential predictors for element concentrations in moss and soil

In order to uncover and rank multivariate relationships of the HM concentrations in moss and natural surface soil with potential influencing environmental factors as predictors of HM concentration in moss and soil samples, classification and regression trees (CART) were computed. Thereby, four approaches (A) should enable investigating whether moss and soil indicate similar environmental conditions: Measured concentrations of Cd, Hg, and Pb in moss samples were set as target variable and related to predictors including (A1) / not including (A2) geostatistically estimated HM concentrations in natural surface soil. Additionally, measured concentrations of Cd, Hg, and Pb in natural surface soil were set as target variable including (A3) / not including (A4) geostatistically estimated HM concentrations in moss samples as environmental predictor. The geostatistical estimation of concentration values have each been carried out because the geographical coordinates of moss and soil sampling sites did not match exactly in all cases. Contrary to approaches 1, 3 and 4, approach 2 was calculated not only for Cd, Hg, and Pb but also for As, Cr, Cu, Fe, Ni, Sb, Ti, V, and Zn. The following characteristics of terrestrial landscapes and drainage basins, respectively, were regarded as predictors: distance to the North Sea [km] as parameter for potential sea spray effect; elevation above sea level [m] (GLOBE, 1 km by 1 km, Hastings et al. 1999); precipitation 1991-2002 [mm / a] (20 km by 20 km, New et al. 2002); percentage of agricultural, forestall and urban land use [%], respectively, each in 1 km and 5 km radius around sampling sites derived from Corine Land Cover maps 2000 and 2006 (Büttner et al. 2012); population density [residents / km^2] (grid data in a 5 km by 5 km resolution on population densities for the years 1990, 1995, 2000 and estimated for 2005, 2010 and 2015, GPW version 3, CIESIN / FAO / CIAT 2005); soil

texture in terms of percentages of clay, silt and sand in the upper soil [%] (1 km by 1 km, FAO / IIASA / ISRIC / ISSCAS / JRC 2009); modelled total atmospheric deposition (EMEP; 50 km by 50 km grid; Gusev et al. 2010): Cd - 3 years' sum [µg m^{-2} a^{-1}], Hg - 3 years' sum [µg m^{-2} a^{-1}], and Pb - 3 years' sum [µg m^{-2} a^{-1}]; geostatistically estimated concentrations of Cd, Hg and Pb in moss and soil [µg g^{-1}].

For the HM concentrations in moss, the median for each of the EMEP 50 km by 50 km raster cells (Gusev et al. 2010) 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 atmospheric total deposition data from that same year was available.

Geostatistical evaluation of spatial validity

To investigate the validity of the monitoring network and, respectively, the 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), geostatistics were applied. To this end, variogram analysis and Kriging procedures were carried through by use of the ESRI ArcGIS 10.1 extension Geostatistical Analyst (ESRI 2011). 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 by 5 km. The quality of estimation was calculated by use of cross-validation and by correlation of measured and geostatistically estimated HM concentrations.

Correlation of measured and geostatistically estimated HM concentrations

The surface maps calculated by use of the Kriging estimation were used to analyse the correlation between both the measured Cd, Hg and Pb concentrations in moss and the spatially estimated HM concentrations in soil, and the measured Cd, Hg and Pb concentrations in soil and the spatially estimated HM concentrations in moss for the surveys 1995 and 2005.

2.2.4 Variation of N concentrations at site level due to canopy drip effects

In analogy to the investigations in Norway, for characterisation of the sampling sites and to identify the most relevant environmental factors associated with the N concentrations in moss, the following geodata were spatially connected with the sampling locations: percentages for agricultural, forested and urban areas within a radius of 1 and 5 km around the moss sampling sites were calculated based on the Corine Landcover map 2006 (Büttner et al. 2012), population density (CIESIN, FAO, CIAT 2005), altitude above sea level (a.s.l.) (Hastings et al. 1999), precipitation (New et al. 2002), distance of the sampling sites to the North Sea, gridded data on modelled atmospheric total N deposition including wet and dry deposition of oxidized and reduced N in a resolution of 50 km by 50 km (provided by EMEP MSC-W; Simpson et al. 2014 a, b). Taking into account the two to three years growth of moss, the modelled atmospheric total N deposition was averaged over the previous three years integrating the respective year of sampling and the previous two years and then intersected with the particular N content in moss (Meyer et al. 2015 b).

3 Results and discussion

The results of the moss surveys are spatially valid not for single measurement points but for large areas such as drainage basins, ecoregions, national territories and Europe as a whole. Up to now, the calculation of element loads of aquatic ecosystems was based on deposition values with little empirical validation (Fuchs et al. 2010). The moss monitoring data are recommended to improve that situation.

3.1 Quality control

According to Dołęgowska and Migaszewski (2015) and Schröder et al. (1991, 2009) environmental studies need a transparent documentation of selecting sampling sites, collection of specimens, chemical and physical measurements and statistical data analysis. Regarding the European moss survey, these requirements are realised pretty good. Generally, data obtained indicated acceptable agreement between laboratories. In 2010, the mean values ranged from 85 % for As to 105 % (Sb) of the recommended values for M2 and from 92 % (Cr) to 113 % (As) for M3. For N, the mean values of M2 and M3 were 101 % and 102 % of the recommended value respectively. Correction factors were applied when both M2 and M3 values were outliers for a specific metal, and sometimes corrections factors were also applied when only one reference value was identified as an outlier (Harmens et al. 2015). Although applying correction factors enhanced compatibility of data between countries, it hardly affected the overall European mean and median values for the elements. As a consequence, it did not significantly affect the temporal trends reported for the whole of Europe. The results of quality control exercises were

reported by Harmens et al. (2010, 2011 b, 2013c, 2014, 2015), Kluge et al. (2013), Meyer et al. (2015 b), and Schröder et al. (2009).

3.2 Calculation of minimum number of sampling sites needed for reliable statistics

The minimum sample size for the European moss surveys 2005 and 2010 was computed ex-post but not a priori and, thus, applied to the already existing networks. Regarding those 40 ELCE units which were covered by the European moss survey 2005, in most cases the number of sampled sites (realized sample size - RSS) reached the number of sites required (MSS) to calculate valid statistically reliable N concentrations in moss. The minimum number of sampling sites required had failed in three out of 27 ECLE units (11.1 %) with N determined in mosses: in these three land classes, 27 sites instead of 12, 6 instead of 2, and 8 instead of 4, should have been sampled, respectively. The determination of minimum numbers of sampling sites needed for calculating reliable mean values for Europe as a whole and for each of the 16 countries participating in the moss survey 2005 revealed a similar picture as found for ELCE landscapes as spatial reference system. The number of sampling sites was shown to be adequate to estimate reliable statistics on the N concentrations in moss sampled in 2005 (Schröder et al. 2014). To capture the spatial variability of atmospheric N deposition and N concentrations in mosses, it should be emphasized that the guidance on sampling density as provided in the moss monitoring manual (ICP Vegetation 2015) should be followed. As indicated above for the ELCE units, the spatial scale of the statistical analysis determines whether the current network density is sufficient or not to obtain reliable statistics.

