STATISTICAL APPROXIMATION AND PREDICTION OF ATMOSPHERIC SULPHURIC ACID CONCENTRATION WITH METEOROLOGICAL AND TRACE GAS MEASUREMENT DATA

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INTRODUCTION

Sulphuric acid is one of the key factors in new particle formation in the atmosphere (Kulmala et al., 2006) and the number concentration of freshly nucleated particles is found to have a strong dependency on sulphuric acid levels (Weber et al., 1997, Sihto et al., 2006, Kuang et al., 2008). The problem is that gas phase sulphuric acid concentration is difficult to measure and in many measurement sites no \( \text{H}_2\text{SO}_4 \) data are available. The purpose of this study is to test how different proxies predict the real sulphuric acid concentration in different datasets, thus widening the study made by Petäjä et al. (2009) for the EUCAARI 2007 campaign data. In total seven datasets, consisting of six campaign datasets and one long term dataset, were analyzed for this study. The campaign datasets were measured in Hyytiälä, Finland, in 2003 and 2007, in San Pietro Capofiume (SPC), Italy in 2009, in Atlanta, USA, in 2002, in Manitou, USA, in 2008, and in Niwot Ridge, USA, in 2007. The long term data were measured in Hohenpeissenberg, Germany within years 1998 to 2000 (Birmili et al., 2003).

METHODS

A proxy for sulphuric acid concentration is based on a production mechanism that is described by the net reaction \( \text{SO}_2 + \text{OH} \rightarrow \text{H}_2\text{SO}_4 + \text{HO}_2 \), and a deposition-based loss mechanism that is described by a first order rate constant, \( CS \), also known as the condensation sink. Integrating the differential equation for sulphuric acid concentration

\[
\frac{d[\text{H}_2\text{SO}_4]}{dt} = k \cdot [\text{OH}] \cdot [\text{SO}_2] \cdot [\text{H}_2\text{SO}_4] \cdot CS,
\]

where \( k \) is temperature dependent reaction constant, gives the sulphuric acid concentration at given time. To simplify the problem, it can be assumed that the \( \text{H}_2\text{SO}_4 \) production is in steady-state, which leads to proxy function given by

\[
[\text{H}_2\text{SO}_4] = k \cdot [\text{OH}] \cdot [\text{SO}_2] \cdot CS^{-1}.
\]

Recent studies have suggested that the \( \text{OH} \) radical concentration is strongly correlated with the intensity of solar radiation (Rohrer and Berresheim, 2006) despite the complex \( \text{OH} \) chemistry in the atmosphere. We therefore use the measurements of global radiation as a proxy for \( \text{OH} \).

A nonlinear fitting procedure was applied to all datasets, with a fit function given by

\[
[\text{H}_2\text{SO}_4] = a \cdot \text{Radiation}^{b} \cdot [\text{SO}_2]^{c} \cdot CS^{d}.
\]

If the steady state applies without any additional chemistry, then all \( a, b \) and \( c \) should be unity, and it turns out to be an adequate approximation. However, the fitting procedure results power \( c \) for \( \text{SO}_2 \) concentration to be approximately 0.5 for every dataset except Manitou and Niwot Ridge where \( c \) was near unity. The
power \( b \) for radiation varied a lot, but it could be approximated with unity without significant decrease in prediction ability for all other datasets but Manitou, and the power \( d \) for condensation sink could be approximated with -1 without significant decrease in prediction ability of the proxy. Only data points where Radiation was higher than 10 W m\(^{-2}\) and \( \text{SO}_2 \) concentration was higher than 0.1 ppb were used. Surprisingly, the prediction ability of the proxy was equal without the CS term for datasets from Hohenpeissenberg and Niwot Ridge but for all other datasets the prediction was even better without the condensation sink and using square root dependency for the \( \text{SO}_2 \) concentration. The prediction ability of the proxy without CS and with the \( c \) being 0.5 varied between datasets from 90% of SPC and Hyytiälä 2003 data and 65% of Hohenpeissenberg. Figure 1 illustrates the prediction ability of the proxies in SPC. The lower prediction ability for the long term data indicates that the change in atmospheric conditions caused by the change of the seasons has to be taken account in the analysis.

![Figure 1. Measured sulphuric acid concentration vs. predictions with two different proxies in SPC. Diagonal line represents the perfect fit.](image)

The reason for the better performance of proxies with square root of \( \text{SO}_2 \) can only be speculated, but it is possible that it has to do with the somewhat unrealistic steady-state approximation or the \( \text{SO}_2 \) concentration acts also as an indicator for some other parameter involved in the process but not present in our data. The development of a proxy without a condensation sink term enables its use also for situations when no particle size distribution data is available.

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REFERENCES


