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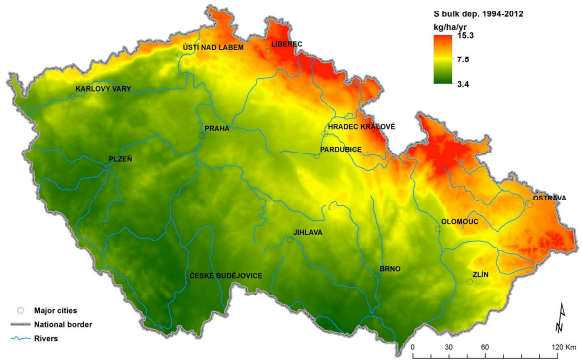

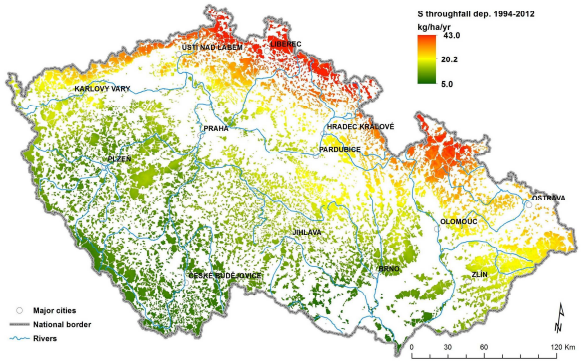

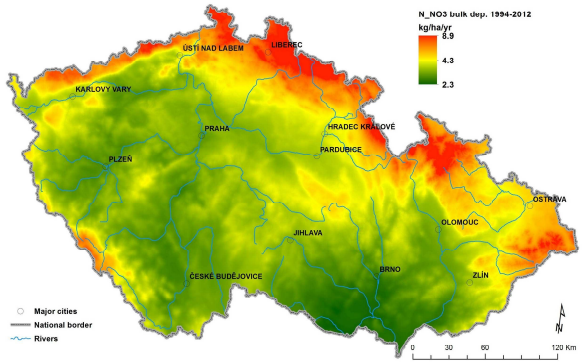

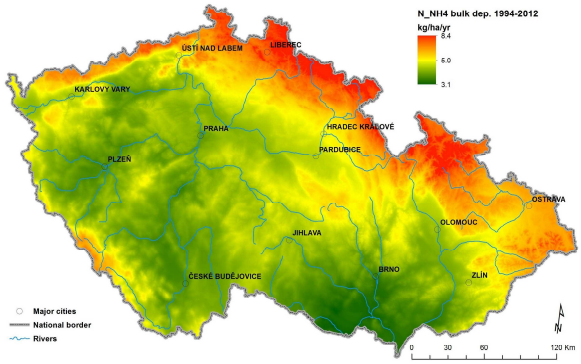

Predicting sulphur and nitrogen deposition using a simple statistical method

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HIGHLIGHTS

- Temporal coherence of precipitation SO_4, NO_3 and NH_4 was demonstrated
- Regional S and N emissions enabled to reconstruct long-term changes in deposition
- Empirically-based interpolation allowed spatial deposition variations to be mapped

ABSTRACT

Data from 32 long-term (1994 – 2012) monitoring sites were used to assess temporal development and spatial variability of sulphur (S) and inorganic nitrogen (N) concentrations in bulk precipitation, and S in throughfall, for the Czech Republic. Despite large variance in absolute S and N concentration/deposition among sites, temporal coherence using standardized data (Z score) was demonstrated. Overall significant declines of SO_4 concentration in bulk and throughfall precipitation, as well as NO_3 and NH_4 concentration in bulk precipitation, were observed. Median Z score values of bulk SO_4, NO_3 and NH_4 and throughfall SO_4 derived from observations and the respective emission rates of SO_2, NO_x and NH_3 in the Czech Republic and Slovakia showed highly significant ($p < 0.001$) relationships. Using linear regression models, Z score values were calculated for the whole period 1900 - 2012 and then back-transformed to give estimates of concentration for the individual sites. Uncertainty associated with the concentration calculations was estimated as 20 % for SO_4 bulk precipitation, 22 % for throughfall SO_4, 18 % for bulk NO_3 and 28 % for bulk NH_4. The application of the method suggested that it is effective in the long-term reconstruction and prediction of S and N deposition at a variety of sites. Multiple regression modelling was used to extrapolate site characteristics (mean precipitation chemistry and its standard deviation) from monitored to unmonitored sites. Spatially distributed temporal development of S and N depositions were calculated since 1900. The method allows spatio-temporal estimation of the acid deposition in regions with extensive monitoring of precipitation chemistry.

Keywords: precipitation, sulphur, nitrogen, deposition, monitoring, upscaling

1 INTRODUCTION

The acidification of sensitive ecosystems by sulphur (S) and nitrogen (N) deposition has been a widespread environmental problem in Europe since the mid 20th century. More recently, there has been increasing concern that elevated atmospheric N inputs are leading to eutrophication of semi-natural ecosystems (Bobbink et al., 2010). Monitoring data for the main driving variables, the deposition of S and N species, are generally available only for a relatively short period (Schöpp et al., 2003). Therefore estimations of S and N deposition levels over longer periods are based on emission trends (Kopacek et al., 2001; Schöpp et al., 2003). Knowledge of the emission history and deposition trends of major acidifying pollutants is a key factor for understanding changes in those ecosystems, and in particular is an important input to process-based models used to predict the long-term impacts of atmospheric deposition on terrestrial and aquatic ecosystems (Bonten et al., 2016; Hofmeister et al., 2008; Oulehle et al., 2015).

On a European scale, the EMEP (European Monitoring and Evaluation Programme) Eulerian acid deposition model (Simpson et al., 2003) is used to simulate sulphur, nitrogen oxides and ammonia deposition in grid cells at a 50 km × 50 km resolution. This model has provided the basis for optimisation of emissions control legislation at a European scale within the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP), most recently the Gothenburg Protocol (UNECE, 2004). However, the low spatial resolution of this model may lead to a high within-grid cell variability, particularly in topographically complex areas, and also provides average rather than ecosystem-specific (e.g. forest versus grassland) deposition. As a result, it is difficult to relate the large-scale model simulations to specific sites or ecosystems.

According to the Gothenburg Protocol, the respective SO_2, NO_x and NH_3 emissions should have been 85%, 61% and 35% lower in the Czech Republic in 2010 compared to the 1990 base line. However, already by 2007, SO_2 emissions had decreased by 88% to 217 kt yr^{-1}, NO_x emissions by 62% to 284 kt yr^{-1} and NH_3 emissions by 62% to 60 kt yr^{-1} (www.emep.int), therefore target emissions have been successfully passed. The decrease of SO_2 emissions in the Czech Republic has been one of the most pronounced examples of pollution reduction anywhere in Europe (Vestreng et al., 2007), and are believed to have had profound consequences for ecosystem biogeochemistry including the carbon and nitrogen cycles (Oulehle et al., 2011).

Many countries provide long-term air quality monitoring including assessment of spatial and temporal changes in precipitation chemistry (wet-only, bulk, throughfall), such as National atmospheric deposition program (NADP) across USA and European Monitoring and Evaluation Programme (EMEP) under CLRTAP. European nation based programs operate across many countries (e.g. SWETHRO in Sweden, UKEAP in the UK or GEOMON in the Czech Republic). Precipitation composition often integrates altered air quality over large parts of landscape, thus common coherence in chemistry trends across different monitoring sites may be expected and explored. However, air quality is influenced by different sources of emissions, thus S deposition might be influenced directly by SO2 emissions cuts from big stationary sources over large areas, whereas N deposition may behave less consistently due to the mixing of emissions from small (local) and large stationary sources, as well as mobile (transport) sources (Waldner et al., 2014). Geographical features (e.g. local topography) may also determine different levels and temporal pattern of S and N deposition at sites in the same area (Rogora et al., 2006). Here, we use all stations with available data on precipitation chemistry in the Czech Republic spanning at least 15 years to examine the spatiotemporal variations in SO_4, NH_4 and NO_3 concentrations and fluxes in bulk precipitation and throughfall (only SO_4) in this central European region. Specifically, we (i) evaluate the degree of underlying coherence in deposition trends across the range of monitoring sites, (ii) develop and test a methodology enabling to infer S and N deposition across the spatio-temporal gradients in a study region from the related emission trends, and (iii) apply this method to reconstruct historical trends in S and N deposition in the Czech Republic back to 1900.

2 MATERIALS AND METHODS

2.1 STATION DATA DESCRIPTION

The monitoring stations of precipitation chemistry are located in the Czech Republic and close border areas (Slovakia and Austria) and comprise 32 stations. For their location see the Supplementary Information (SI; Figure S1). Site elevations varied between 180 (Praha-Podbaba) and 2023 m a. s. l. (Chopok station, Slovakia) and mean annual precipitation depths varied between 503 and 1641 mm yr^{-1} during 1961 – 2012. The number of years with available volume weighted mean chemistry varied from 15 to 35 years for individual stations and cover the period from 1978 to 2012 (Table S1). Monitoring stations differ in frequency of precipitation sampling and type of precipitation samplers. The rain water collection comprises daily, weekly and monthly sampling, dependent on site manager. We used only annual weighted means. Precipitation collectors comprise open bulk collectors and wet only collectors. Fifteen stations provide throughfall (under the Norway spruce - the dominant tree in the Czech forests) precipitation chemistry data.

We used sulphate (SO_4), nitrate (NO_3) and ammonium (NH_4) concentrations. In general, SO_4 and NO_3 were measured by ion chromatography, NH_4 either by potentiometry or by manual/automatic spectrophotometric determination by the indophenol blue method (analytical procedures have changed since 1976, thus for further details visit: http://www.chmi.cz/files/portal/docs/uoco/web_generator/locality/precipitation_locality/index_GB.html). The reliability of the chemical data was controlled by means of an ionic balance for the annual average concentrations. Data with differences between the sum of cations and the sum of anions lower than $\pm$ 10% of the total ionic content were used without any other control. If the difference exceeded $\pm$ 10%, the data were checked for errors using a trend analysis. If the concentration of some ion was outlying the trend and at the same time this difference from the trend explained the error in the ionic balance control, we excluded this ion from other analyses, but used the rest of the data on chemical composition.