In the European moss survey 2010 moss were sampled at 4.499 sites in 25 countries and 14 elements were determined. For each of the elements the minimum sample size was calculated and compared to the realised sample number for Europe as a whole, each participating country and landscape-specific across Europe (Table 1) and each participating country (Table 2) , to provide an indication of statistical reliability at different spatial scales. Regarding Europe as a whole, the realized sample size (RSS) reaches the required minimum sample size (MSS) in all cases of the 14 considered elements. However, this holds not true when considering lower spatial levels. On a national scale, only two (N, S) of the 14 considered elements comply with the required sample size in 100 % of the countries in which the respective elements were collected. For all other elements the MSS is reached by 58 % to 90 % of the participating countries. On the other hand, 6 out of the 25 participating countries, so nearly 24 %, reach the MSS for all elements that were collected by the respective country. When considering the ELCE units (Figure S1 and Table S1), which in contrast to the administrative areas of the national states constitute not do be continguous areas, some differences compared to the national level were found. Moss sites are located in 32 of the 40 ELCE units (Table 1). However, none of the 14 examined elements reach the MSS in all ELCE units where moss specimens

were sampled. The lowest percentage was calculated for Al reachimg the MSS in only 34 % of the ELCE units containing sample sites with Al measurements. But by taking a differentiated look at the particular ELCE units at least four of the 32 ecoregions containing sampling sites comply with the MSS for all elements measured within the respective ecoregion. On the other hand, in comparison to the national level, ecoregions with very low percentage of sufficient MSS per element were found: Unit F4_1 (11 %) and Unit L_2 (8 %) and Unit D_10 (7 %). In unit M_6, none of the measured elements reaches the MSS. Concerning the level of compliance of the particular ELCE units as shown in Table 2 for Cd, Hg, Pb and N, three-digit absolute values for MSS were reached within many ecoregions, which corresponds with the results on the national scale. Highest compliance was calculated for unit F4_2 in case of N.

Table 1. Element-specific minimum and realised sample size for different landscapes across Europe by example of Cd, Hg, Pb and N, survey 2010

Considering the lowest spatial scale – the ELCE units within each participating country – it turned out that none of the elements reaches the MSS in 100 % of the ELCE units of the single participating countries. As ELCE units are not continuous across Europe, one specific unit may occur in more than one country. Thus, the "total n" may contain one specific ELCE unit several times. Therefore, "total n" exceeds the number of different ELCE units within Europe as a whole (n = 40). Based on "total n", deviations were calculated to examine for each element, the absolute number (MSS complied (n) and MSS not complied (n)) and the relative number (MSS complied (%) and MSS not complied (%)) of ELCE units within the single participating countries that fulfill the required MSS or do not, respectively. As Table 2 shows, a maximum was calculated for N and S for which at least 76 % and 80 % of the landscapes within the single countries reach the MSS. But more than half of the 14 analysed elements do not reach even 50 %. Regarding the ELCE units within the single countries particularly, in 8 % of the cases MSS was reached for all elements sampled within the respective unit of a certain country. In 13 % of the cases the MSS was not reached for all sampled elements. Furthermore, the analysis revealed that indeed some landscapes comply with the MSS regarding the European level. However, when examining the same landscape within a single participating country, this fact is not holding true anymore in some cases.

Table 2. Element-specific minimum and realised sample size for different landscapes within each participating country for 14 elements, survey 2010

The computations indicate that the compliance achieved for Europe as a whole and single countries, respectively, is now lower when statistics are conducted at the landscape level. This suggests that MSS is dependent on the scale of interest of a

study, hence, following the MSS guidance from a higher spatial level would be not valid if one would like to determine concentrations in mosses reliably at the landscape or even a smaller scale as for instance protected habitats or sites. In summary, from the results shown, it is clear that the requirement for MSS is very much dependent on the aim and scale of a study and the questions it is trying to answer.

3.3 Trends of HM (1990-2010) and N (2005-2010) concentrations in moss sampled across Europe

In general, mosses from countries in Northern Europe had the lowest HM concentrations, whereas countries in Eastern and South-eastern Europe had the highest. Averaged across Europe, since 1990, the median concentration in moss specimens has declined the most for Pb (77 %), followed by V (57 %), Cd (51 %), Cr (43 %), Zn (34 %), Ni (33 %), Fe (27 %), As (21 %, since 1995), Hg (14 %, since 1995) and Cu (11 %) (Harmens et al. 2013, c, 2015) (Table 3). The average modelled Cd and Pb deposition in the EMEP domain has declined by 51 % and 74 %, respectively. Between 1995 and 2010, the average Hg concentration in mosses has decreased by 23 %, whereas the average modelled Hg deposition (EMEP) has declined by 27 %. For other metals, the decline in concentrations in mosses also follows the decline in reported emissions since 1990, with the lowest decline being reported for Cu concentrations in mosses and absolute emissions.

Table 3. Decline in the average median HM and N concentrations in moss specimens since the start of the European moss survey in 1990a and since the survey in 2005b (Harmens et al. 2013 c, 2015)

As in previous surveys, the lowest concentrations of HM in moss sampled 2010 were generally found in Northern Europe. Low to intermediate HM concentrations in moss were generally observed in western and Central Europe. The highest concentrations were often found in (South-)Eastern Europe. The spatial patterns of Hg and Zn concentrations in moss were more homogeneous across Europe. On a national or (eco)regional scale deviations from the general European trend occur (Schröder et al. 2013, 2014). Therefore, even in times of generally decreasing metal deposition across Europe, temporal trends can differ between geographical scales.

From 2005 to 2010, the average N concentration in moss declined by 5 %. The spatial pattern of the N concentration in mosses in 2010 / 11 was similar to that in 2005 / 2006, with lower values being observed for Finland than the rest of Europe. High concentrations of N were found in western and central Europe. The small decrease in the average median N concentration in mosses is in agreement with the 7 % decline reported by EMEP for modelled total N deposition in the EU27 since 2005. Analyses of the relationship between nitrogen concentration in mosses and EMEP-modelled total nitrogen

deposition showed considerable scatter with saturation occurring at a total nitrogen deposition rate of ca. 15 kg N ha^{-1} a^{-1}. However, in some countries a linear relationship has been observed between the total N concentration in mosses and measured bulk N deposition at the site level (Harmens et al. 2015, 2011 b).

