Atmos. Chem. Phys. Discuss., 8, S12362–S12366, 2009
www.atmos-chem-phys-discuss.net/8/S12362/2009/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Sulfuric acid and OH concentrations in a boreal forest site" *by* T. Petäjä et al.

T. Petäjä et al.

Received and published: 14 August 2009

The authors gratefully acknowledge the referee for critical comments, which improved the manuscript considerably.

The article "Sulfuric acid and OH concentrations in a boreal forest site" by Petäjä et al. report on a three-month data set of H2SO4 and OH measurements at the Hyytiälä SMEAR station using the CIMS technique, and its comparison with the corresponding modelled species. The authors provide several proxy calculations of the sulphuric acid concentrations based on measured SO2, solar radiation and aerosol size distributions. Because sulphuric acid is a trace gas which is delicate to measure, it is important to know if proxies can adequately replace the actual measurements when not available. Hence, the scientific topic of this paper addresses important questions which fit into the scope of Atmospheric Chemistry and Physics. However, it is not clear whether it

presents novel concepts, ideas or data.

The authors do not give proper credit to related work and clearly indicate their own new/original contribution. While these are not the first H2SO4 measurements at the SMEAR station, they seem to cover the longest period of measurements. Of course, this can not be the only reason for a high level scientific publication.

The aims are now more clearly presented in the introduction with the relevant credits given to the previous work. The key objective of this study was to develop physically feasible proxies for sulphuric acid based on the long measurement time series.

Therefore, I highly recommend to the authors to clearly specify how new their analysis is. Is it the first time that such a proxy calculation is performed from H2SO4 measurements? If not, how different the conclusions are from previous measurements at the same place or different places?

Correct. Proxy calculations have been performed in many studies, including e.g. Hohenpeissenberg meteorological observatory. We added the following paragraph to the end of the introduction.

The question of the variability of the k1, k2 and k3 empirical factors with space is of high relevance, in order to enable the reader to use them with more or less confidence (in case they do not have any possibility to measure it directly).

The scaling factors for the different proxies were revisited. See comments below.

The scientific approach and applied method seem to be valid although a few precisions should be mentioned before publication. The authors state that k2 and k3 are calculated based on the ratios between the proxy and observed sulphuric acid concentrations (p 20202). Later, they state that only the 09:00-15:00 LT data was used to scale the k2 and k3, in order to better fit the maximum daily concentrations. Therefore, I do not understand how the proxies can over-estimate the sulphuric acid daily maxi-

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mum concentration (page 20203). Does it mean that the "shape" of the proxy diurnal variation does not follow the shape of the real sulphuric acid concentration? Figure 3, the correlation are this time performed with the 06:00 to 18:00 data. Is this the main reason for the discrepancy to the 1:1 line?

The proxy scaling factors were revisited and the discrepancies discussed in more detail. The overall shapes of the diurnal cycles of the proxy and measured sulphuric acid concentrations follow each other as presented in Figure 8 of the manuscript.

Page 20204: do the authors have any explanation why the modelled H2SO4 correlate better with the measurements when the whole data set is considered, compared to when only the daytime concentrations are considered?

More data analysis was done related to the measured and modelled sulphuric acid concentrations. Instead of utilizing standard least squares fitting, a bi-variate fitting was used (e.g. Cantrell, 2008). This method assumes that there are errors in both x- and y-directions, whereas the standard least squares fitting assumes errors only in the x-direction. This is more feasible since there are errors in both the measurements and in the modelled concentrations.

Figure 4 was replaced with a new figure, which presents the bi-variate fits for day-night separated data. Clearly the day-time concentrations are larger as compared to the night-time concentrations and the model agrees well with the measurements with a slope close to unity. In the night-time the model seems to under-estimate the sulphuric acid concentrations.

Technical comments:

Page 20196: Experimental setup The authors should mention the dates of the measurement campaign, even if it is stated in the abstract and it can be found from the figures.

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The measurement period was already presented in section 2.1, first paragraph, but now it is moved already to the section 2 while discussing the EUCAARI measurement campaign in general.

Page 20197: ..From the main inlet flow a sample (typically 10 lpm) is extracted via a thin walled 1.27 cm ... Is the extraction performed perpendicularly to the main inlet?

There was an error in the inlet diameter. It is 1.91 cm instead of 1.27 cm. The extraction is performed coaxially. This is now mentioned in the text.

Page 20199 How were losses evaluated? Were calibrations performed by taking into account these losses in the main and secondary inlet?

The calibrations take into account the losses in the secondary inlet and within the CIMS itself. The losses in the primary inlet are considered negligible.

Page 20202 line 10: .. typical of Hytiälä

Corrected.

Page 20203 line 10: Medians of the daily maximum...The median of the measured sulphuric

Corrected.

Page 20206 line 17: The observation period is the longest period in Hyytiälä, over which sulphuric acid has been measured.

Corrected.

Page 20207 line 6: ...since it is the longest available sulfuric acid measurement data base in Boreal environment.

Corrected.

References

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Cantrell, C. A. (2008) Technical Note: Review of methods for linear leastsquares fitting of data and application to atmospheric chemistry problems, Atmos. Chem, Phys., 8, 54778211;5487.

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