



# Effect of industrial dust on precipitation chemistry in the Czech Republic (Central Europe) from 1850 to 2013



Jiří Kopáček<sup>a, b, \*</sup>, Josef Hejzlar<sup>a</sup>, Pavel Krám<sup>c</sup>, Filip Oulehle<sup>c</sup>, Maximilian Posch<sup>d</sup>

<sup>a</sup> Biology Centre CAS, Institute of Hydrobiology, Na Sádkách 7, 37005 České Budějovice, Czech Republic

<sup>b</sup> Faculty of Science, University of South Bohemia, Branišovská 1760, 37005 České Budějovice, Czech Republic

<sup>c</sup> Czech Geological Survey, Klárov 3, 11821 Prague 1, Czech Republic

<sup>d</sup> Coordination Centre for Effects, RIVM, P.O. Box 1, NL-3720 BA Bilthoven, The Netherlands

## ARTICLE INFO

### Article history:

Received 23 December 2015

Received in revised form

6 July 2016

Accepted 9 July 2016

Available online 11 July 2016

### Keywords:

Sulphate

Nitrate

Chloride

Ammonium

Base cations

pH

Czech Republic

## ABSTRACT

Using statistical relationships between the composition of precipitation at eight long-term monitoring stations and emission rates of sulphur (S) and nitrogen (N) compounds, as well as industrial dust in the Czech Republic and Slovakia (Central Europe), we modelled historic pH and concentrations of sulphate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), chloride ( $\text{Cl}^-$ ), base cations (BC), and bicarbonate ( $\text{HCO}_3^-$ ) in bulk precipitation from 1850 to 2013. Our model suggests that concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{HCO}_3^-$  were similar (11–16  $\mu\text{eq l}^{-1}$ ) in 1850. Cations were dominated by  $\text{NH}_4^+$  and BC (24–27  $\mu\text{eq l}^{-1}$ ) and precipitation pH was  $>5.6$ . The carbonate buffering system was depleted around 1920 and precipitation further acidified at an exponential rate until the 1980s, when concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$  and BC reached maxima of 126, 55, 16, 76, and 57  $\mu\text{eq l}^{-1}$ , respectively, and pH decreased to 4.2. Dust emissions from industrial sources were an important source of BC. Without their contribution, pH would have decreased to 4.0 in the 1980s, and the carbonate buffering system would have been depleted already in the 1870s. Since the late 1980s, concentrations of strong acid anions and BC have decreased by 46–81% (i.e. more than in Europe on average) due to a 53–93% reduction in regional emissions of S and N compounds and dust from industrial and agricultural sources. The present composition of precipitation is similar to the late 19th century, except for  $\text{NO}_3^-$  concentrations, which are similar to those during 1926–1950. Precipitation pH now exceeds 5.0, the carbonate buffering system has been re-established, and  $\text{HCO}_3^-$  has again become (after almost a century) a significant component of precipitation chemistry.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Atmospheric acidic deposition from anthropogenic sources has affected the biogeochemistry of aquatic and terrestrial ecosystems in many areas (Psenner and Catalan, 1994). Knowledge on the history and possible future development of precipitation chemistry is a key factor for understanding and modelling ecosystem response to air pollution (e.g., Cosby et al., 1985; Posch et al., 2012) and provides important information, which can be used to support policies to control pollutant emissions and their adverse effects on ecosystems (e.g. Reis et al., 2012).

Continuous long-term data on precipitation chemistry in Europe

starting prior to the 1970s are sparse, scattered, and usually not including all major ions (e.g., Egnér and Eriksson, 1955; Mackú et al., 1959; Brimblecombe and Stedman, 1982). The assessment of past and future changes in atmospheric chemical composition can be, however, based on the use of historical and projected pollutant emissions scenarios due to a high degree of underlying temporal coherence between emission and deposition rates of major pollutants (Schöpp et al., 2003). Close relationships have been found between measured sulphur and nitrogen depositions and their respective regional emissions and widely used either in simplified versions (e.g. source–receptor matrices) of atmospheric transport models (e.g., Simpson et al., 2012) or correlative studies (Kopáček et al., 2012). These relationships enable estimates of earlier levels of sulphate, nitrate, and ammonium depositions, using long-term sequences of emissions of sulphur dioxide ( $\text{SO}_2$ ), nitrogen oxides ( $\text{NO}_x$ ), and ammonia ( $\text{NH}_3$ ). Historical S and N emissions into the atmosphere can be successfully reconstructed