N concentrations in herbarium moss specimens collected between around 1860 and 2000 in the Czech Republic, Finland, France and Switzerland did not change before 1960. After 1960, the total N concentration in mosses has increased in these countries. Total N deposition rates modelled by EMEP / MSC-West show a similar trend with not much change in total N deposition rates up to 1960 (apart from the Czech Republic) and a clear rise since 1960 (Harmens et al. 2006). Highest exceedances of critical loads for acidification of freshwaters and forests by atmospheric deposition occurred in 1980. At that time, the critical loads for acidification of ecosystems were exceeded on 43 % of the EU-28 area. By 2020, the area where critical loads are expected to be exceeded and the absolute magnitude of exceedances is expected to be as low as they were in 1880, i.e. 4 % of the EU-28 area (EEA 2014). Nevertheless, the recovery from acidification will take decades even if they receive deposition lower than the critical loads (Skjelkvåle and de Wit 2011). The largest coverage with exceedances of critical loads for eutrophication was reached in 1990 with 79 % of the EU-28 area. This percentage is expected to decrease to 54 % in 2020, and the absolute magnitude of exceedances will also be reduced in most areas. North-western Germany will be one of the remaining hot spot areas for N. Even if all technically feasible reduction measures are implemented, the area at risk of eutrophication would still be 51 % in the EU-28 in 2030 (EEA 2014). Simpson et al. (2014 b) projected the area of ecosystems exceeding critical loads to 50% and in case of a possible climate-induced increase to 57 % for NH_3 emission rising by 30 %. However, it should be noted that for 2005, the atmospheric deposition measured and spatially modelled by the Norwegian Institute for Water Research was 69 % higher for sulphur and 98 % higher for N than the EMEP deposition. Considering the modelled EMEP deposition, the exceedances of critical loads amount for 8 % (2005) and 2% (2020), respectively. The corresponding values using deposition data from the Norwegian Institute for Air Research are 18.5 % and 9.5 %. Thus, in European overviews based on EMEP deposition (EEA 2014), the situation in Norway and other countries may appear better than it really is (Austnes 2015). Assuming the implementation of abatement techniques under *C*urrent *LE*gislation in 2010 (*CLE*2010) and in 2020 under *F*ull *I*mplementation of the Aarhus protocol (*FI*2020), a comparison of the critical loads and atmospheric depositions of Cd, Hg and Pb in these years revealed that Cd deposition is not a widespread risk in any years. However, Pb deposition was calculated to be acceeded about 22 % and 16 % of natural European area in 2010 and 2020, respectively, and Hg deposition to affect an area of more than 74 % in both years (Hettelingh et al. 2015).

Filtering atmospheric deposition and recycling water, forests are of great importance for the quantity and quality of water in drainage basins and their terrestrial and aquatic sediments (Likens and Bormann 1995). Long-term monitoring clearly

documents that surface waters respond to changes in atmospheric deposition: From 1990 to 2008 the concentrations of sulphate and nitrate (NO_3^-) in precipitation and surface waters have decreased in large areas in Europe and North America due to emission reductions which were more distinct between 1990 and 1999 than from 1999 to 2008. NO_3^- did not show uniformly decreasing trends despite the decrease in N deposition. The acidity of lakes and rivers decreased due to the decrease in sulphate. Although recovery of aquatic biological communities could be monitored a return to pre-industrial biodiversity is unlikely in most cases because original species were extinct. That is why in several regions of Europe a good water quality will not be achieved with current legislation of emissions of acidifying components (Futter et al. 2014; Skjelkvåle and de Wit 2011).

Even if the atmospheric deposition of HM declined throughout the last 25 years across Europe, it still remains high in the south-eastern European countries (Harmens et al. 2010). The HM pools in soils were and will be progressively filled up and constitute a latent risk to aquatic ecosystems (Bringmark et al. 2013). This gets obvious when assessing the toxicological potential of Hg (EU 2002). In fish, levels of Hg usually exceed the European environmental quality standard as set by the WFD to 20 µg Hg kg^{-1} fresh weight, whereby recent pollution was mainly ascribed to the diffuse atmospheric input. In Bavaria, for example, 98 % of the fish muscle samples exceeded the environmental quality standards for Hg between 2007 and 2009 (Lepom et al. 2013; Schäfer et al. 2015). Hg concentrations in fish collected during 2005-2010 from European lakes (Como, Geneva, Iseo, Lugano, Maggiore) and rivers (Rhine, Rhone) exceeded the above mentioned quality standard by 2- to 16-fold (Vignati et al. 2013). Akerblom et al. (2014) investigated Hg levels in Swedish freshwater fish during almost 50 years based roughly 44927 observations from 2881 waters. The EU environmental quality standard was exceeded in all waters. Trend analyses approaches indicated an overall decline of at least 20 % during 1965–2012. A clear regional pattern could not be found.

3.3 Correlation of HM concentrations in moss and organic surface soil sampled across Norway 1990-2010

Basic descriptive statistical measures (number of sites, minimum, maximum, median) for the concentrations of As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Ti, V, and Zn in moss collected in 1990, 1995, 2000, 2005, and 2010 as well as for natural surface soil specimen sampled in 1995 and 2005 were computed. For Cd, Hg and Pb, the highest medians as well as maximum values in moss can be observed in the 1990 survey. Between 1990 and 2010 Pb concentrations in moss decreased from 9.3 µg g^{-1} in 1990 to 1.5 µg g^{-1} in 2010. The median concentration of Hg in 2010 (0.064 µg / g) was almost the same as in 1990 and 1995 (0.068 µg g^{-1}). The highest median concentrations in soil were calculated for Cd and Pb in 1995. In case of Pb, there was a slight but significant decrease over time reaching from 34.6 µg g^{-1} in 1995 to 25.8 µg g^{-1} in 2005 ($\alpha = 0.01$). The