2.2 SO_2, NO_x AND NH_3 EMISSIONS

Historical Czech and Slovak (CS) emission trends for SO_2, NO_x, and NH_3 are based on data from the official databases of EMEP (www.ceip.at/emission-data-webdab) for the 1980 – 2012 period, and on data calculated by (Kopacek and Vesely, 2005) for the 1900 – 1990 period. The calculated CS emissions of anthropogenic SO_2, NO_x, and NH_3 were on average 7 % higher, 2 % lower, and 8 % higher, respectively, than the EMEP data for the overlapping 1980 – 1990 period. Data on central European (Austria + Germany + Poland + CS) emissions of SO_2 and NO_x and NH_3 after 1980 were taken from the EMEP database; emissions of SO_2 and NO_x before 1980 are from Mylona (1996) and Schöpp et al. (2003), respectively. Data on central European emissions of NH_3 prior to 1980 were calculated for individual countries using inventories of livestock, use of synthetic N-fertilizers (FAO database, http://faostat.fao.org), and data on population, using the per-capita emission model (Kopáček and Posch, 2011).

The long-term trend in CS emissions of SO_2 was similar to the central European trend, except for 1970 - 1990, when CS emissions increased more sharply due to high emission rates in the region (Figure 1). The CS emission rate of NH_3 was lower than that in the central Europe and decreased more in the 1990s, due predominantly to lower areal livestock density and its larger reduction in CS than in Germany. Central European emissions of NO_x were slightly lower in the 1980s and trends were similar to the CS trend in 1990s.

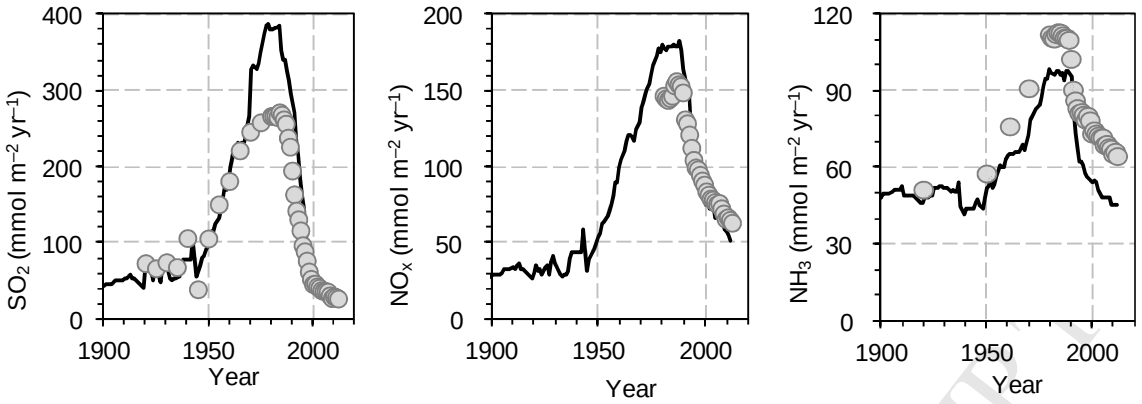


Figure 1. Historical trends (1900 - 2012) in emissions of SO_2, NO_x and NH_3 in the area of the Czech and Slovak Republic (CS, black line) and in central Europe (circles; Austria, Germany, Poland and CS).

2.3 TIME SERIES STANDARDISATION

2.3.1 Precipitation chemistry data processing

Recalculation of wet only SO_4, NO_3 and NH_4 concentrations to bulk precipitation was based on parallel measurements of wet - only and bulk precipitation on eleven stations. For SO_4, 64 parallel annual measurements (Figure 2) were available and a linear regression model was obtained:

$$SO_4 \text{ bulk } (\mu eq\ L^{-1}) = 1.04 \times SO_4 \text{ wet } (\mu eq\ L^{-1}) + 21.99 \quad (1)$$

For NO_3, 51 parallel annual measurements (Figure 2) were obtained and the linear regression model was:

$$NO_3 \text{ bulk } (\mu eq\ L^{-1}) = 0.87 \times NO_3 \text{ wet } (\mu eq\ L^{-1}) + 14.87 \quad (2)$$

For NH_4, 45 parallel annual measurements (Figure 2) were obtained and the linear regression model was:

$$NH_4 \text{ bulk } (\mu eq\ L^{-1}) = 1.01 \times NH_4 \text{ wet } (\mu eq\ L^{-1}) + 18.93 \quad (3)$$

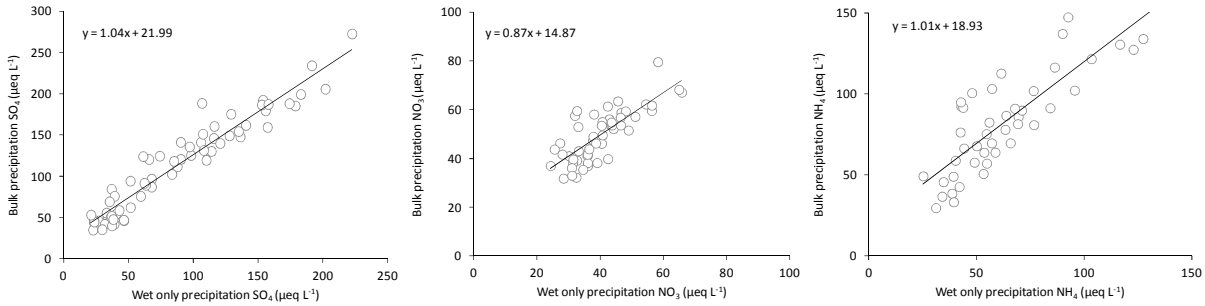


Figure 2. Relationships between available annual volume weighted mean concentrations of SO_4, NO_3 and NH_4 in wet-only and bulk precipitation in the Czech Republic.

2.3.2 Site standardization

Despite large variance in precipitation chemistry across sites, underlying patterns of temporal variation show strong similarities. To demonstrate these underlying patterns, measured annual concentration of SO_4, NH_4 and NO_3 at each sampling site *s* on respective year *t* (*Cst*) were standardised over time, by subtracting the site mean (*Cs*) for the whole time series (1994–2012) and dividing by the site standard deviation (σs) according to:

$$Zst = \frac{Cst - Cs}{\sigma s} \quad (4)$$

The time series of standardised concentrations (*Zst* referred to as 'Z score') thus have a zero mean and a standard deviation equal to 1. This implies that temporal effects are essentially multiplicative, so that sites with generally high concentrations will tend to have high variability over time in absolute but not in relative terms (Evans et al., 2010). The degree of observed between - site coherence was quantified as the mean annual 10^{th} - 90^{th} percentile Z score range for all sites over the monitoring period, following the method of Evans et al. (2010).

2.3.3 Historical trends estimations

Median Z scores for SO_4, NH_4 and NO_3 in bulk precipitation and for SO_4 in throughfall for each year across the whole set of sites was calculated according to Eq. 4. Obtained median values were than related to emissions by linear regression method for the period 1994 - 2012. We used logarithmically transformed emission data because they were better fitted by the regression model than non-transformed data. For the modelling we used the CS emission trends because they provided closer relationships with the deposition data than the central European trends. The obtained equations were then used to calculate median SO_4, NH_4 and NO_3 Z scores for their concentrations in the whole 1900 - 2012 period according to the respective emission rates of SO_2, NH_3 and NO_x (Figure 1).
The median time series of Z scores for whole set of sites was then back-transformed to give estimates of *Cst* for each individual site for the whole period 1900–2012 according to Eq. 5, and following the notation of Eq. 4:

$$Cst = (Zst \times \sigma s) + Cs \quad (5)$$

The *Cs* and the σs were calculated from the measured data between 1994 and 2012.

2.3.4 Model validation

Results obtained for individual sites according to Eq. 5 were compared with measured concentrations. The precision of the model outputs was calculated by three measures; the Root Mean Square Error (RMSE), Nash-Sutcliffe Coefficient of Determination (NSCD) and a linear regression coefficient (R^2) were used to assess explained variability of model estimations (De Vries et al., 2010; Janssen and Heuberger, 1995; Nash and Sutcliffe, 1970).

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(Pi - Oi)^2}{N}} \quad (6)$$

$$NSCD = \sqrt{\frac{\sum_{i=1}^{N}(Oi - Pi)^2}{\sum_{i=1}^{N}(Oi - O)^2}} \quad (7)$$

Where *Pi* is predicted value, *Oi* is observed value, *O* is average of observed values and *N* is number of observations.

RMSE describes the deviations between the measurements and the predictions in a quadratic way and is thus rather sensitive to extreme values. RMSE has the same units as the quantity being estimated. An NSCD of 0 indicates that the model predictions are as accurate as the mean of the observed data; the closer the model is to 1, the more accurate the model is.

Finally, we used long-term precipitation chemistry (with years of observations before 1994) from bulk precipitation ANE, JEZ, LYS, NAC, SLA and PCJ (for site abbreviations see SI, Table S1) sites to compare model outputs with measured chemistry within the period 1978 - 2012. This comparison highlighted the model performance at the time of the highest measured S and N depositions across Central Europe.

2.4 SPATIAL PRECIPITATION CHEMISTRY MODEL

The large number of sites with measured precipitation chemistry across the study region allowed us to test whether site characteristics (coordinates, elevation, precipitation amount) may be used to calculate site *Cs* and *σs,* and thus to estimate site precipitation chemistry at any given position and year within the period 1900 and 2012, according to Eq. 5.

We used multiple regression analysis to study the relationship between dependent (response) variables and independent variables (predictors) derived from 32 stations. Selection of predictors was based on stepwise regression with forward selection method. The forward selection method, at each step, selects the candidate variable that increases R^2 the most. It stops when none of the remaining variables are significant. Outliers can have a large impact on this stepping procedure, so we made some attempt to remove outliers from dataset before applying this method.

Independent variables entering the stepwise regression model were: latitude (*X*), longitude (Y), precipitation depth (*P*; mm) and elevation (*E*; m a.s.l.). Latitude and longitude are expressed in Křovák's projection (JTSK).

2.4.1 Model validation

Results obtained for individual sites (Cs_{SO4}, Cs_{SO4thf}, Cs_{NO3}, Cs_{NH4}, ΔCs_{SO4}, ΔCs_{SO4thf}, ΔCs_{NO3}, ΔCs_{NH4}, σs_{SO4}, σs_{SO4thf}, σs_{NO3}, σs_{NH4}), where ΔCs represents annual rate of solute change in μeq L^{-1} $year^{-1}$, were compared with measured concentrations. The precision of the model outputs was calculated by Nash-Sutcliffe coefficient of determination (NSCD) and RMSE was used to assess explained variability of model estimations (Janssen and Heuberger, 1995; de Vries et al., 2010; Nash and Sutcliffe, 1970).