\* Corresponding author. Biology Centre ASCR, Institute of Hydrobiology, Na Sádkách 7, 37005 České Budějovice, Czech Republic.

E-mail address: [jkopacek@hbu.cas.cz](mailto:jkopacek@hbu.cas.cz) (J. Kopáček).

many decades back on the basis of statistical data on industrial and agricultural activities, which are often available in national statistical yearbooks (e.g., Mylona, 1996; Olivier et al., 1998). Preliminary data suggested that close relationships also could be found between measured depositions of non-marine chloride ( $\text{Cl}^-$ ) and base cations ( $\text{BC} = \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$ ) and emissions of  $\text{SO}_2$  and dust, respectively, in areas where these emissions predominantly originate from anthropogenic sources, and their deposition is not significantly affected by marine aerosols and/or aeolian-derived dust (Kopáček et al., 2015).

Atmospheric depositions of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in Central Europe originate predominantly (65–85%) from the emissions of  $\text{SO}_2$ ,  $\text{NO}_x$  and  $\text{NH}_3$  from the same region (Berge, 1997), and the contribution of sea salt and dust from arid or desert areas to precipitation chemistry is negligible (Van Leeuwen et al., 1996; Tsyro et al., 2011; Vet et al., 2014). Consequently, Central Europe represents an area without such ‘noise’ and with robust relationships between emissions from industrial and agricultural activities and deposition fluxes and thus the long-term effects of the anthropogenic pollution of the atmosphere on precipitation chemistry can be evaluated.

Using the Czech Republic, located in the middle of Central Europe, as example, we show that the knowledge on emission rates of major anthropogenic pollutants (S, N, and industrial dust), based on statistical data, can be used to successfully reconstruct long-term trends in precipitation chemistry, including not only major ions but also pH and concentrations of bicarbonate ( $\text{HCO}_3^-$ ). We also show how precipitation chemistry in this region was influenced by politically and economically induced changes in industrial and agricultural activities and modified by dust emissions from industrial sources.

## 2. Materials and methods

### 2.1. Measured trends in precipitation chemistry

In this study, we used annual precipitation amounts and annual volume-weighted mean composition of bulk ( $n = 5$ ) and wet-only ( $n = 3$ ) deposition of major ions from eight stations situated in the Czech Republic and Slovakia (CS) at elevations between 273 and 2008 m. All stations were located in open area without trees with distance from the nearest forested area  $>50$  m. For more details on their locations and type of sampling (bulk; wet-only) see Supplementary Information (SI), Fig. SI-1. Measurements at individual stations started in 1978 ( $n = 4$ ; Chopok, Jezeří, Slapy, Svratouch), 1983 ( $n = 2$ ; Košetice, Hradec Králové) and 1991 ( $n = 2$ ; Čertovo Lake, Lysina) and continued until the end of this study in 2013, except for one station (Hradec Králové) that was operated only until 2010. Annual volume-weighted mean concentrations of major ions in wet-only deposition were recalculated to bulk deposition according to Oulehle et al. (2016), using relationships between available parallel data on composition of wet-only and bulk precipitation in the CS region.