concentrations of Cd, Hg, and Pb in moss significantly decreased over time, except for Cd comparing 1990 / 1995, 1990 / 2005, and 2000 / 2010 and for Hg 1990 / 1995, 1990 / 2010, 1995 / 2010, and 2000 / 2005. The concentrations of As, Cr, Cu, Fe, Ni, Ti, Sb, V, and Zn (for details see Meyer et al. 2015 b) in moss mostly showed significant slight decrease across the surveys. However, this trend is not significant for As 1990 / 1995, 2000 / 2005, 2000 / 2010, and 2005 / 2010; for Cr 2005 / 2010; for Cu 1990 / 1995 and 2000 / 2010; for Fe 1995 / 2000 and 2005 / 2010; for Ni 1990 / 1995 and 2000 / 2010; for Sb 2005 / 2010; for V 1990 / 1995, 2000 / 2010, and 2005 / 2010; and for Zn 1990 / 2005, 2000 / 2005, 2000 / 2010, and 2005 / 2010. The mean HM concentrations in natural surface soil slightly decrease significantly between 1995 and 2005, except for As ($p = 0.78$, not significant (n.s.)), Cd ($p = 0.21$, n.s.), Cu ($p = 0.05$, n.s.), Ti ($p = 0.67$, n.s.), and V ($p = 0.04$, n.s).

Spearman correlation analysis revealed significant statistical associations between measured HM concentrations in moss and soil. Highest coefficients were computed for Pb (r_s around 0.8), followed by Cd ($r_s \approx 0.5$). Correlations between Hg concentrations in moss and soil samples ranged between $r_s \approx 0.3$ and $r_s \approx 0.4$. 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 moss show the same tendency and are slightly higher as those derived only from measured values. The highest coefficients were found for Pb ($0.81 \leq r_s \leq 0.88$), followed by Cd ($0.65 \leq r_s \leq 0.78$) and Hg ($0.35 \leq r_s \leq 0.39$). These findings together with the results from cross-validation corroborate the spatial validity of surface estimations and of the surveys (Nickel et al. 2014).

Based on this, the correlation of measured Cd, Hg and Pb concentrations either in moss and in soil samples and potential influencing factors such as sea spray effect, elevation above sea level, precipitation, land use, population density, soil texture (percentage of clay, silt and sand) and modelled total atmospheric deposition of Cd, Hg and Pb (EMEP) are of special interest (for details see Meyer et al. 2014). Regarding the element concentrations in moss, the modelled deposition values by far showed the highest significant (alpha = 0.01) correlations especially for Pb ($0.69 \leq r_s \leq 0.82$ for all years) and Cd ($0.61 \leq r_s \leq 0.73$ for all years). Like in the case of natural surface soil, for Hg, the weakest correlations among all three elements were identified ($0.26 \leq r_s \leq 0.46$ for all years). 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. Here, the corresponding coefficients are lower ($r_{s\,max} < \approx 0.5$) in all cases. The percentages of agriculture land use ($r_{s\,max} \approx 0.2$ for Pb in 1995) and forest areas ($r_{s\,max} \approx 0.3$ 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 ($r_s < \approx -0.3$) 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 (Pb 0.69 ≤ r_S ≤ 0.82, Cd 0.61 ≤ r_S ≤ 0.73, Hg r_S = 0.16). Population density was significantly correlated with the three HM in focus (Pb 0.40 ≤ r_S ≤ 0.45, Cd 0.23 ≤ r_S ≤ 0.25, Hg r_S = 0.28). Urban land use within a 5 km radius around sampling sites was most strongly, but low, correlated with concentrations of Cd (r_S = 0.2 in 2005) and Pb (r_S = 0.29 in 1995, 2005).

Multivariate relations between HM concentrations in moss and soil specimen and environmental characteristics were investigated by 4 approaches: CART computations including the HM concentrations in soil as potential environmental factor (approaches 1 and 3 described in Section 2.2.3) proved that the geostatistically estimated HM concentrations in natural surface soil was the most powerful predictor for measured concentrations of Cd, Hg and Pb in moss. In computations which did not include the HM concentrations in soil (approach 2, 4 described in Section 2.2.3), the modelled atmospheric HM deposition ´replaced´ the HM concentrations in soil as mostly influencing Cd, Hg and Pb concentrations in moss. Thus, moss and soil indicate the same phenomenon (Meyer et al. 2015 b; Steinnes et al. 2011).

For As, Cu, Sb, and V, the population density was the most powerful predictor between 1990 and 2010 (approach 2, Meyer et al. 2015 b). Following Weckwerth (2001), the use of Sb in brake pads of motor vehicles and the intensified use of automobiles in densely populated areas is probably the main reason for higher Sb levels in moss. Considering the maximum value of Sb, there was an increase of Sb in both moss (1990: 0.6 µg g^{-1}, 2010: 1.2 µg g^{-1}) and in natural surface soil from 5.4 µg g^{-1} in 1995 to 24.8 µg g^{-1} in 2005. The reduction of Sb emissions due to combustion processes in recent years was compensated by an increased number of motor vehicles (Steinnes et al. 2011). V, mainly emitted by combustion of fuel oils, only showed a small reduction of concentration in moss and natural surface soil with time (Meyer et al. 2015 b). Cu increased in, both, moss and natural surface soil from 1990 to 2010. The results of the CART analyses correspond to Steinnes et al. (2011) associating high population densities with increasing industrial activities. For Cr and Fe, the percentages of urban areas 5 km around the moss sampling sites is the predictor with the strongest association to the respective HM concentrations in moss – the higher the population density, the higher the concentrations in moss. Both the Fe and the Cr concentrations in moss increased over time, whereby Fe is mainly associated with mineral dust blown by the wind and Cr with domestic sources (Steinnes et al. 2011). The highest Cr and Ni concentrations collected across are respectively 6 and 20 times higher than the median concentration values of European countries and probably originated from industrial

emission of ferrochromium metallurgy, mine industry and the wind blowing soil dust from Cr and Fe-Ni mineral open slag dumps (Qarri et al. 2013).

The case study showed a decrease of HM concentrations in both moss and soil specimen collected across Norway. However, in case of moss samples the decrease is more pronounced and statistically significant. The spatial patterns of Cd and Pb concentrations in moss and soil specimens in 1995 and 2005 are similar. For Cd and Pb, the spatial differentiation of concentrations in moss is higher than in soil, while the opposite is true for Hg. Response times, especially of Pb concentration in soil, appear to be generally delayed compared to those of moss. Thus, risk assessments relying on terrestrial moss sampled across drainage basins help monitoring whether emission reductions result in decreasing atmospheric deposition for protecting terrestrial and aquatic sediments and biota. The integration of (organic) surface soil samples seems to be important for assessing effects of atmospheric deposition on compartments that respond more slowly than moss. At ICP Integrated Monitoring sites, the decline of Cd and Pb in the humus and top soil layers was accompanied by an increase in deeper soil layers in recent decades. Hg concentrations in deeper soil layers have also increased, demonstrating continued soil accumulation of heavy metals (WGE 2015).

