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Finding a proxy for sulphuric acid concentration with statistical analysis

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Sulphuric acid is known to be a significant factor in the 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 (Sihto et al., 2006). The problem is that gas phase sulphuric acid concentration is difficult to measure and in many measurement sites no H_2SO_4 data are available. The purpose of this study is to test how the different proxies predict the real sulphuric acid concentration in four different datasets and to widen the study made by Petäjä et al. (2009) for EUCAARI 2007 campaign data. Three campaign datasets, measured in Hyytiälä, Finland, in 2003 and 2007 and in San Pietro Capofiume, Italy in 2009, and a long term data measured in Hohenpeissenberg, Germany within years 1998-2000 (Birmili et al., 2003) were used.

A proxy for sulphuric acid concentration is based on chemical reaction SO_2+OH→H_2SO_4+HO_2. Integrating the differential equation for sulphuric acid concentration $d[H_2SO_4]/dt = k\cdot[OH]\cdot[SO_2]-[H_2SO_4]\cdot CS$, where CS is condensation sink and$k$ is temperature dependent reaction constant gives the sulphuric acid concentration at given time. To simplify the problem, it can be assumed that the H_2SO_4production is in steady-state, i.e. $d[H_2SO_4]/dt=0$, which leads to a proxy function given by
$[H_2SO_4]=k\cdot[OH]\cdot[SO_2]\cdot CS^{-1}$. Measurements show that OH concentration is highly correlated with intensity of solar radiation, and if [OH] is not available, like in some of the datasets we are using, it is possible to use a proxy given by $[H_2SO_4]=k\cdot Radiation\cdot[SO_2]\cdot CS^{-1}$.

A nonlinear fitting procedure was applied to all datasets, with a fit function given by
$[H_2SO_4]=a\cdot Radiation^b\cdot[SO_2]^c\cdot CS^d$, resulting in a power c for SO_2 concentration of approximately 0.5. The power b for radiation was near to unity for all datasets and the power d for condensation sink could be fixed to -1 without significant decrease in prediction ability of the proxy. A good prediction was attained with $[H_2SO_4]=a\cdot k\cdot Radiation\cdot[SO_2]^{0.5}\cdot CS^{-1}$ for all of the datasets, but for the Hyytiälä campaigns the prediction was better without the CS term. For the shorter campaign datasets the proxy explains 80-90% of the total variation of the measured sulphuric acid concentration but for the long term data from Hohenpeissenberg the prediction ability was not that high. This indicates that the change in atmospheric conditions caused by the change of the seasons has to be taken account in the analysis of the longer time series.

The reason for the better performance of proxies with square root of SO_2 can only be speculated, but it is possible that it has to do with the somewhat unrealistic steady-state approximation or the SO_2concentration acts also as an indicator for some other parameter involved in the process but not present in our data.

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