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Atmospheric
Chemistry
and Physics
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.

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We thank the reviewer for valuable comments.

The study aims to evaluate the kinetic sulphuric acid and organic-induced nucleation theories. It is obvious, that the model simulations still depend on several unknown parameters. We believe that the readers are able to see the limitations and the hypothetical nature of our study. However, the simulations indicate that kinetic sulphuric acid nucleation cannot be responsible for new particle formation (even if we vary several model parameters) while organic-induced nucleation is a possible candidate.

We aim to present one possible organic-induced formation path.

Both reviewers notify, that the higher generation reaction products of organics are more volatile than the first generation products. Therefore we have multiplied the organic reaction rates by 0.5. We see that this has imporoved the consistence with the observations (Fig. 3).

We have improved the language of the manuscript.

1)...Therefore, to strengthen their case, the authors should conduct a set of sensitivity 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.

As the simulated particle formation is based on several unknown parameters, several sensitivity tests have been carried out. Now we have presented some results from sensitivity simulations in Fig. 3 and write: “The concentration gradient between the ABL and the residual layer decreases if the nucleating and condensing reaction products of organics are higher generation products, in other words, if the nucleating organic products are formed slower than the first order products (Fig. 3a). However, this does not affect the particle concentration above the residual layer in the free troposphere. We have tested the model variables, e.g., different condensing fraction of organics, different prefactors for nucleation, possibility that organics do not condense on particles below 3 nm or organics are nonvolatile. As we can expect, the number concentration of particles (> 10 nm) increases, if a reduced amount of organics is able to condense on particles. Also the gradient between the ABL and the residual layer seems to be stronger in this case. All tested cases produce a surface event or a vertical profile (Fig. 3b) which is less consistent with the observations than our basic case. In the case of kinetic nucleation, the particle concentration in the free troposphere is overestimated without an exception."

We have written about SO_2 profile, which is the most essential vapour in our study: "…kinetic nucleation cannot be the prime particle formation mechanism in the lower troposphere at the boreal forest site. The conclusion does not change even if we assume a uniform SO_2 distribution only within the ABL, and the concentration above the ABL is set to 0.5 of the observed value. "

We have attached two updated figures (Fig. 3 in the manuscript): Observed and simulated particle number concentration $N_{>10\ \mathrm{nm}}$ on 13 March 2006 when the particles are formed by organic and kinetic nucleation. The ABL height is shown by black dotted horizontal line. a) The shaded areas show the range of concentration when reaction rate of organics is multiplied by 0.2–1. b) The shaded areas show the range of particle concentration when 2–10 % of organic vapours can condense on particles (red). Profile when i) organics cannot condensate on particles below 3 nm (cyan), ii) organics are nonvolatile (blue) and iii) organics are nonvolatile and $P = 10^{-3}$ cm^{-3} (green).

2) 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.

We agree and have replaced the term organic nucleation with organic-sulphuric acid nucleation or organic-induced nucleation.

3) Are the two prefactors for organic nucleation needed or could they be combined for

clarity (as has been done with kinetic nucleation)?

P is a constant, but ν is presented as a function of temperature and pressure and therefore it depends on altitude, even though weakly. We have parameterized the nucleation rate in the model as a function of these two variables and therefore we prefer the presented form.

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

We moved from section 4.2.2 to section 3.3: "In the presented simulations we have assumed that 5 % of organic oxidation products are able to condense on particles. The value has led to good agreement with observed growth rates in earlier (Boy et al., 2006) and present study."

5) 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.

The nucleating and condensing vapours are simulated using similar chemical paths, in other words the same model variable. Even if we estimate nucleating and condensing (nano-Köhler) vapour concentrations using the same model variable, the actual vapour components can differ from each other, e.g. vapours may be different generation organics if the concentrations do not differ from each other drastically. In addition, comparison between formation mechanisms (Fig. 2c and 2d) showed that the nano-Köhler growth was not able to regulate particle formation and therefore it was not a significant step in our particle formation simulations. As the vapours are not strictly defined and the nano-Köhler step is insignificant in our study, we use the same organic vapour for nucleation and nano-Köhler growth.

6) How is the model run initialized (e.g. spin-up)? How were the initial vertical profiles of vapour concentrations determined (e.g. SO_2, H_2SO_4, 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?

We run the meteorology scheme 11 days from the beginning of the month. So, the meteorology should be well adjusted to forcing. We write: "The initial vapour concentrations of most species, especially the organic reaction products, were set to zero at the start of the model run." Now we continue, "The concentration of reactions products of organics achieve steady state in few hours after the onset of emissions", and have reformulated: "For several other gases like CO, SO_2, NO, NO_x and ozone, measurements from the SMEAR II station were used as inputs through the model simulation duration. The vertical profiles of input gases were set to be uniform. "

We do not have H_2SO_4 measurements for March 2006 but we mention now: "Sulphuric acid was calculated from oxidation of observed SO_2, and organic vapours originated from the calculated canopy emissions. H_2SO_4 was not measured at the SMEAR II station on March 2006 but the simulated concentrations (10^4–10^7 cm^{-3}) are consistent with observations on spring 2007 (Petäjä et al., 2009)." H_2SO_4 concentration is higher above the ABL than in the ABL, because the simulated particle concentration and thereby concentration sink is higher at the surface than in the FT.

7) 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.

Added: "Recent laboratory experiments (Hao et al., 2009) indicate that reaction products from OH oxidation of organics are more probable to participate nucleation than reactions products from O_3 oxidation."