Sediments result from chemical and physical weathering of rocks, subsequent transport by wind, water, mass movement or ice and, finally, accumulation of weathering products on land surfaces or in aquatic ecosystems such as lakes, rivers, and oceans (Jenny 1941 / 1994; White et al. 1998). Their biological, chemical and physical condition is mainly influenced by respective characteristics of their catchment basins including not only their soil and vegetation coverage and land use but also atmospheric deposition (Baron et al. 2013). That is why a catchment-based approach for monitoring and protection of aquatic ecosystems is needed (Breuer et al. 2008; Sharpley et al. 2015; Wolanski et al. 2004). Consequently, the European Water Framework Directive (WFD, Directive 2000 / 60 / EC) aims at protecting aquatic systems including their sediments by protecting their drainage basins (Noges et al. 2006; Reible and Lanczos 2006). The WFD aims to reach a “good ecological status” of aquatic ecosystems by water management at the river basin level. Similarly to concepts of ecological integrity and ecosystem health, “ecological status” means the quality of the structure and functioning of aquatic ecosystems and is to be assessed by biological, hydromorphological, and physico-chemical characteristics and evaluated using a scale graded by different deviations from the reference condition associated with no or very low anthropogenic pressure (Noges et al. 2006). To this end, the implementation of the WFD needs monitoring data from the above ICPs.

Atmospheric deposition is one of the pressures affecting directly and, via surface and sub-surface runoff, indirectly the chemical condition of waters and their sediments (Driscoll et al. 2007; EEA 2014; Eisele and Leibundgut 2002; Gassama and

Violette 2012; Langedal et al. 1998; Lepori and Keck 2012; Moldan et al. 2006; Oulehle et al. 2013; Prechtel et al. 2001; Rogora et al. 2012; Waller et al. 2012). Even if more than 90 % of the Quaternary[1] deposits in Norway have been transported and deposited offshore large areas are covered with at least a thin sediment cover (Olsen et al. 2013): Generally, Norway has large areas of exposed bedrock or bedrock with a thin cover of Quaternary sediments. A thin layer of sediments enhances the vulnerability to acidification on the one hand and decreases the time for responding to changing atmospheric deposition (Skjelkvåle and de Wit 2011). The South-eastern parts of Norway, the Jæren area in Southwest Norway and Finnmarksvidda in northern Norway have extended areas with a continuous cover of sediments. The average thickness of the till deposits which cover about 25 % of the mainland of Norway is about 6 m. Brown trout populations in thousands of lakes and native salmon populations from seven major rivers, such as the Tovdal River, got extinct due to atmospheric deposition of acidic pollutants and HM toxicity. A survey conducted in the 1990s in Fenno-Scandia documented that acidification has impaired fish populations at least 10 000 lakes (Holen et al. 2013). Simultaneous surveys, conducted 1995 in Norway, proved the same geographic patterns of HM concentrations in moss, soils (humic layers), lake sediments, and surface waters (Skjelkvåle et al. 2006).

In the lake Dümmer region in North-western Germany, where cyanobacteria regularly causes severe ecological problems, the atmospheric N deposition amounted to roughly 21 kg N ha^{-1} a^{-1} as estimated from moss specimens sampled in 2005. This yields a direct yearly input to Lake Dümmer of about 25 t N. The N deposition into the catchment area of Lake Dümmer is, taking the moss estimates, about 738 t a^{-1} and 1107 t a^{-1} according to deposition modelling (Holy et al. 2011). As holds true for the Dümmer catchment area, sediments spatially dominate the drainage basins and the territory of Germany (357387 km^2): Limnic sediments cover 1 %, magmatic and metamorphic rocks each 4 % as well as unconsolidated sediments 55 % and 36 % consolidated sediments (Stegger 2015 based on the Hydrologic Atlas of Germany, table 1.5 `lithology´, BMU 2003). This sedimentary coverage is exposed to environmental contamination through atmospheric deposition.

3.4 Variation of N concentrations in moss at site level due to canopy drip effects

Considering the N concentration in moss collected across North-Western Germany (Kluge et al. 2013; Meyer et al. 2015 a, 2015 b), the average concentration at sites with canopy drip was both significantly higher in 2013 (mean: 2.50 % in dry weight which, applying a regression model, corresponds to 31.3 kg ha^{-1} a^{-1}) compared to 2012 (2.27 %, 26.4 kg ha^{-1} a^{-1}) and significantly higher compared to the N concentration in moss sampled at adjacent sites without canopy drip (mean 2012:

[1] The Quaternary Period is the current period in the geologic time scale of the International Commission on Stratigraphy.It is divided into two epochs: the Pleistocene (ca. 2.6 million years ago to ca. 12 thousand years ago) and the Holocene (ca. 12 thousand years ago to today.

1.11 %, 7.3 kg ha^{-1} a^{-1}, 2013: 1.39 %, 10.9 kg ha^{-1} a^{-1}). The maximum within the forest stands accounted for ~ 56 kg ha^{-1} a^{-1} in 2012 and 43 kg ha^{-1} a^{-1} in 2013. Compared to N values in mosses collected across in 2005, there was a decline of the average N deposition by 2.4 kg N ha^{-1} a^{-1} in open fields. However, the average N deposition within forests stands in 2012 remained nearly the same since 2004 (29 kg N ha^{-1} a^{-1}). The atmospheric N deposition derived from the N concentration in moss averaged for 2012 and 2013 ranged between the minimum and maximum critical load value at 21 of 30 sites with canopy drip (70 %) and exceeded the maximum critical load value at 30 % (Meyer et al. 2015 a).

The deposition values estimated from the moss concentrations in North-western lowland of Germany are rather high compared to those reported for the Bavarian Forest site within the ICP Integrated Monitoring. Here, the bulk deposition collected during 2003 -2012 in beech and spruce forests located at 825 m a.s.l. and 720 m a.s.l. amounted to 10 kg ha^{-1} a^{-1}. Deposition values collected under beech and spruce canopies did not differ significantly, neither from each other nor from open land sites. Averaged modelled values for total deposition were 10-13 kg ha^{-1} a^{-1} (beech) and 11-17 kg ha^{-1} a^{-1}, and the maximum total deposition 15 kg ha^{-1} a^{-1} (beech) and 22 kg ha^{-1} a^{-1} (spruce) (Beudert and Breit 2014).

