

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

T. Petäjä et al.

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

General comments: This paper reports an interesting data set. However, the data analysis is largely missing a clear presentation and a diligent and in-depth discussion, a proper comparison with similar studies published by other research groups, and a thorough evaluation of the experimental methods. A major revision is required before final publication can be recommended.

Major revision is applied to the results section of this paper considering all the referee comments. Point-by-point replies are presented below.

Specific comments: The authors fail to refer to previously published OH and H₂SO₄

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long-term measurements at Hohenpeissenberg station (e.g., Rohrer and Berresheim, Nature, 442, 184-187, 2006; Berresheim et al., Int. J. Mass Spec., 202, 91-109, 2000) which discussed in detail the validity of proxy variables such as J(O1D) and UV-B and the precision and accuracy of the experimental technique, respectively.

The introduction was amended and the previous work is now cited, both in terms of long-term measurements presented in Rohrer and Berresheim (2006) as well as proper credit is given to previous work presenting sulphuric acid proxies in Berresheim et al. 2000 as well as in Weber et al. 1997.

No J(O1D) measurements were made in the present study, and global radiation and other parameters used here can only be relatively weak proxies for OH, and /or H₂SO₄. Correlations with UV-B need to be clearly discussed in comparison with other studies previously published.

The authors agree that J(O1D) would provide a better source term in conjunction with the measured precursors in comparison with UV-B or global radiation. The UV-B and global radiation are, however, more commonly measured parameter and thus it was selected. Also in a cloud free situation the J(O1D) and global radiation have a similar diurnal cycle (e.g. Handisides et al. 2003)

Figure 1 is hard to read, Figure 2 does not make much sense, at least with respect to night-time data (no radiation). Figures 3, 4, and 6 are all log-log formats obscuring much of the information in the data. Regressions should instead or in addition be shown in detail within particular linear scales. The authors should clearly state how the correlation coefficients were determined. Are they derived from log-log or exponential regression of the data?

Figure 1 is enhanced. The scaling factors were derived matching the measured and the proxy data. The Williamson-York method (e.g. Cantrell, 2008) was used in the linear fits, which assumes errors both in the x and y-directions.

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It is not clear which CIMS instrument was used in this study. Since each prototype has its own precision and accuracy of measuring OH and H₂SO₄, this needs to be done systematically and in detail in this study, unless it has been described previously. I assume this was not the same instrument as used by Tanner et al. (1997), and corresponding estimates should not be adopted from previous versions of CIMS instruments.

More details also need to be reported on the operational stability, especially calibration factors. Background OH signal is not always identical with ambient H₂SO₄ signal, this should be examined. SO₂ measurements also need to be presented or at least discussed. How many data were below detection limit? The caption of Figure 6 states the same detection limit for OH as for H₂SO₄. This must be wrong! The authors should clearly state the detection limits for both compounds based on standard deviation and signal integration time (see also Figure 9 and section 2.1.1). The typical DL for OH of the CIMS instrument is 3e5 molec/cc for 5 min, for H₂SO₄ it is about one order of magnitude lower.

The ground-based CIMS instrument used in this study is the instrument described in Mauldin et al. 2001. As the geometries of all of the OH, H₂SO₄ CIMS instruments used by this group are the same, it is reasonable to assume that the precision and accuracy are of the same level. As discussed in Mauldin et al. 1999, OH is measured by first converting it to H₂SO₄ and then subsequently measuring the H₂SO₄. Isotopically labeled ³⁴SO₂ is added to the sample flow to convert the OH into H³⁴SO₄ thus allowing for the measurement of OH and ambient H₂SO₄ simultaneously. The detection limits of OH and H₂SO₄ are the same as the same integration time was used for both during the 30 sec measurement time used during the study. The 3e5 molec/cc LOD reported is for a single 30 sec measurement. By averaging these values over 5 minute the LOD drops to 5e4 molec/cc. The calculated calibration coefficient during this study was (4.7 +/- 0.5)e9 molec/cc 2 sigma.

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Concerning the background measurements, the referee is correct. There are ambient compounds other than OH (e.g. Criegee radicals, etc) which can also oxidize SO₂ into H₂SO₄. As discussed in Mauldin et al. 1999, 2001, the presence of these compounds is accounted for by the measurement of an "OH Background". This background is the H₃SO₄ (isotopic H₂SO₄ = OH) signal measured with propane added to remove all OH. This background value does change over time, albeit slowly, due to changes in the ambient concentrations of these other oxidants. A more strict analysis of the OH background measurement and the identities of these compounds while of interest, is left to a future study.

Since Hyytiälä is a clean background site, the SO₂ concentrations are low, very often close to the detection limit of the SO₂-analyzer. The UV- and global radiation already limits the use of the proxies to day-time. The low SO₂ concentrations further limit the data set, but as can be seen from Figure 3, the span of proxy concentrations is covers the measured sulphuric acid concentration range.

A description of the OH model is missing and should be included along with measured ranges of NO_x and VOC concentrations. In section 3.1 no discussion is given regarding possible mechanisms of H₂SO₄ generation at nighttime (which may also proceed at daytime) as previously mentioned in the above literature (e.g., peroxy radical or Criegee radical reactions with SO₂).

The model is described in Boy et al. 2005, more details are now added to the text.

The re-analysis of the data led to completely rewritten results and discussion sections. Based on existing literature, more discussion is provided with respect to comparison between the Hohenpeissenberg and Hyytiälä. The authors feel that an in-depth analysis of the night-time chemistry as well as further comparison between the measurement sites should be left for a future study.

Estimated nighttime OH production rates are not presented. Measured OH concentra-

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tions (section 3.2) are relatively low compared to, e.g., Hohenpeissenberg (latitude ?) and no seasonal cycle seems to be apparent. A discussion of both points should be included. Hohenpeissenberg should not be characterized as "more polluted" (section 3.3), rather a comparative discussion of NO_x, SO₂, VOC, UV-B and ozone data time series from both stations should be made and included in the OH model with reference to the previous publications by the Hohenpeissenberg group given above. Just quoting values and assuming a qualitative difference in pollution levels is unacceptable.

The model description was extended. The results in comparison with Hohenpeissenberg are now discussed in more detail. See above.

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