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

Reformulated: "The value has led to good agreement e.g. with observed growth rate in an earlier (Boy et al., 2006) and present study."

9) 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.

We have rewritten and continued discussion:"Dilution cannot be positively identified in our measurements because he observed particle concentrations of 25–100 and 100–1000 nm particles vary in a short time scale. The concentrations decrease simultaneously before the onset of particle formation only on 13 March (Fig. 4). The simulations show more clearly dilution at the top of the ABL followed by a weaker dilution effect at the surface. The simulated dilutions occur at noon after the onset of new particle formation and therefore the decreasing sink, due to dilution of background aerosol concentration, cannot activate particle formation in our simulation. The simulated number concentration of the largest particles follows well the trend of measurements but the short scale variation cannot be captured (Fig. 4c). The simulated concentration of the smallest particles starts to increase simultaneously with the measured concentration but the growth is slightly weaker than the measurements indicate (Fig. 4a,b). The early increase of the observed Aitken mode concentration on 13 March results from the new particle formation event on previous day (see Fig. 2a).“

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

Size-segragated particle flux measurements have very large random uncertainty and does not allow for direct comparison with model results. However, we have compared the simulated deposition velocities with observed, characteristic, median values and now we continue: “We calculated the total removal flux of particles due to deposition in the vegetational column. Dividing the total flux by the particle concentration above the canopy we can compare the results with observed deposition velocities. In the simulations the median normalised deposition velocity v_d/u_* is 8×10^{-3} for 10 nm particles and the minimum 6×10^{-4} is achieved around 140 nm. The results are consistent with observations even if the values are slightly smaller than the observed median values (Grönholm et al., 2007; Pryor et al., 2008).”

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

Now we write: “On afternoon, the flux of 3–6 nm particles turns downwards before 3–25 nm particle flux. This can be understood as the number concentration of 6–25 nm particles increases near the surface still after 3–6 particles have achieved the maximum concentration. In other words, due to favourable particle growth at the surface, the vertical distribution of 3–25 nm particles evens out slower and the flux continues upwards longer than for the smallest studied size range.”

12) 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

We removed following sentences: “Petroff et al. (2008) showed that deposition of Aitken mode particles is mainly controlled by Brownian diffusion. The simulated wind velocity inside canopy was only up to few meters per second which decreases especially influence of interception of largest particles. Therefore deposition as particle sink inside forest affected mainly nucleation mode particles.”

We reformulated: “Deposition affected mostly particle concentration near the surface, and especially concentration of the smallest particles, but ignoring the deposition process did not change particle fluxes substantially.”

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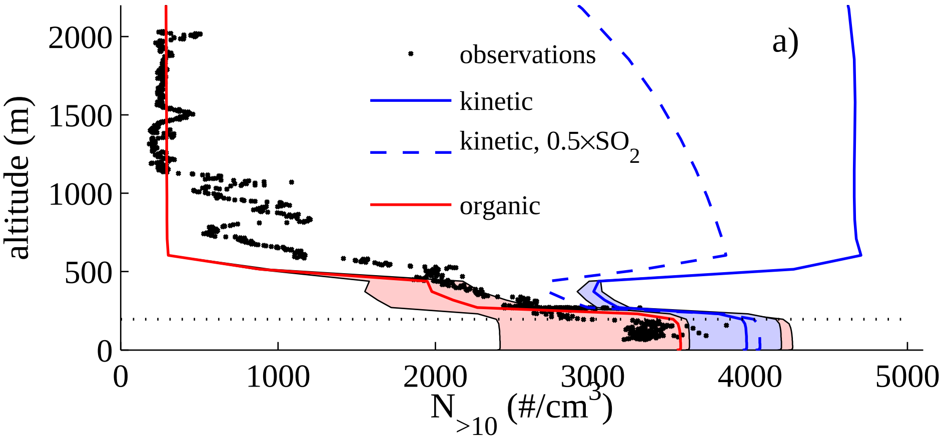

Fig. 1. Fig. 3 in the manuscript. See the answer to 1).

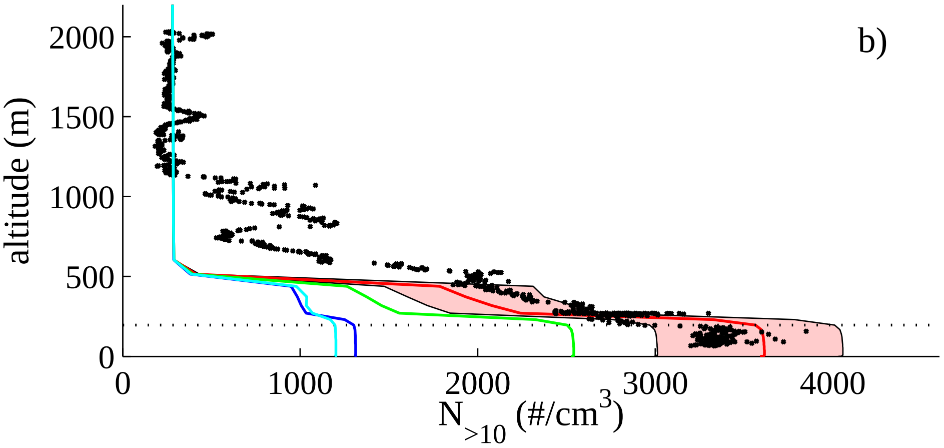

Fig. 2. Fig. 3 in the manuscript. See the answer to 1).