2.4.2 Average precipitation estimates and deposition calculations

Precipitation data were estimated from a dataset of about 200 stations (obtained from Czech Hydrometeorological Institute) distributed around the Czech Republic. After the quality control and homogenization (methods are described e.g. in Štěpánek et al., (2013)) new series for given individual sites were calculated. The calculation of the "new" series was based on geostatistical interpolation methods, improved by standardization of neighbouring stations values to altitude of a given location by means of regional regression analysis (Štěpánek et al., 2011). Parameters settings of the calculation differ for each meteorological element and optimal settings were found by means of cross validation. In this case, series for a given site were obtained from up to 6 nearest stations within maximum distance of 50 km, with the allowed maximum difference in altitude of 700 m. Before applying inverse distance weighting, data at the adjacent stations were standardized relative to the altitude of the base grid point (station location). The standardization was carried out by means of linear regression, dependence of values of a particular meteorological element on altitude, for each day individually, and regionally. Each standardized value was checked to ensure that it did not differ excessively from the original value. Modelled precipitation was used to calculate deposition of

S and N based on estimated SO_4, NO_3 and NH_4 concentrations in precipitation. Median calculated bulk deposition for the Czech Republic was based on 1599 points regularly distributed across the Czech Republic, thus each point represented an area of 49 km^2. Median calculated throughfall S deposition for the Czech Republic was based on 499 points, representing forested areas.

3 RESULTS AND DISCUSSION

3.1 MEASURED TRENDS OF SO_4, NH_4 AND NO_3 CONCENTRATIONS

Annual mean SO_4, NH_4 and NO_3 concentrations in precipitation differed significantly across individual sites (Table S1). Despite high between-site variability of mean concentrations, standardization highlights the degree of underlying temporal coherence in the measured dataset (Figure 3). A highly significant decline in SO_4 annual average precipitation concentration (R^2 = 0.86 versus year, $p < 0.001$), as well as throughfall concentration (R^2 = 0.81 versus year, $p < 0.001$), was observed during the 1990s and 2000s. Moreover, both bulk precipitation and throughfall SO_4 concentrations showed high inter-site coherence (mean annual 10^{th} - 90^{th} percentile range of 1.04 and 0.74 standardised units, respectively). For NO_3 concentrations in bulk precipitation, a significant decline was observed in median trend (R^2 = 0.72 versus time, $p < 0.001$), with higher inter-site variability (mean annual 10^{th} - 90^{th} percentile range of 1.80) (Figure 3). A less consistent and coherent decrease in annual average concentrations in bulk precipitation was recorded for NH_4 (R^2 = 0.58 versus time, $p < 0.001$, mean annual 10^{th} - 90^{th} percentile range 1.94). Measured declines in SO_4 concentrations were most pronounced during the 1990s whereas the NO_3 concentration decrease was steepest after 2005 and NH_4 concentration has been decreasing linearly since 1994 (Figure 3).

The higher observed 10^{th} - 90^{th} percentile Z scores ranges for NH_4 and NO_3 concentration in bulk precipitation (compared to those observed for SO_4) led us to test significance of the NO_3 and NH_4 decrease in bulk precipitation at individual sites. For NH_4 concentrations, significant ($p < 0.05$; linear regression versus year) decreases in bulk precipitation were observed at 15 out of 30 sites. The NO_3 concentration significantly decreased at 22 sites ($p < 0.05$; linear regression versus year) out of 30. Throughfall NO_3 and NH_4 concentrations were not included in the assessment. The absence of a significant overall change of throughfall DIN indicates that canopy N transformation plays a significant role in N delivery to the forest floor (Lovett and Lindberg 1993; Kopáček et al. 2009) and was more or less independent of actual N deposition level over the short to medium term.

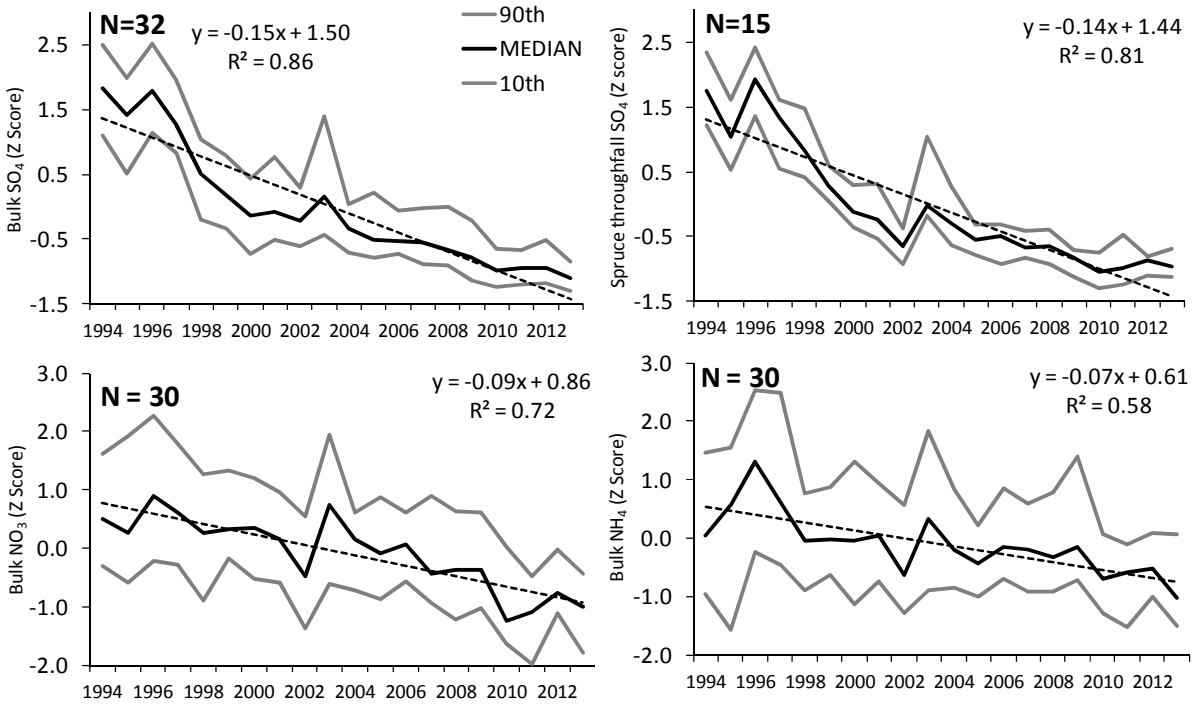


Figure 3. Standardised annual mean (Z score) time series for bulk and throughfall SO_4, bulk NO_3 and NH_4 concentrations for sites listed in Table S1. Bold central line shows median annual Z score for all sites, outer lines show 10th and 90th percentile values. Dashed lines show linear regressions between median annual Z scores and time.

3.2 Estimation of measured historical SO_4, NH_4 and NO_3 concentrations

3.2.1 Reconstruction of SO_4 precipitation concentrations

The high degree of overall temporal coherence observed among sites in annual mean precipitation SO_4 as well as throughfall SO_4 concentrations, and to a lesser extent precipitation NO_3 and NH_4 concentrations, allowed the use of standardised median concentration as a representative measure of change in respect of emission rates. For SO_4 in bulk precipitation, a strong relationship with log transformed SO_2 emission rate was found ($R^2 = 0.97$, $p < 0.001$; Figure 4). According to this log-linear regression equation, annual median SO_4 Z scores for precipitation were calculated from emission rates for the whole period of emissions reconstruction (1900 - 2012). Modelled SO_4 concentration (Figure 5) was compared with measured data across all years (including measurements before 1994) and sites. Prediction of SO_4 had RMSE values ranging from 5.6 to 31 µeq L^{-1} at individual sites (10th and 90th percentile), with a median of 12.3 µeq L^{-1} (20 % of median SO_4 concentration) across all sites and years. Explained variability in the measured SO_4 concentration ranged between 41 % and 94 %, with a median of 81 %. NSCD ranged between 0.32 and 0.92 with a median of 0.73 (Figure 6).

Similar results were obtained for throughfall SO_4 (Figure 5). The standardised Z score of SO_4 throughfall was tightly related to the log transformed SO_2 emissions ($R^2 = 0.96$, $p < 0.001$; Figure 4). Predicted RMSE of SO_4 throughfall varied between 18.5 and 87 µeq L^{-1} (median 42 µeq L^{-1}, which is 22% of median concentration across sites). Explained variability in the measured throughfall SO_4 concentration ranged between 55 % and 97 %, with a median of 82 %. NSCD ranged between 0.51 and 0.94 with a median of 0.79 (Figure 6).

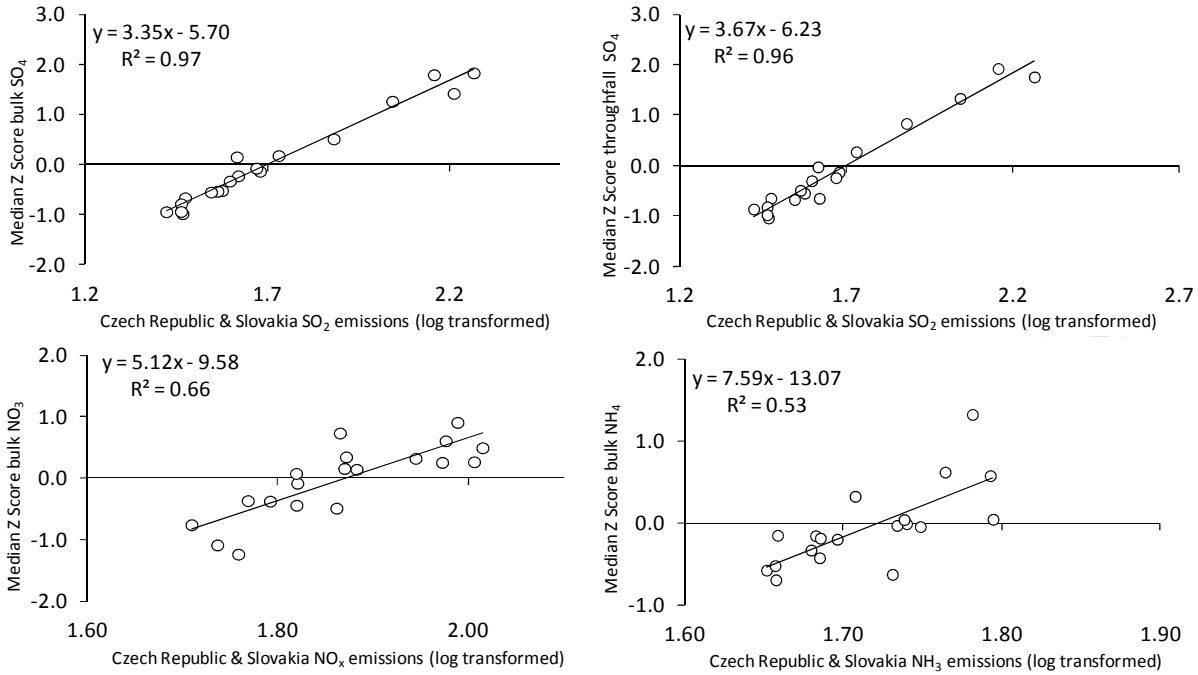


Figure 4. Linear regressions between median Z score of bulk and throughfall SO_4, bulk NO_3, and bulk NH_4 and the CS emission rates (log transformed mmol m^{-2} yr^{-1}) of the respective S and N compounds.

