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Predicting sulphur and nitrogen deposition using a simple statistical method

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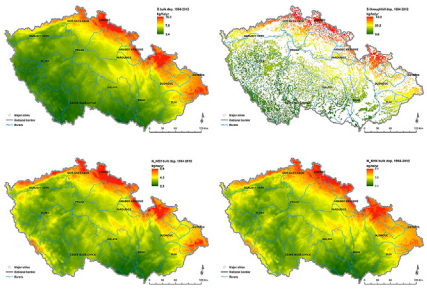
HIGHLIGHTS

- 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.

GRAPHICAL ABSTRACT



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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 standardised 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

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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.

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%–217 kt yr^{-1}, NO_x emissions by 62%–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 SO_2 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; Fig. 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 ±10% of the total ionic content were used without any other control. If the difference exceeded ±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.