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Atmospheric
Chemistry
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Discussions

Interactive comment on "Particle concentration and flux dynamics in the atmospheric boundary layer as the indicator of formation mechanism" *by* J. Lauros et al.

Anonymous Referee #1

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The manuscript presents a 1D modelling study of new particle formation at Hyytiälä, Finland, and compares many of the simulated results to measurements. The main conclusions of the manuscript are that 1) based on measurements of particle vertical profiles, sulphuric acid nucleation alone cannot be responsible for nucleation in Hyytiälä and that organic nucleation from monoterpene oxidation is likely to explain the observed events, and 2) understanding the mixing characteristics of the atmosphere is important when quantifying new particle formation in the troposphere.

I find these two results interesting to the atmospheric nucleation community. However, I am not fully convinced that the current simulations warrant especially the first conclusion to be made. Therefore, I recommend that the manuscript can be accepted for publication if the following comments are carefully addressed by the authors.

Major comments:

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1) Although recent lab and field evidence suggests that organics (terpenes, amines?) very likely play a role in atmospheric nucleation, the presented simulations as such do not warrant very strong conclusions about the actual nucleation mechanism.

The modeled nucleation rates and profiles are likely to be highly sensitive to several model features and chosen parameters: accuracy of the simulated vertical profiles of the vapours (which hasn't been discussed in detail), nucleation mechanisms and prefactors (which are deduced from >3nm particles and may not be very accurate), assumptions made about the condensation of organics to sub-3nm clusters ("nano-Köhler" is not a truly validated mechanism and its effects are dependent on chosen parameters), or fraction and properties of monoterpene oxidation products taking part in nucleation, etc. In addition, should the nucleating organics be produced not in the first but second or higher generation reactions, the time after emission they were formed could increase notably. This means that they could be formed in or transported to the free troposphere in higher abundance than assumed here. This could be an issue especially combined to the fact that, as the authors acknowledge, the model underestimates mixing above the boundary layer.

It is likely that despite these uncertainties, kinetic nucleation cannot explain the observed vertical profile. However, it is very possible that the atmospheric nucleation mechanism is different from the organic one suggested in this study. Therefore, to strengthen their case, the authors should conduct a set of sensitivity simulations, in which they vary the relevant nucleation parameters for both kinetic and organic nucleation within the whole uncertainty range. Some sensitivity runs have apparently already been made but they are not presented in the manuscript. The varied parameters

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should include at least the nucleation prefactors; organic condensation assumptions (e.g., nano-Köhler vs. nonvolatile vs. not condensing below 3 nm); fraction of organics from monoterpenes that can nucleate and condense; some way to mimic the possibility that the organics are second or higher generation reaction products (e.g. slow down monoterpene oxidation by adjusting oxidation rate coefficients).

The results from the sensitivity runs could be presented e.g. in Figure 3 as a shading around the current "basecase" simulations.

Furthermore, the uncertainties arising from model features that cannot be easily controlled in sensitivity simulations (such as possible problems with vertical profiles of vapour concentrations) should be discussed in the text. Given the uncertainties, conclusions about the nucleation mechanism should also be toned down (e.g. "cannot be responsible", "allows to conclude that — is responsible for particle formation").

2) The manuscript requires a careful language revision. While the text is for the most part relatively straightforward to follow, there are unsuitable choices of vocabulary and phrasing in several places as well as numerous articles missing (too many to be listed here). The punctuation should also be improved for clarity.

Minor comments:

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3) I find the term "organic" nucleation misleading since the mechanism includes also sulphuric acid. Calling it e.g. organic-sulphuric acid nucleation would be clearer.

4) Are the two prefactors for organic nucleation needed or could they be combined for clarity (as has been done with kinetic nucleation)?

5) Explain already in section 3.3 that only a certain fraction of monoterpene products take part in nucleation.

6) Are condensing vapours formed in reactions of other organics than monoterpenes?

Are the condensing vapours from monoterpene oxidation the same as the nucleating ones? If so, it doesn't make much sense to assume that the products are non-volatile enough to nucleate but still follow nano-Köhler mechanism for condensation.

7) How is the model run initialized (e.g. spin-up)? How were the initial vertical profiles of vapour concentrations determined (e.g. SO2, H2SO4, VOCs)? How well do they compare throughout the simulation to measurements at this or similar sites? Why is H2SO4 higher in the FT than in the BL?

8) There are several lab-based studies that indicate organic OH reactions (rather than O3 reactions) as the source of low-volatile, nucleating compounds (e.g. Hao et al., 2009, ACP). These papers should be cited in section 4.2.2.

9) p. 20015, lines 12-15: observations of which properties?

10) p. 20016, first full paragraph: I cannot follow what is meant here. Please reformulate.

11) p. 20016, lines 17-19: In the model, dilution happens after the onset of nucleation. However, it is not evident in the measurements in Figure 4. Furthermore, the clear deviations from measurements in Figure 4 should be briefly discussed in the text.

12) The modeled particle fluxes in section 4.3.1 should be compared against the size-segregated particle flux measurements made at the site.

13) p. 20017, lines 11-12: please reformulate "new particles achieve larger sizes later than smallest sizes".

14) Conclusions: The segment on deposition should be shortened (now 40% of conclusions) to better correspond to its importance in the results section. Some of the material could be moved to section 4.3.2

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