Sampling frequency varied from one day to one month. Precipitation was stored in dark at  $4^\circ\text{C}$  until analysis. Even though the stations were operated by four different institutions (Table SI-1), ionic concentrations were measured using similar methods (mostly ionic chromatography and atomic absorption spectrometry, but prior to the 1990s the data were partly based on colorimetric methods; for methodological details see Part SI-1). In addition to major ions, concentrations of dissolved organic carbon (DOC) have been determined at four stations (Slapy, Jezeří, Lysina, and Čertovo) and acid neutralizing capacity (ANC, Gran titration) at three stations (Slapy, Čertovo, and Lysina) since the late 1990s. 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 (without organic acid anions) lower than  $\pm 10\%$  of the total ionic content were used without any other control. If the difference exceeded  $\pm 10\%$  ( $n = 33$ , i.e. 13% of all data), 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, we excluded this ion from statistical analyses, but used the rest of the data on chemical composition. If we were not able to detect an error, we excluded all chemical data from that year ( $\sim 3\%$  of all data).

### 2.2. Reconstructed trends in emissions of $\text{SO}_2$ , $\text{NO}_x$ , $\text{NH}_3$ , and dust

Historical emission trends for  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_3$  in the CS region (Fig. 1a) are based on data from the official databases of EMEP ([www.ceip.at/emission-data-webdab](http://www.ceip.at/emission-data-webdab)) for the 1980–2013 period, and on data reconstructed by Kopáček and Veselý (2005) for the 1850–1979 period on the basis of statistical data on energy production and its sources ( $\text{NO}_x$ ), fossil fuel combustion ( $\text{SO}_2$ ), and livestock production and the production and use of synthetic N-fertilizers ( $\text{NH}_3$ ). Thus calculated CS emissions of  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_3$  were on average 7% higher, 2% lower, and 8% higher, respectively, than the EMEP data during 1980–1990. We did not correct our estimated trends prior to 1980 for these differences.

Trends in the CS emissions of dust (total particulate matter) are based on official databases (CS Statistical Offices and Ministry of Environment of the Czech Republic) from 1970 to 2013 and calculated from statistical data on the mining and combustion of lignite and hard coal in the area of the present Czech Republic and Slovakia (data from Yearbooks of the Austrian and CS Statistical Offices before and after 1918, respectively) for the 1850–1969 period (Fig. 1b). A relationship between coal combustion and dust emissions, used for computing dust emissions prior to 1970, was obtained for data from 1970 to 1982; i.e. the period prior to effective controls of dust emission from power production and industrial sources. The average ( $\pm$ standard deviation) dust emission was  $103 \pm 9 \text{ g m}^{-2} \text{ Mg}^{-1}$  of the used fuel during this period. For this estimate, we assumed that (i) dust emissions from agriculture, transportation, and natural sources were stable throughout 1850–2013 (due to the absence of detailed data on these sources) and (ii) dust emissions from cement production (responsible for less than one third of total industrial emissions of  $\text{Ca}^{2+}$  in Europe; Lee et al., 1999) were proportional to the energy production, i.e. coal combustion in the CS region. All emission trends used in this study are given on an areal basis related to the CS region, i.e. in  $\text{mmol m}^{-2} \text{ yr}^{-1}$  for S and N compounds and in  $\text{g m}^{-2} \text{ yr}^{-1}$  for dust. For more details on reconstruction and description of the emission trends see SI, Part SI-2.

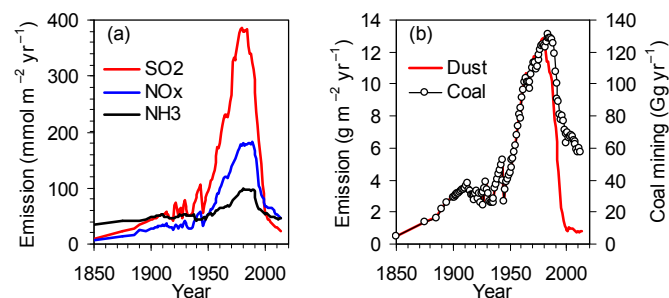


Fig. 1. Reconstructed trends in areal emission rates of (a)  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{NH}_3$ , and (b) dust (and coal mining) in the present area of the Czech Republic and Slovakia.

Download English Version:

<https://daneshyari.com/en/article/6364425>

Download Persian Version:

<https://daneshyari.com/article/6364425>

[Daneshyari.com](https://daneshyari.com)