Ranking interacting factors associated with N concentration in moss sampled during 2012 and 2013 in North-Western Germany by use of CART confirmed the canopy drip to be the factor most associated to the N concentration in moss integrating all site-specific factors (sampling site category: site with / without canopy drip; moss species: *Pleurozium schreberi*, *Scleropodium purum*; sampling year: 2012, 2013; tree height; distances to emission sources: traffic, industry, agriculture; percentages of urban, agricultural and forested areas in 1 km, 5 km, 10 km and 25 km around the sampling sites; population density; precipitation; distance to North Sea). The CART model presented explains 82 % of the variance in the data set comprising 112 measurements. This result was corroborated by a CART and Random Forest modelling based on the merged data sets published by Harmens et al (2015) and Meyer et al. (2015 b). Both models explained 71 % and 77 % of the variance (Meyer et al. 2015 b).

Merging the data from above mentioned sites sampled during 2012 and 2013 in North-Western Germany (Meyer et al. 2015 a) with data from moss collected across Europe (Harmens et al. 2014) yielded an average N content of 11.9 mg g^{-1} at open sites and by 20.0 mg g^{-1} at throughfall sites. Modelled atmospheric deposition rates were also higher at throughfall (18.0 kg ha^{-1} a^{-1}) compared to open sites (15.4 kg ha^{-1} a^{-1}). Taking the different countries into account, the highest average N content measured in *moss* at open sites was 13.9 mg g^{-1} in Slovenia. Germany showed the second highest average N content in moss with 12.6 mg g^{-1} followed by Austria (12.2 mg g^{-1}), Switzerland (12.0 mg g^{-1}) and Finland (8.2 mg g^{-1}). Regarding the average values at throughfall sites, Germany had by far the highest average N content (22.5 mg g^{-1}) followed

by France (13.5 mg g^{-1}) and Spain (11.9 mg g^{-1}). The overall average N content at sampling locations inside the peripheral tree canopy was 20.0 mg g^{-1}. Thus, the average N content measured in moss deviated from the total average value by 11 % (Germany), -48 % (France) and -68 % (Spain) (Meyer et al. 2015 b). On the whole, these findings are in line with NH_4^+ and NO_3^- measurements in bulk deposition (Harmens et al. 2015; Meyer et al. 2015 b): The highest average NH_4^+ concentration was measured at open sites in Germany followed by Austria, Slovenia, Switzerland and Finland. Under canopy, in Germany again the highest NH_4^+ and NO_3^- concentrations in bulk deposition were determined. In France, the NH_4^+ and NO_3^- concentrations were second highest followed by Spain.

Often either element concentrations are measured at sites below canopies *or* beyond them and not at both, open *and* throughfall sites as conducted by Skudnik et al. (2014, 2015) and Meyer et al. (2015 a, 2015 b). These studies yielded factors calculated by regression analysis enabling to estimate open site values from measured throughfall data and vice versa. Measured and estimated N contents neither at open sites nor at throughfall sites differed significantly (p: 0.81, Wilcoxon signed-rank test).

4 Conclusions

Pollutants emitted into the atmosphere are deposited at Earth´s surface where they accumulate in biota and sediments of terrestrial and of aquatic ecosystems. In Germany, most of the pollutant load of aquatic systems is derived from atmospheric deposition. Thus, assessing risks for aquatic sediments necessarily needs spatial valid information on atmospheric deposition onto land surfaces of drainage basins (Böhm et al. 2000; Fuchs et al. 2010). There, atmospheric deposition can be collected by technical devices (Hansen et al. 2013) and, as demonstrated in this article, by moss. In contrast to measurements with technical deposition samplers moss surveys allow covering a broad range of spatial scales with the same method in a high spatial density. From the investigations presented can be concluded that the European moss surveys comprise enough sample sites for reliable statistics for Europe as a whole, single countries and – with specific restrictions - ecologically defined land classes covering Europe (methods Sections 2.2.1, results: Section 3.2). The results for the minimum sample size needed on the landscape level in some cases might give reason to discuss the number of sampling sites needed depending on the aim of the analysis to be done. Pesch et al. (2008) developed a methodology to optimize the German moss monitoring network without reduction of statistical reliability. Accordingly, the German moss survey network for 2005 was designed and will again be re-structured for the campaign 2016. Ecological land lassifications such as ELCE are important on regional level because usually ecological maps are not synchronized between countries. However, on small

scale, similar maps as $ELCE_{40}$ could be less accurate then national ecological or nature protection maps and, because of this, countries are encouraged to do similar analysis also on the country level for regional and local important ecological classes. Alternatively, to this end ELCE versions with up to 230 classes are available and could be used.

Undoubted, the current spatial resolution of the European moss survey yields data at unrivalled high spatial densityenabling to detect spatial valid long-term trends of HM and N atmospheric deposition of HM (1990-2010) and N (2005-2010 (HM) (methods Sections 2.1.1 and 2.2.2, results: Section 3.3). Further, HM concentrations in moss were proved correlated with HM concentrations in organic surface soil and, thus, due to leaching of HM from soil, indicate a potential risk for aquatic ecosystems and their sediments (methods Sections 2.1.2 and 2.2.3, results Section 3.4). Even if we observed a (minor) decline of Pb in the humic surface layer from 1995 to 2005, organic-rich surface soils in Norway and elsewhere have accumulated metals from air pollution over centuries, and some of these metals, Pb in particular, are only slowly released to adjacent surface waters as they accumulate in deeper soil layers. Others, such as Zn and Cd, are strongly accumulated by plant roots and hence retained in the terrestrial ecosystem for a long time. Thus, the relations between these metals in surface soil and surface water / sediment are likely to be much weaker than correspondingly for moss samples - if evident at all. Additionally, the investigation corroborated that the moss biomonitoring technique seems to be able to reliably detect *site*-specific variance due to the filter effect of vegetation canopies (methods Sections 2.1.3 and 2.2.4, results Section 3.5). Further validation of this issue will be the focus of the upcoming moss survey in Germany 2016.