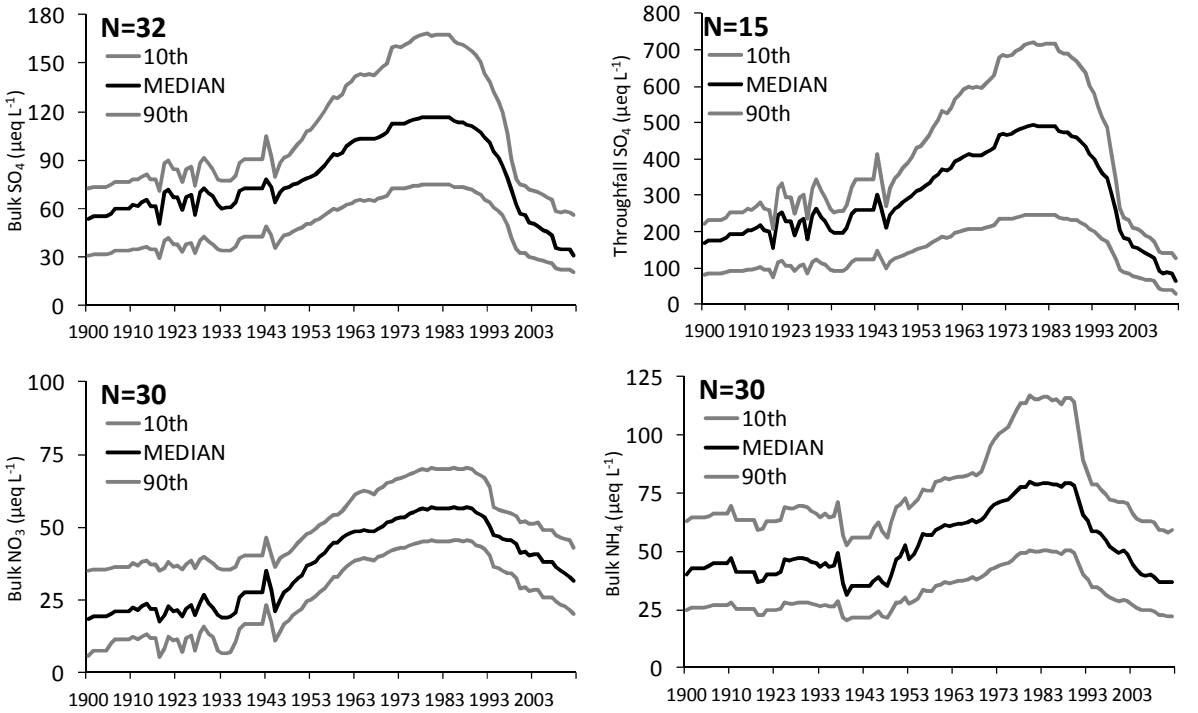


Figure 5. Modelled concentrations of bulk and throughfall SO_4 and bulk NO_3 and NH_4. Bold central line shows median for all sites, outer lines show 10th and 90th percentile values.

3.2.2 Reconstruction of NO_3 and NH_4 precipitation concentrations

For NO_3, a significant relationship ($R^2 = 0.66$, $p < 0.001$) between median Z score and log transformed NO_x emissions was observed (Figure 4). Variation of NO_3 RMSE was between 4.5 and 19 µeq L^{-1} (median 7.5 µeq L^{-1}, which is 18 % of median concentration across sites). Explained variability in the measured NO_3 concentration ranged between 2 % and 68 %, with a median of 33 %. NSCD ranged

between -0.38 and 0.61 with a median of 0.32 (Figure 6). There was no obvious relationship between model performance and site location. For NH_4, a weaker but still significant relationship (R^2 = 0.53, p < 0.01) between median Z score and log transformed NH_3 emissions was found (Figure 4). The RMSE of modelled NH_4 ranged between 7.1 and 41 µeq L^{-1}, with median of 13.5 µeq L^{-1} (28 % of median concentration across sites). Explained variability in the measured NH_4 concentration ranged between 3 % and 73 %, with a median of 27 %. NSCD ranged between -0.42 and 0.48 with a median of 0.16 (Figure 6).

The somewhat poorer correlations between NH_4 and NO_3 concentrations in precipitation and their respective emissions compared to those observed for SO_4 are probably caused by a higher degree of year-to-year variability in the NH_4 concentration in precipitation, as well as higher degree of inter site trend heterogeneity as demonstrated in section 3.1. Moreover, components of NO_x (NO and NO_2) are much more reactive than SO_2, and therefore the atmospheric chemistry associated with NO_x is more complex than for SO_2 (Seinfeld and Pandis, 1998). The non-linearity between NO_x emissions and precipitation concentration may therefore be more strongly influenced by changes in other atmospheric chemical constituents than the equivalent relationship between SO_2 emissions and S precipitation (Fagerli and Aas, 2008). A lack of significant temporal changes in bulk nitrogen deposition was confirmed for Sweden (Pihl Karlsson et al., 2011) and for the UK (Kernan et al., 2010). On the other hand, significant correlations between precipitation concentration and emissions were found in the eastern USA for both NO_x and SO_2 (Butler et al., 2005; Likens et al., 2001).

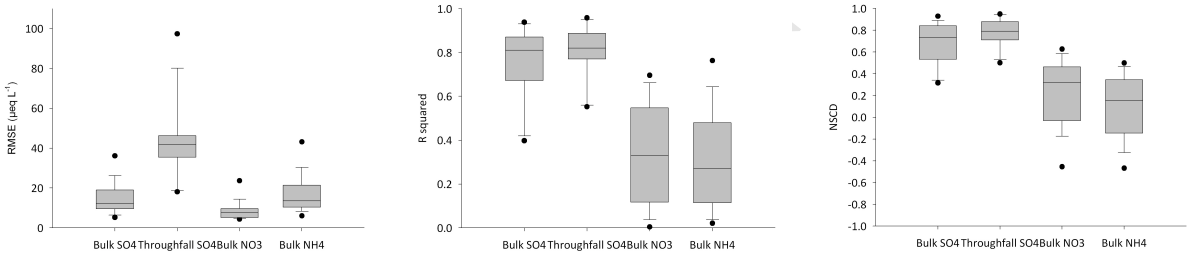


Figure 6. Box plots showing distribution of statistical results for root mean square error (RMSE), coefficient of determination (R^2), and Nash-Sutcliffe coefficient of determination (NSCD) obtained for individual sites. Median, 25th and 75th percentiles, whiskers indicate 5th and 95th percentiles and minimum maximum values are denoted with dots.

3.2.3 Precipitation SO_4, NO_3 and NH_4 concentrations during the peak of acid deposition

The non-linear relationships between standardised SO_4, NH_4 and NO_3 concentrations and their respective emissions were highlighted when long-term precipitation data (measurements from 1970s and 1980s) were used for comparison (Figure S3). Such a dataset was available for the ANE, JEZ, LIZ, NAC, SLA and PCJ for the period 1978-2012. This period covered the peak of emissions reported for central Europe (Figure 1). Taking into account that CS emissions of SO_2 and NO_x were disproportionately higher during this period than for central Europe as a whole (Figure 1), the balance of "emission export" from CS minus "emission import" from surrounding countries was higher during the 1980s and 1990s then currently. On the other hand, NH_3 emissions were significantly lower in CS than in surrounding countries, probably leading to a net import. Log transformation appears to correct for the discrepancy between CS and central European emissions, by reducing modelled deposition estimates during the peak of CS emissions, leading to more accurate fit between observed precipitation chemistry and emission rates. In future, it is expected that further reductions in emissions should be followed by more linear responses in precipitation concentrations. Similarly, long-term (1965 - 2000) precipitation monitoring at Hubbard Brook Experimental Forest in U.S. showed non-significant relationships between SO_4 bulk precipitation

concentrations and SO_2 emissions during the 1965 - 1980 period. A clear strong curvilinear relationship was apparent only for the whole period 1965 - 2000 (Likens et al., 2005), again suggesting a weaker relationship between concentration and emission during the period of peak SO_2 emissions.

