

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.

This paper presents measurements of H₂SO₄ and OH concentrations at a boreal forest site in Finland using Chemical Ionization Mass Spectrometry, a previously established technique for the measurement of these compounds. The main focus of the paper appears to be the testing of several proxies for sulfuric acid concentrations and the evaluation of a chemical for both sulphuric acid and OH concentrations. This is an important area of research due to the importance of gas phase sulfuric acid in atmospheric particle formation. The data set presented in the paper is interesting and worthy of eventual publication in ACP. I do have several comments that the authors should take into consideration in their revisions of the manuscript.

1) The authors state that the nominal detection limit for sulfuric acid is 5×10^4 cm⁻³ on page 20198. However, the manuscript does not state the minimum detectable OH concentration, although it appears from the data presented that the precision of the instrument for OH measurements is similar to that for H₂SO₄. However, the authors should clarify the limit of detection for OH during the campaign.

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 3×10^5 molec/cc LOD reported is for a single 30 sec measurement. By averaging these values over 5 minute the LOD drops to 5×10^4 molec/cc.

Are the nighttime concentrations of OH significant?

Considerable amount of new data analysis was conducted to examine the night-time OH as well as sulphuric acid concentrations. The results are presented in new Figures 4 and 8 for sulphuric and OH, respectively.

Typically the measured night-time OH stayed under 1×10^5 molec cm⁻⁵. When the measured OH during night-time was larger than approx 7×10^4 molec cm⁻³, the model under-estimated the OH concentrations whereas typically the model tended to over-estimated the OH (Figure 8).

The time interval of the measurements shown in Figures 1 and 5 should also be clarified, although it appears to be 5-min integrations.

Clarified.

2) There is no discussion of the pseudo-steady state model used for the calculation of sulfuric acid and OH concentrations. This is especially important for the interpretation of the modeled OH concentrations. What reactions were included in the model?

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

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3) Similar to previous studies, the modeled OH concentration tend to overestimate the measured concentrations, and the authors claim that the discrepancy is likely due to missing VOC chemistry in their model. However, there is little information given to put this discrepancy into context.

What was the range of VOC and NO_x concentrations observed during the campaign?

The VOC and NO_x variability in is now discussed in a general manner in the Results and Discussion section.

The measured/modelled discrepancy appears to be greater at higher temperatures, and the authors suggest that increased biogenic VOC emissions at higher temperatures might explain the discrepancy. However, as mentioned above, there is little discussion to support this statement. What type of VOCs were measured during the campaign, what were the range of individual concentrations, and how did these concentrations change with temperature? The paper would benefit from an expanded discussion of the measurement/model discrepancies.

The authors agree with this comment. The discussion is expanded with the taking into account typical concentration range in Hyytiälä. Since this is scientifically really an important, the authors feel that a more detailed analysis is worth a follow-up paper, where the PTR-MS derived VOC data and CIMS sulfuric acid and OH are analyzed.

4) On page 20203, the authors state that the sulfuric acid proxies relying on the measured OH concentrations underestimated the sulfuric acid concentrations by a factor of two, while the proxies relying on radiation tend to overestimate the sulfuric acid concentration. This is not clear to me from Figure 3, where it appears that the UV-B proxy also underestimates the sulfuric acid concentration based on the overall fit to the data set, although it does appear to overestimate at higher sulfuric acid concentrations.

Similarly, the authors state on page 20204 that all three proxies tend to overestimate

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the measured sulfuric acid concentration on average, while it appears from Figure 3 that that two of the three tend to underestimate the measured concentrations on average. This should be clarified in the revised manuscript.

Clarified.

References

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