These findings are of relevance for the risk assessment of aquatic sediments, since, like in terrestrial ecosystems, sediments are sinks for atmospheric deposition in aquatic systems. Under changing environmental conditions such as pH and oxidation-reduction potential at the interface between the sediment and the water body HM may be desorbed from the sediment and released to the aqueous phase (Förstner 1995; Soares et al. 1999). The accumulation of potentially hazardous substances such as HM in an organism relative to its level in the ambient medium (bioaccumulation) is of major environmental concern, especially when referring to aquatic ecosystems (Schäfer et al. 2015). Their drainage areas capture and spatially concentrate materials derived from large terrestrial areas and even larger areas by atmospheric long-range transport and subsequent deposition. Atmospheric transport and deposition of global emissions may complicate the response of HM such as Hg levels in fish to regulation and remediation (Bhavsar et al. 2010; Gandhi et al. 2014). Taking Hg as an example, the response of concentrations in freshwater fish to changes in anthropogenic emissions depends on several factors affecting Hg cycling and bioaccumulation such as drainage basin characteristics causing considerable variation of transferring atmospheric deposition to fish (Akerblom et al. 2014). Therefore, the protection of aquatic ecosystem including their sediments needs the spatially differentiated characterisation of watersheds by mapping atmospheric deposition (moss, technical samplers, modelling), land

use (Corine: EU and national level), soils (nation-wide soil maps, FAO soil map on European level), ecoregions (Pardo et al. 2015; Schröder et al. 2007, 2013, 2014) and ecosystem types coverage based on structures and functions (Schröder et al. 2015). In this context, moss data could be used to estimate the atmospheric input of pollutants into sediments of catchment basins and aquatic ecosystems and, thus, contribute to risk assessment in context with the WFD. For this purpose, comparisons between moss data and results from numeric modelling of atmospheric deposition (Nickel et al. 2015 b) as a basis for dealing with uncertainties in N and HM balances are of great importance.

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Table

Table 1. Element-specific minimum and realised sample size for different landscapes across Europe by example of Cd, Hg, Pb and N, survey 2010

ELCE unit	Cd			Hg			Pb			N		
	MSS	RSS	Formula	MSS	RSS	Formula	MSS	RSS	Formula	MSS	RSS	Formula
B_1	478	73	[1]	44	**67**	[2]	236	73	[1]	25	13	[2]
B_2	58	**110**	[2]	26	**110**	[2]	66	**110**	[1]	7	**19**	[2]
C_0	88	**253**	[2]	41	**239**	[1]	454	252	[1]	15	**51**	[1]
D_10	22	11	[2]	17	11	[2]	40	11	[2]	11	10	[2]
D_13	919	99	[1]	31	**76**	[1]	519	99	[1]	10	**89**	[2]
D_14	16	**82**	[1]	19	**77**	[1]	25	**78**	[1]	9	**38**	[2]
D_16	8	4	[2]	7	4	[2]	2	**4**	[2]	-	-	-
D_17	54	**115**	[1]	41	**71**	[1]	14	**89**	[1]	10	**40**	[1]
D_18	121	**255**	[1]	21	**248**	[1]	92	**255**	[1]	7	**59**	[1]
D_19	14	**258**	[1]	35	**165**	[2]	17	**258**	[2]	8	**205**	[1]
D_21	2	**2**	[1]	0	**2**	[1]	1	**2**	[1]	-	-	-
D_22	25	**168**	[2]	11	**166**	[2]	57	**168**	[1]	8	5	[2]
D_7	16	**186**	[1]	39	**135**	[1]	93	**186**	[1]	4	**76**	[2]
D_8	28	**42**	[2]	28	**34**	[2]	24	**42**	[1]	12	**29**	[2]
F1_1	76	**87**	[1]	13	**87**	[1]	86	**87**	[2]	7	**70**	[2]
F1_2	113	**308**	[1]	12	**308**	[1]	41	**192**	[1]	8	**143**	[2]
F2_5	50	**66**	[1]	11	**65**	[2]	55	**66**	[1]	4	**66**	[2]
F2_6	162	**264**	[1]	68	**238**	[1]	51	**264**	[1]	7	**254**	[2]
F3_1	41	**201**	[1]	19	**189**	[1]	108	**201**	[1]	6	**191**	[2]
F3_2	58	**115**	[2]	15	**113**	[2]	37	**115**	[1]	5	**114**	[1]
F4_1	14	**17**	[2]	11	**17**	[2]	64	17	[2]	10	**10**	[2]
F4_2	78	**468**	[1]	86	**394**	[1]	608	468	[1]	7	**416**	[1]
G1_0	195	126	[1]	94	63	[2]	661	126	[1]	11	**85**	[2]
G2_0	463	186	[1]	564	174	[1]	1087	162	[1]	9	**132**	[2]
J_2	55	**60**	[2]	56	**60**	[1]	38	**59**	[2]	9	**50**	[2]
L_2	19	4	[2]	0	**2**	[1]	110	4	[2]	-	-	-
M_5	9	**15**	[1]	-	-	-	23	16	[1]	-	-	-
M_6	-	-	-	-	-	-	-	-	-	-	-	-
Other	86	45	[2]	148	42	[1]	50	45	[2]	6	**27**	[2]
S_0	61	54	[2]	27	**44**	[2]	29	**54**	[2]	8	**31**	[2]
U_1	49	47	[1]	19	**47**	[2]	54	47	[2]	8	**46**	[2]
U_2	64	**81**	[2]	50	**73**	[1]	96	80	[1]	12	**68**	[2]
MSS complied (n)		21			25			18			24	
MSS complied (%)		68			83			58			89	

bold numbers = MSS met or exceeded
MSS = Minimum Sample Size
RSS = Realized Sample Size
Formula [1] = according to ICP (2014)
Formula [2] = according to Wosniok (2015)

Table 2. Element-specific minimum and realised sample size for different landscapes within each participating country for 14 elements, survey 2010

	Al	As	Cd	Cr	Cu	Fe	Hg	N	Ni	Pb	S	Sb	V	Zn
MSS complied (n)	44	42	65	49	89	52	81	89	49	55	59	25	56	86
MSS not complied (n)	112	111	106	135	80	128	71	28	134	113	13	59	122	99
Total n	156	153	171	184	169	180	152	117	183	168	72	84	178	185
MSS complied (%)	28	27	38	27	53	29	53	76	27	33	82	30	31	46
MSS not complied (%)	72	73	62	73	47	71	47	24	73	67	18	70	69	54

Table 3. Decline in the average median HM and N concentrations in moss specimens since the start of the European moss survey in 1990a and since the survey in 2005b (Harmens et al. 2013 c, 2015)

Element	Decline since 1990[c] (%)	Decline since 2005 (%)	Element	Decline since 1990[c] (%)	Decline since 2005 (%)
Aluminium	n.a.	28	Lead	77	36
Antimony	n.a.	23	Mercury	14	20
Arsenic	21	25	Nickel	33	12
Cadmium	51	7	Vanadium	57	27
Chromium	43	23	Zinc	34	7
Copper	11	6			
Iron	27	15	Nitrogen	n.a.	5