3.3 SPATIAL ESTIMATION OF PRECIPITATION CHEMISTRY AT UNMONITORED SITES

3.3.1 Spatial distribution of SO_4 concentrations in precipitation

To calculate mean precipitation SO_4 concentration (Cs_{SO4}) all site characteristics (latitude, longitude, precipitation and elevation) entered the regression model. All four predictors together explained 72 % of variability in the measured Cs_{SO4} across 32 sites within the Czech Republic:

$$Cs_{SO4} = 10 \wedge (4.321 + 1.093x10^{-4} x E - 3.24x10^{-4} x P + 9.541x10^{-7} x Y + 1.607x10^{-6} x X)$$

Latitude and longitude explained 40 % of variability and reflects a well known spatial gradient in precipitation chemistry within the Czech Republic, due to the cluster of major emission sources in the NW part of the country, i.e. a part of the former Black Triangle (Černý and Pačes, 1995). Annual precipitation amount added 27 % of explained variability in the regression model – sites with higher precipitation tend to have lower concentrations due to dilution effects. Tight coherence in precipitation SO_4 trends across all sites (Figure 3) and fairly high explanatory power of the regression model (72 %) led us to incorporate the modelled Cs_{SO4} as next predictor for calculations of other chemistry constituents (throughfall SO_4, NO_3 and NH_4).
The rate of change in precipitation SO_4 concentration (ΔCs) was a function of Cs_{SO4} (34 % of explained variability), latitude (north-south gradient) and elevation.

$$\Delta Cs_{SO4} = 1.927 - 9.317x10^{-4} x E - 5.639 x \log(Cs_{SO4}) - 5.048x10^{-6} x X$$

Relatively higher annual decreases in bulk SO_4 concentration were modelled for northern sites with higher SO_4 concentrations (Figure S4). All together 44 % of variability in ΔCs was explained. Site standard deviation (σs_{SO4}) was then calculated based on tight relationship between σs *and* ΔCs (Figure S2):

$$\sigma s_{SO4} = -6.24 x \Delta Cs_{SO4} + 1.57 \qquad (R^2 = 0.92)$$

Model performance is highlighted in Figure 7. Modelled RMSE values were 16 % of site average value for Cs_{SO4}, 32 % of site mean change for modelled ΔCs_{SO4}, and 34 % of mean site standard deviation for modelled σs_{SO4}.
Mean throughfall SO_4 concentration (Cs_{SO4thf}) across 15 sites with available data was best explained with three predictors (Cs_{SO4}, precipitation and latitude).

$$Cs_{SO4thf} = 10 \wedge (1.557 + 1.165 x \log(Cs_{SO4}) - 3.57x10^{-4} x P + 8.941x10^{-7} x X$$

All together 90 % of the variability in Cs_{SO4thf} was explained, from which 73 % was related to the respective bulk SO_4 concentration. Thus, sites with high SO_4 concentration in precipitation tend to have high throughfall (Figure 8). Rate of change in throughfall SO_4 concentration (ΔCs_{SO4thf}) was a function of Cs_{SO4thf} (83 % of explained variability) and longitude (Figure S4).

$$\Delta Cs_{SO4thf} = 43.263 - 23.581 x \log(Cs_{SO4thf}) + 8.399x10^{-6} x Y$$

Sites located in the west and with high throughfall SO_4 concentrations experienced the steepest declines in throughfall SO_4 concentration. Altogether 86 % of the variability in ΔCs_{SO4thf} was explained by Cs_{SO4thf} and longitude. Site standard deviation (σs_{SO4thf}) was then calculated according to linear regression from the Figure S2:

$$\sigma s_{SO4thf} = -6.83 \times \Delta Cs_{SO4thf} - 2.35 \quad (R^2=0.98)$$

Modelled RMSE values were 26 % of site average value for Cs_{SO4thf}, 19 % of site mean change for modelled ΔCs_{SO4thf}, and 21 % of mean site standard deviation for modelled σs_{SO4thf} (Figure 7).

3.3.2 Spatial distribution of NO_3 and NH_4 concentrations in precipitation

Mean precipitation NO_3 concentration (Cs_{NO3}) across 30 sites with available data was best explained with two predictors:

$$Cs_{NO3} = 10 \wedge (1.123 + 5.156\times10^{-3} \times Cs_{SO4} - 2.643\times10^{-7} \times Y)$$

Mean bulk SO_4 concentration explained 49 % in variation of mean bulk NO_3 concentration, another 12 % of explanatory power added longitude. Sites with high SO_4 concentration in the west part of the territory tend to have higher NO_3 concentration in bulk precipitation (Figure 8). This further reflects importance of the proximity from large stationary sources of NO_x emissions that dominated NO_x emissions in the Czech Republic in the 1980s and 1990s (Kopacek and Vesely, 2005).
Absolute change in the NO_3 concentration was related to latitude (14 % of explained variability in ΔCs_{NO3}), precipitation and elevation. All together 36 % of variability in ΔCs_{NO3} was explained.

$$\Delta Cs_{NO3} = -4.687 - 8.589\times10^{-4} \times E + 4.515\times10^{-4} \times P - 3.775\times10^{-6} \times X$$

Higher decreases were observed in northern sites (Figure S4). Site standard deviation (σs_{NO3}) was then calculated based on linear regression from the Figure S2.

$$\sigma s_{NO3} = -5.35 \times \Delta Cs_{NO3} + 3.44$$

Compared to SO_4 assessment, predictive performance of regression models were poorer, with the modelled RMSE values of 15 % of site average value for Cs_{NO3}, 36 % of site mean change for modelled ΔCs_{NO3}, and 29 % of mean site standard deviation for modelled σs_{NO3} (Figure 7).
Mean precipitation NH_4 concentration (Cs_{NH4}) across 30 sites with available data was best explained with four predictors.

$$Cs_{NH4} = 10 \wedge (0.316 - 6.733\times10^{-5} \times P + 7.505\times10^{-3} \times Cs_{SO4} - 4.950\times10^{-7} \times Y - 6.026\times10^{-7} \times X)$$

Bulk SO_4 concentration alone explained 58 % of Cs_{NH4} variability across sites, precipitation added 12 % to explained variability and 8 % was explained by the coordinates. Cs_{NH4} tends to be higher at sites with high SO_4 concentration, reflecting the role of NH_4 as a counter-ion to SO_4 in $(NH_4)_2SO_4$ aerosol. Furthermore, in contrast to NO_3, NH_4 tends to be higher in the SW territory of the Czech Republic (Figure 8). This is in good spatial agreement with the distribution of industrial and agricultural areas across the Czech Republic, as well as with closer proximity of NH_3 emission sources in Germany that are higher than the CS sources (EMEP; www.ceip.at/emission-data-webdab) due to higher density of livestock production (FAO; http://faostat.fao.org).
The concentration change was related to Cs_{SO4} (29 % of explained variability) and to precipitation and elevation. Overall, 45 % of annual change in NH_4 concentration was explained.

$$\Delta Cs_{NH4} = 0.413 - 1.334x10^{-3} \times E + 1.075x10^{-3} \times P - 3.279x10^{-2} \times Cs_{SO4}$$

The steepest decline tends to be at sites with highest SO_4 concentrations (Figure S4). Site standard deviation (σs_{NH4}) was then calculated based on the linear regression from the Figure S2.

$$\sigma s_{NH4} = -5.59 \times \Delta Cs_{NH4} + 7.2$$

Modelled mean Cs_{NH4} RMSE was 25 % of site average value, modelled ΔCs_{NH4} RMSE was 56 % of site mean change and modelled σs_{NH4} RMSE was 39 % of mean site standard deviation (Figure 7). Concentrations of inorganic nitrogen were less satisfactorily predicted than SO_4 concentrations in precipitation. Related to the previous discussion, higher degree of year-to-year variability in the N concentration in precipitation and higher degree of inter site trend heterogeneity caused poorer performance of regression models compared to the well constrained trends in SO_4 concentrations. However, calculated spatial distribution of precipitation chemistry (*Cs*, σs) can be used to estimate historical deposition gradients across the Czech Republic.

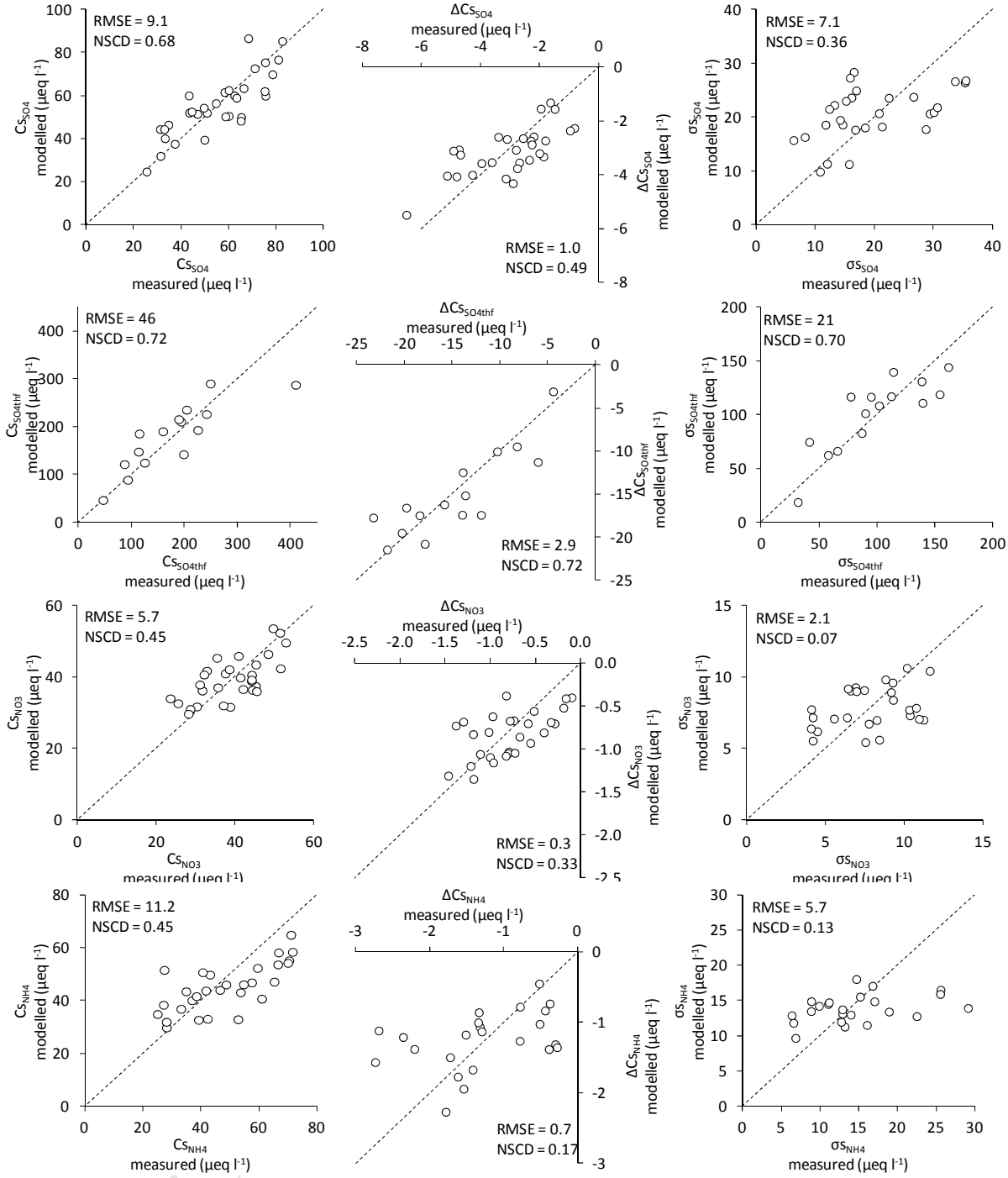


Figure 7. 1:1 plots of modelled vs. measured mean SO_4, NO_3 and NH_4 concentrations (*Cs*) at the study sites, annual rate of change (*ΔCs*), site standard deviation (*σs*). Root mean square error (RMSE) and Nash-Sutcliffe coefficient of determination (NSCD) are displayed.

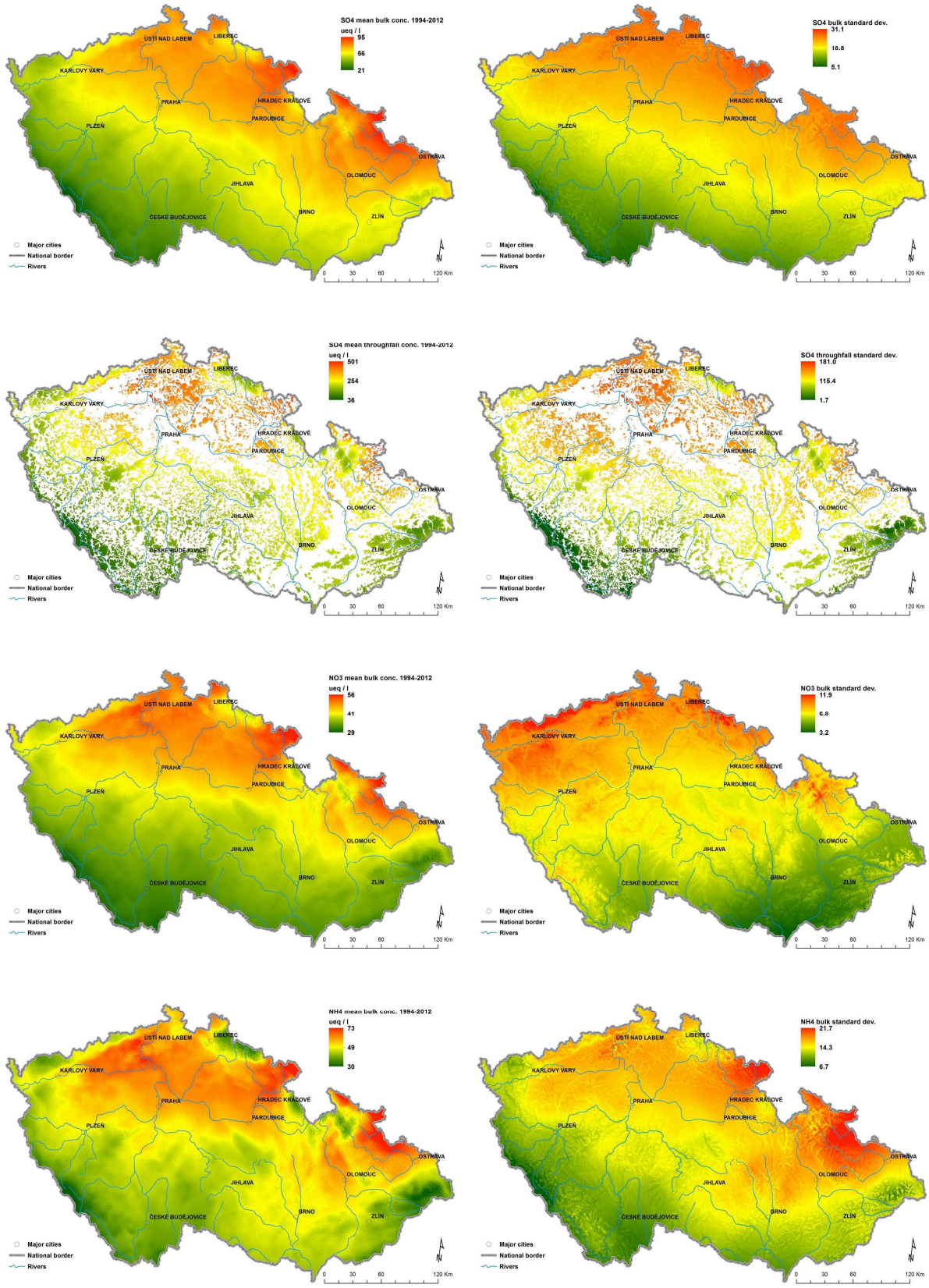


Figure 8. Spatial distribution of calculated mean Cs and σs across the Czech Republic.

3.4 SPATIAL ESTIMATION OF S AND N DEPOSITION ACROSS THE CZECH REPUBLIC BETWEEN 1900 AND 2012

3.4.1 Temporal development of S deposition

Estimated average S bulk deposition across the Czech Republic was a product of the spatial distribution of modelled Cs_{SO4} and mean precipitation depth. Highest S bulk deposition was modelled for northern part of the Czech Republic, especially in the mountainous landscape. For the calibration period (1994 - 2012), average S bulk deposition ranged between 3.5 and 15 kg S ha^{-1} yr^{-1} across the Czech Republic (Figure 9). Over the 20th century, estimated median S bulk deposition increased from 5 kg S ha^{-1} yr^{-1} (1900) to 11.6 kg S ha^{-1} yr^{-1} (1979) and then declined to 3.8 kg S ha^{-1} yr^{-1} (2012) (Figure S5). Current S bulk deposition is thus lower than estimated deposition in 1900. Between peak of the bulk S deposition and the year 2012, deposition declined by 67 %. Between 1979 and 2012, the rate of decline in bulk S deposition (ΔCs_{SO4}) ranged between -0.19 and -0.48 kg S ha^{-1} yr^{-1} (median of -0.29 kg S ha^{-1} yr^{-1}) (Figure S4). Over the 20th century (1900 – 2012) cumulative CS (Czechoslovakia area based) SO_2 emissions were on average ~5025 kg S ha^{-1} and the modelled bulk S deposition (for the same area) was 945 kg S ha^{-1} for the same period.

Forests in the Czech Republic cover ca. 34 % of country area and consist mainly of production forests (75 %) with predominantly conifer species (73 %). During the 20th century forest area increased by ca. 5 %. Because canopy exchange of S is negligible, higher throughfall versus bulk deposition can be attributed to dry S deposition, such that throughfall provides a good measure of the total atmospheric deposition of S (Lindberg and Lovett, 1992). Average S throughfall (total) deposition was highest in the northern part of the Czech Republic, with the highest estimated deposition in the mountain areas. Between 1994 and 2012, average S total deposition under the spruce canopy ranged between 5 and 43 kg S ha^{-1} yr^{-1} (Figure 9). Over the 20th century, estimated country median S total deposition increased from 14 kg S ha^{-1} yr^{-1} (1900) to 41 kg S ha^{-1} yr^{-1} (1979) and then declined to 7.3 kg S ha^{-1} yr^{-1} (2012) (Figure S5). Between peak of the S total deposition and year 2012, the throughfall S deposition declined by 82 %, i.e. faster than bulk S deposition. Between 1979 and 2012 the rate of decline in total S deposition (ΔCs_{SO4thf}) ranged between -0.9 and -2.3 kg S ha^{-1} yr^{-1} (median of -1.3 kg S ha^{-1} yr^{-1}). The most pronounced decline in S total deposition was modelled for forests close to the biggest stationary SO_2 sources (mostly brown coal burning powerplants) in the NW part of the Czech Republic (Figure S4)(Hůnová et al., 2014). On average, cumulative S deposition in Czech forests is estimated to be 3048 kg S ha^{-1} during the 20th century. In total, due to the majority of non-forested landscape (66 %) with relatively low dry deposition on vegetation surfaces, 34 % of emitted S in the Czech Republic has been deposited within its own territory as bulk or throughfall deposition since 1900. Currently, 70 % of Czech SO_2 emissions is deposited within the country boundaries. However, during the peak of SO_2 pollution, 20 % of emitted S in the Czech Republic has been deposited within its own territory.

Based on the analysis, enrichment of throughfall deposition over the bulk deposition (DDF – dry deposition factor) varied between 1.7 and 6.6, with the highest ratio in the NW of the Czech territory. Again, sites closest to the S emission sources had the highest DDF (Figure 10). Over the last hundred years, median DDF peaked in the 1980s at 3.4 (10th and 90th percentile range of 2.9 and 3.8) and declined to 1.7 in 2012 (10th and 90th percentile range between 1 and 2.6) (Figure S5).