[a] Based on data from countries that participated in at least four out of five surveys. For As countries were included that participated in four survey years since 1995. For Hg some countries were included that had data for three out of four surveys since 1995.
[b] Based on data from countries that participated in both survey years.
[c] Decline since 1995 for As and Hg.
n.a. = not available

Figure S1. Map of Ecological Land Classes of Europe ($ELCE_{40}$) (Hornsmann et al. 2008) (Legend: **Table S1**)

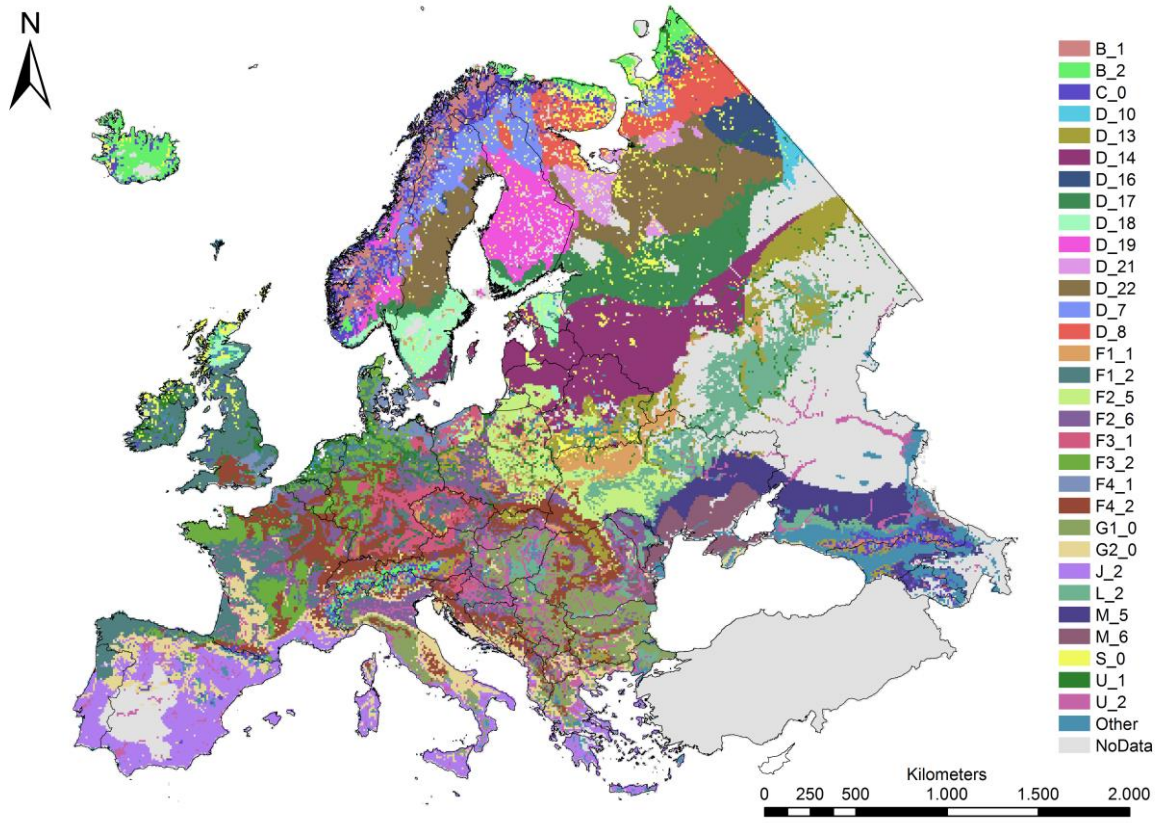

Table S1. Legend of the map on Ecological Land Classes of Europe ($ELCE_{40}$) (Hornsmann et al. 2008)

ELCE *Code*	***Main distribution***	***Area*** *[km²]*
B_1	Western and northern Scandinavia, northwest Russia	178800
B_2	The Alps, Iceland, northwest Russia	311400
C_0	The Alps, Iceland, western and northern Scandinavia, Kola Peninsula, northwest Russia, Caucasus	321800
D_7	Scandinavia, northwest Russia	185700
D_8	Kola Peninsula, northwest Russia	287800
D_10	Russia	96700
D_13	The Alps, dispersed small areas in eastern and southeast Europe	377500
D_14	Baltic States, Belarus, western Russia	537900
D_17	Scandinavia, western Russia	336000
D_18	Southern Scandinavia, northern Baltic States	150500
D_19	Southern/central Finland, Norway	227100
D_21	Northwest Russia	92800
D_22	Sweden, northwest Russia	534000
F1_1	Poland, northwest Ukraine	162000
F1_2	Ireland, Great Britain, western and central Europe	431000
F2_5	Southern Baltic States, eastern Poland, western and southwest Ukraine	231400
F2_6	Central Europe, easterm and southeast Europe	345200
F3_1	Germany, northwest Poland, Czech Republic, northern Austria, Slovenia, the Balkans	154800
F3_2	Western Europe (including northern Spain, France, Benelux countries, western Germany), Denmark	225100
F4_1	Southeast Great Britain, southeast Denmark, northeast Germany, northwest Poland	79900
F4_2	Western/central and southern Europe (including southern Great Britain, eastern France, southern Belgium, Luxembourg, the Alps, Italy), eastern and southeast Europe (including the Carpathian Mountains, the Balkans)	483300
G1_0	Italy, southeast Europe	303000
G2_0	Iberian Peninsula, southern and southeast Europe	296200
J_2	Iberian Peninsula, coastal areas by the Mediterranean Sea	438200
L_2	Eastern Europe (Hungary, Romania, Moldova, Ukraine, Russia)	352500
M_5	Eastern Ukraine, Southwest Russia, Caukasus	233800
M_6	Eastern Romania, southern Ukraine	131100
S_0	Northern parts of Europe (including parts of Iceland, Ireland, Great Britain, Scandinavia, northwest Russia, the Blatic states and Belarus)	271600
U_1	Dispersed small areas within a stripe reaching form Ireland via central Europe and the Byelorussian-Ukrainian borderline to Russia	199300
U_2	Dispersed small areas in southern Europe reaching form the Iberian Peninsula via southeast Europe including e.g. the Balkans, the Carpathians, Greece and northern Turkey to southwest Russia	239900
Others	Southwest Russia, Georgia, Azerbaijan, Armenia and further small areas all across Europe	347800

ELCE = 30 Ecological land classes and other ELCE which were summarized to one class (“Others”);