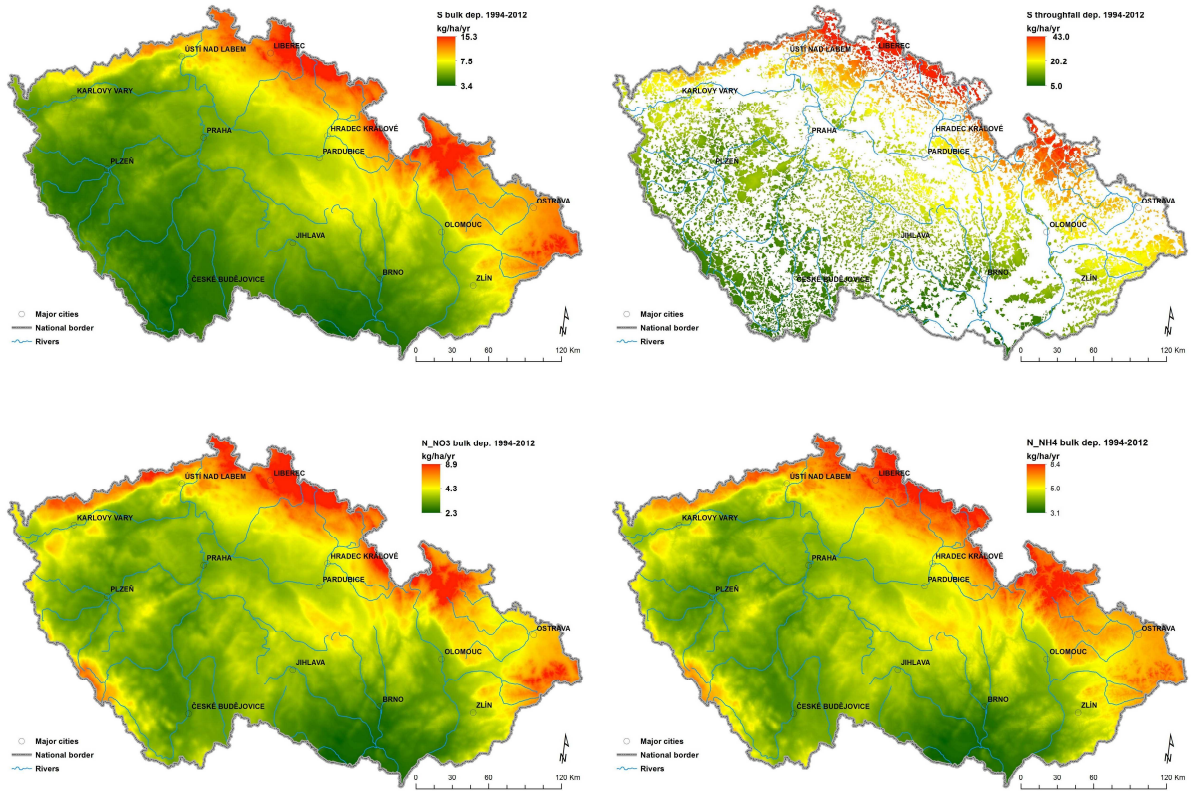


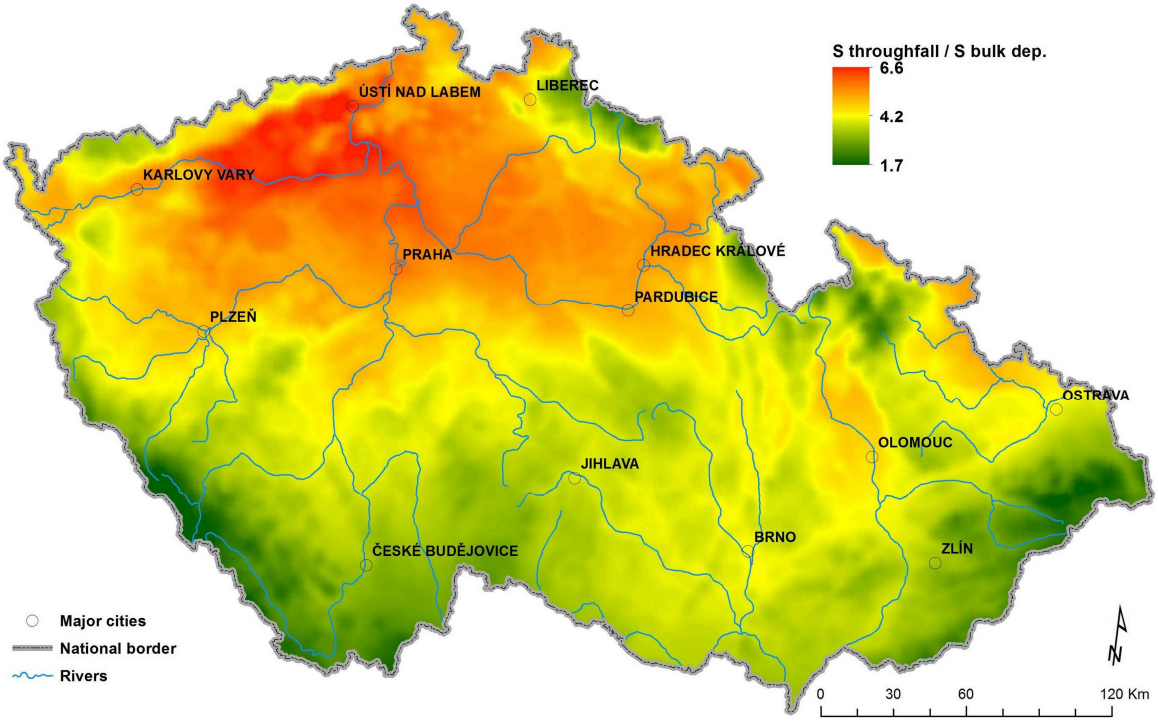
Figure 9. Modelled average deposition (kg ha^{-1} yr^{-1}) of S (bulk and throughfall) and N (bulk) compounds in the Czech Republic during 1994–2012.

3.4.2 Temporal development of N deposition

Spatial distribution of both NO_3 and NH_4 bulk concentration was statistically related to SO_4 concentration in precipitation. Although modelled Cs_{SO4} as a predictor of spatial distribution of Cs_{NO3} and Cs_{NH4} may induce additional error in regression modelling, both N species concentrations were statistically related to the SO_4, likely reflecting common sources (SO_2 and NO_x emissions) or/and linked atmospheric chemistry (SO_4 and NH_4). Modelled deposition of NO_3 was highest in the mountain areas across the Czech Republic, with a south – north gradient. The average NO_3 deposition ranged between 2.3 and 8.9 kg N-NO_3 ha^{-1} yr^{-1} from 1994 – 2012 (Figure 9). Bulk NO_3 deposition was 2.4 kg N ha^{-1} yr^{-1} in 1900, which is lower than its current level. The peak of NO_3 deposition occurred in 1988, with a median value of 5.3 kg N ha^{-1} yr^{-1}. Since then, NO_3 deposition declined by 38 % to 3.3 kg N ha^{-1} yr^{-1} (Figure S5). The median decline was calculated as -0.07 kg N ha^{-1} yr^{-1} (range between -0.05 and -0.11 kg N ha^{-1} yr^{-1}). The most pronounced declines in NO_3 deposition were modelled for western and north-western part of the Czech Republic (Figure S4). Cumulative NO_3 deposition over the 1900–2012 period was 409 kg N ha^{-1}, which accounted for 33 % of the emissions of oxidized N forms.

The modelled spatial distribution of ammonium deposition was similar to NO_3, with less deposition in the eastern part of the Czech Republic. The average NH_4 deposition ranged between 3.1 and 8.4 kg N ha^{-1} yr^{-1} (Figure 9). Bulk NH_4 deposition was 4.2 kg N ha^{-1} yr^{-1} in 1900, i similar to its current deposition (Figure S5), and peaked in 1984 with a median of 7.2 kg N ha^{-1} yr^{-1}. Since then, NH_4 deposition declined by 46 % to 3.9 kg N ha^{-1} yr^{-1}. Modelled decline ranged between -0.11 and -0.2 kg N ha^{-1} yr^{-1} (median of -0.14 kg N ha^{-1} yr^{-1}). The most pronounced declines occurred in northern and north-eastern parts of the country (Figure S4). Cumulative NH_4 deposition was estimated to 576 kg N ha^{-1} during 1900 – 2012, which accounted for 62 % of the CS emissions of NH_3. Spatially distributed NO_3 and NH_4 precipitation concentrations reflects the nature of country land use, with higher NH_4 to NO_3 ratios in lowland, agricultural landscapes (Figure 10). Temporal development of the NH_4 to NO_3

ratio in precipitation reflects different temporal changes in energy production (sources and amount) and agricultural activities (mostly livestock production) (Kopáček and Veselý, 2005). Two distinct period of time highlight those changes – after the 2nd World War and then after the political changes in 1989 (Figure S5) (Kopáček et al., 2013).



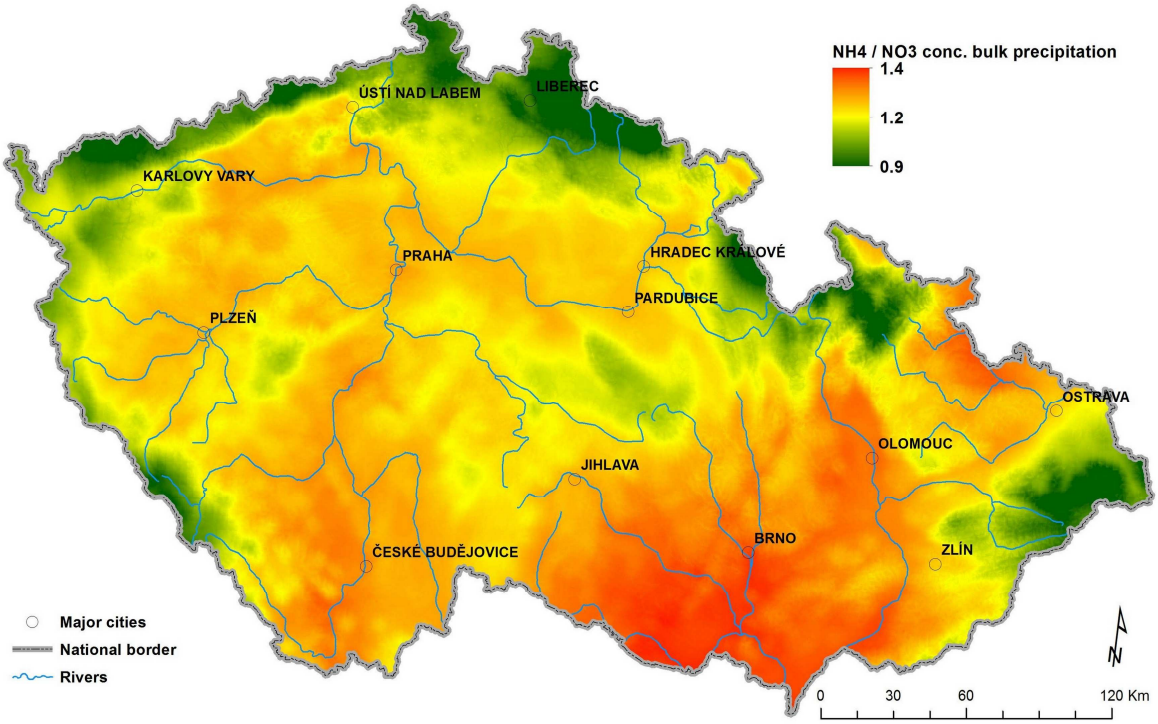


Figure 10. Mean modelled ratio between throughfall and bulk S deposition and NH_4 to NO_3 molar ratio in bulk precipitation in the Czech Republic in the period 1994 – 2012.

4 CONCLUSIONS

The methodology described in this paper represents a novel approach to the temporal reconstruction and spatial interpolation of atmospheric deposition chemistry, based on a simple statistical analysis of precipitation and throughfall monitoring data. Standardisation of precipitation chemistry to annual mean Z scores provides a robust method for comparing sites with different levels of absolute concentrations, and relationships between these Z scores and regional S and N emissions enabled us to reconstruct long-term changes in total deposition at the scale of the Czech Republic for the entire 20th century. Empirically-based interpolation, taking into account of key variables such as altitude, precipitation depth and geographical coordinates, allowed spatial variations in deposition to be mapped at a high resolution based on just 30 monitoring sites. The combination of temporal extrapolation and spatial interpolation allowed us to generate whole-country S and N budgets for the Czech Republic, which indicate that the country has undergone a transition from a strong net exporter of S to one in which the majority of (much lower) S emissions are now redeposited within the country.

Our results demonstrate that long-term measurements of atmospheric deposition, in combination with a statistical method that exploits observed spatiao-temporal coherence in deposition chemistry, provides a robust approach for upscaling the observed data to other locations. As an important anthropogenic driver in many regions, the capacity to estimate site-specific S and N deposition over long time periods is a requirement for many models that seek to predict the historic and future trajectory of change in natural and semi-natural ecosystems, and a prerequisite for understanding the ecological changes that have occurred in many ecosystems affected by atmospheric pollution over the last 100 years.

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References

Bobbink, R., Hicks, K., Galloway, J., Spranger, T., Alkemade, R., Ashmore, M., Bustamante, M., Cinderby, S., Davidson, E., Dentener, F., Emmett, B., Erisman, J.W., Fenn, M., Gilliam, F., Nordin, A., Pardo, L., De Vries, W., 2010. Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. Ecol. Appl. 20, 30–59.

Bonten, L.T.C., Reinds, G.J., Posch, M., 2016. A model to calculate effects of atmospheric deposition on soil acidification, eutrophication and carbon sequestration. Environ. Model. Softw. 79, 75–84. doi:10.1016/j.envsoft.2016.01.009

Butler, T., Likens, G., Vermeylen, F., Stunder, B., 2005. The impact of changing nitrogen oxide emissions on wet and dry nitrogen deposition in the northeastern USA. Atmos. Environ. 39, 4851–4862. doi:10.1016/j.atmosenv.2005.04.031

Černý, J., Pačes, T. (Eds.), 1995. Acidification in the Black Triangle Region. Czech Geological Survey, Prague.

De Vries, W., Wamelink, G.W.W., van Dobben, H., Kros, J., Reinds, G.J., Mol-Dukstra, J.P., Smart, S.M., Evans, C.D., Rowe, E.C., Belyazid, S., Sverdrup, H.U., van Hinsberg, A., Posch, M., Hettelingh, J.P., Spranger, T., Bobbink, R., 2010. Use of dynamic soil-vegetation models to assess impacts of nitrogen deposition on plant species composition: an overview. Ecol. Appl. 20, 60–79.

Evans, C.D., Cooper, D.M., Monteith, D.T., Helliwell, R.C., Moldan, F., Hall, J., Rowe, E.C., Cosby, B.J., 2010. Linking monitoring and modelling: can long-term datasets be used more effectively as a basis for large-scale prediction? Biogeochemistry 101, 211–227. doi:10.1007/s10533-010-9413-x

Fagerli, H., Aas, W., 2008. Trends of nitrogen in air and precipitation: model results and observations at EMEP sites in Europe, 1980--2003. Environ. Pollut. 154, 448–61. doi:10.1016/j.envpol.2008.01.024

Hofmeister, J., Oulehle, F., Krám, P., Hruška, J., 2008. Loss of nutrients due to litter raking compared to the effect of acidic deposition in two spruce stands, Czech Republic. Biogeochemistry 88, 139–151. doi:10.1007/s10533-008-9201-z

Hůnová, I., Maznová, J., Kurfürst, P., 2014. Trends in atmospheric deposition fluxes of sulphur and nitrogen in Czech forests. Environ. Pollut. 184, 668–75. doi:10.1016/j.envpol.2013.05.013

Janssen, P.H.M., Heuberger, P.S.C., 1995. Calibration of process-oriented models. Ecol. Modell. 83, 55–66.

Kernan, M., Battarbee, R.W., Curtis, C., Monteith, D.T., Shilland, E.M., 2010. UK Acid Waters Monitoring Network 20 Year Interpretative Report. Report to DEFRA. London, UK.

Kopáček, J., Hejzlar, J., Posch, M., 2013. Factors Controlling the Export of Nitrogen from Agricultural Land in a Large Central European Catchment during 1900–2010. Environ. Sci. Technol. 47, 130528133920004. doi:10.1021/es400181m

Kopáček, J., Posch, M., 2011. Anthropogenic nitrogen emissions during the Holocene and their possible effects on remote ecosystems. Global Biogeochem. Cycles 25, GB2017. doi:10.1029/2010GB003779

Kopáček, J., Posch, M., Hejzlar, J., Oulehle, F., Volková, A., 2012. An elevation-based regional model for interpolating sulphur and nitrogen deposition. Atmos. Environ. 50, 287–296. doi:10.1016/j.atmosenv.2011.12.017

Kopacek, J., Vesely, J., 2005. Sulfur and nitrogen emissions in the Czech Republic and Slovakia from

1850 till 2000. Atmos. Environ. 39, 2179–2188. doi:10.1016/j.atmosenv.2005.01.002

Kopacek, J., Vesely, J., Stuchlik, E., Kopáček, J., Veselý, J., Stuchlík, E., 2001. Sulphur and nitrogen fluxes and budgets in the Bohemian Forest and Tatra Mountains during the Industrial Revolution (1850-2000). Hydrol. Earth Syst. Sci. 5, 391–405.

Likens, G.E., Buso, D.C., Butler, T.J., 2005. Long-term relationships between SO2 and NOx emissions and SO4(2-) and NO3- concentration in bulk deposition at the Hubbard Brook Experimental Forest, NH. J. Environ. Monit. 7, 964–8. doi:10.1039/b506370a

Likens, G.E., Butler, T.J., Buso, D.C., 2001. Long-and short-term changes in sulfate deposition: Effects of the 1990 clean air act amendments. Biogeochemistry 52, 1–11. doi:10.1023/A:1026563400336

Lindberg, S.., Lovett, G.., 1992. Deposition and forest canopy interactions of airborne sulfur: Results from the integrated forest study. Atmos. Environ. Part A. Gen. Top. 26, 1477–1492. doi:10.1016/0960-1686(92)90133-6

Mylona, S., 1996. Sulphur dioxide emissions in Europe 1880-1991 and their effect on sulphur concentrations and depositions. Tellus 48B, 662–689.

Nash, J.E., Sutcliffe, J.V., 1970. River flow forecasting through conceptual models part I — A discussion of principles. J. Hydrol. 10, 282–290. doi:10.1016/0022-1694(70)90255-6

Oulehle, F., Cosby, B.J., Austnes, K., Evans, C.D., Hruška, J., Kopáček, J., Moldan, F., Wright, R.F., 2015. Modelling inorganic nitrogen in runoff: Seasonal dynamics at four European catchments as simulated by the MAGIC model. Sci. Total Environ. 536, 1019–28. doi:10.1016/j.scitotenv.2015.05.047

Oulehle, F., Evans, C.D., Hofmeister, J., Krejci, R., Tahovska, K., Persson, T., Cudlin, P., Hruska, J., 2011. Major changes in forest carbon and nitrogen cycling caused by declining sulphur deposition. Glob. Chang. Biol. 17, 3115–3129. doi:10.1111/j.1365-2486.2011.02468.x

Pihl Karlsson, G., Akselsson, C., Hellsten, S., Karlsson, P.E., 2011. Reduced European emissions of S and N--effects on air concentrations, deposition and soil water chemistry in Swedish forests. Environ. Pollut. 159, 3571–82. doi:10.1016/j.envpol.2011.08.007

Rogora, M., Mosello, R., Arisci, S., Brizzio, M.C., Barbieri, A., Balestrini, R., Waldner, P., Schmitt, M., Stähli, M., Thimonier, A., Kalina, M., Puxbaum, H., Nickus, U., Ulrich, E., Probst, A., 2006. An Overview of Atmospheric Deposition Chemistry over the Alps: Present Status and Long-term Trends. Hydrobiologia 562, 17–40. doi:10.1007/s10750-005-1803-z

Schöpp, W., Posch, M., Mylona, S., Johansson, M., 2003. Long-term development of acid deposition (1880-2030) in sensitive freshwater regions in Europe. Hydrol. Earth Syst. Sci. 7, 436–446.

Seinfeld, J.H., Pandis, S.P., 1998. Atmospheric chemistry and physics: From air pollution to climate change. Wiley, New York.

Simpson, D., Fagerli, H., Jonson, J.E., Tsyro, S., Wind, P., Tuovinen, J.P., 2003. Transboundary acidification and eutrophication and ground level ozone in Europe: Unified EMEP Model Description, EMEP Status Report 1/2003 Part I, EMEP/MSC-W Report. Oslo.

Štěpánek, P., Zahradníček, P., Farda, A., 2013. Experiences with data quality control and homogenization of daily records of various meteorological elements in the Czech Republic in the period 1961-2010. Idojaras 117, 123–141.

Štěpánek, P., Zahradníček, P., Huth, R., 2011. Interpolation techniques used for data quality control and calculation of technical series: An example of a Central European daily time series. Idojaras

115, 87–98.

UNECE, 2004. Handbook for the 1979 convention on long-range transboundary air pollution and its protocols. New York and Geneva.

Vestreng, V., Myhre, G., Fagerli, H., Reis, S., Tarrasón, L., 2007. Twenty-five years of continuous sulphur dioxide emission reduction in Europe. Atmos. Chem. Phys. 7, 3663–3681.

Waldner, P., Marchetto, A., Thimonier, A., Schmitt, M., Rogora, M., Granke, O., Mues, V., Hansen, K., Pihl Karlsson, G., Žlindra, D., Clarke, N., Verstraeten, A., Lazdins, A., Schimming, C., Iacoban, C., Lindroos, A.-J., Vanguelova, E., Benham, S., Meesenburg, H., Nicolas, M., Kowalska, A., Apuhtin, V., Napa, U., Lachmanová, Z., Kristoefel, F., Bleeker, A., Ingerslev, M., Vesterdal, L., Molina, J., Fischer, U., Seidling, W., Jonard, M., O'Dea, P., Johnson, J., Fischer, R., Lorenz, M., 2014. Detection of temporal trends in atmospheric deposition of inorganic nitrogen and sulphate to forests in Europe. Atmos. Environ. 95, 363–374. doi:10.1016/j.atmosenv.2014.06.054

HIGHLIGHTS

- Temporal coherence of precipitation SO_4, NO_3 and NH_4 was demonstrated
- Regional S and N emissions enabled to reconstruct long-term changes in deposition
- Empirically-based interpolation allowed spatial deposition variations to be mapped