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Interactive comment on “New insights into nocturnal nucleation” *by* I. K. Ortega et al.

I. K. Ortega et al.

ismael.ortegacolomer@helsinki.fi

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We would like to thank the referee for his useful comments; certainly they help us to improve the quality of the manuscript. Please find below a detailed reply to these comments:

1) The introduction and conclusions should reflect that the new result of this study is not so much the fact that monoterpenes can cause nocturnal nucleation events (studies showing nucleation from ozonolysis of monoterpenes at atmospherically relevant concentrations are likely available in the literature). Instead one main achievement of this study is that the conditions, i.e. time dependence of ozone, monoterpene and condensation sink concentration, which influence the resulting nucleation type are probed and analyzed in a more systematic and quantitative way than previously available. In view of this fact it would also be desirable to have these findings emphasized

by e.g. summarizing the boundary conditions to a certain type of nucleation event for each nucleation type in tabular or graphical form. Such a scheme may then even be used to put the results from these laboratory experiments further in atmospheric context regarding the questions why a certain nucleation type is most favourable in the nocturnal atmosphere and why Tumbarumba is so favourable for nocturnal nucleation.

We have re-written the paragraph defining the overall and more specific goals of this manuscript (the last paragraph in the introduction), in order to bring the goals more in line with the suggestions given by the reviewer above. The suggestion of summarizing the boundary conditions for each nucleation type in tabular or graphical form is very good one but, unfortunately, with do not have enough measurement data to provide all the required boundary conditions. We have, however, modified the discussion in section 3.2.1 to discuss the conditions leading to different even types in more detail, and to explain why two of the five event types mentioned in Figure 7 were not encountered in our experiments. What it comes to Tumbarumba, very few data are available regarding ozone and organic concentrations there, so we do have immediate answer on why these kind of nocturnal events are so pronounced in there. Again, we have reformulated our goals bring up that our main emphasis is to get new insight into overall characteristics of nocturnal nucleation event, not just to explain our observations in Tumbarumba.

2) The following statement is made on p. 31331, l. 22-26: “This ozone trigger level was directly related with oxidation rates (Calogirou et al., 1998): monoterpenes having a higher oxidation rate required a smaller ozone concentration for initiating an event and vice versa. This kind of pattern points to the oxidation products of the monoterpenes being responsible for the observed events.”, And it is stated on p. 31332, l. 16-19: “Like with the ozone trigger level, this time difference seemed to correlate with the monoterpene oxidation rate, with smaller time differences observed for monoterpenes having higher oxidation rates.” I wonder whether this simple reduction on “monoterpene oxidation rates” is an oversimpliïňĄcation. Simply speaking I would expect that

the concentrations of sulphuric acid and nucleating organic species both show up in the nucleation rate. The temporal evolution of the sulfuric acid concentration differs substantially between the experiments (Fig. 9), which will influence the threshold ozone concentration for nucleation onset. Furthermore, the concentration of the nucleating organic species at the onset of nucleation will depend on the product of monoterpene precursor times ozone integrated over time starting from the beginning of the experiment, if the losses of the nucleating organic species are negligible before nucleation onset (not to speak of the fact that the subset of nucleating ozonolysis reaction products may differ between different precursors). Figure 1 shows that the monoterpene concentrations differed substantially between the experiments. And how does it look like with reproducibility of the experiments? Only one set 1 experiment is shown for each precursor (even though more might be available). Some more discussion is certainly needed in this context.

The referee has raised many interesting points regarding the ozone trigger statement. We agree that the discussion, as presented in the paper, was an oversimplification. We have entirely rewritten the text starting from line 14 on page 31 331 and continuing up the line 19 on page 31332 in section 3.1. The text now reads:

“The most interesting experiments turned out to be the ones having an initially low ozone concentration that then increased with time (Set 1, see Tables 1 and 2). In these experiments, monoterpenes were introduced into the chamber using the direct method when the ozone concentration was about 6–8 ppb. Figure 1 shows the time evolution of the concentrations of the total particle number, ozone and monoterpenes during the experiments. Formation of new particles started earlier for monoterpenes having higher reaction rates with ozone (for the reaction rates, see Calogirou et al., 1998), the minimum ozone level for nucleation to take place being 10 ppb for limonene, 15 ppb for alpha-pinene and 19 ppb for 3-carene. Figures 2, 3 and 4 show the number size distributions of particles and ions in the experiments. The duration and shape of the nucleation events produced by different monoterpenes were quite different, as were also the particle formation and growth rates and maximum total number concentrations newly-formed particles (Table 3). Of the three experiments, that with limonene (carene) had the highest (lowest) formation rate of 2-nm particles, the highest (lowest) total particle number concentration resulting from nucleation, and the shortest (longest) time difference between the introduction of a monoterpene into the chamber and the beginning of the nucleation event. The limonene experiment showed a relatively high particle growth rate (GR) in all the size classes from <3 to 25 nm, whereas in the alpha-pinene experiment the GR increased strongly with the increasing particle diameter. The carene experiment had the lowest overall GR of the three experiments. In the case of alpha-pinene (Figure 2), we kept the organic source in the chamber, which produced a continuous event after the strong initial event, and this latter event lasted as long as the alpha-pinene source was in the chamber. Daytime atmospheric nucleation tends to be driven by photochemistry and resulting sulfuric acid production (Kerminen et al., 2010; Sipilä et al., 2010). The Set 1 experiments discussed above confirm the important role of ozone and associated monoterpene oxidation in night-time nucleation taking place under dark conditions. Unfortunately, our experiments tell little about the actual nucleation mechanism or identify of the nucleating compounds. It is quite possible that nucleation in the chamber was affected not only by the organic compounds produced from monoterpene oxidation, but also by sulphuric acid produced by the reaction of sulphur dioxide with the OH radical produced inside the chamber (see section 3.5). Furthermore, reaction of ozone with nitrogen dioxide is expected to produce nitrate radicals, the reaction of which with monoterpenes might also contributed to nucleation and particle growth. The dominance of negative ions over positive ones in the observed events is an indication of the important role of acids (that will be charged negatively) in the nucleation process. This issue will be investigated further in section 3.4.”

We also modified slightly the discussion in section 3.5, in which the results were further interpreted with help of MALTE model simulations, as well as our concluding remarks in section 4 (last paragraph).

3) p. 31333, Sect. 3.2 and Fig. 7: It is no quite clear whether the results presented here are from a new evaluation of previous field experiments or just a repetition of relevant information from a previous study. Please clarify and provide appropriate references.

The Tumbarumba experiments and analysis of nucleation events there have been presented in the publication by Suni et al (2008). Classification of nocturnal events, as presented in Figure 7, has not been published before in peer-reviewed scientific literature. We added a short note to the paper by Suni et al. in the beginning of section 3.2.

Minor comments

1) p. 31329, l. 22-23: "Some minimal changes to the KPP-produced code were preformed. For the OH-yield from the ozonolysis of the monoterpenes, we used the following values: 0.77 for alpha-pinene, 0.7 for limonene and 0.86 for carene. A comparison with the full MCM chemical mechanism for alpha-pinene gave a nearly perfect agreement for the simulated hydroxyl radical concentrations." - Was this adjustment solely a tweak introduced to tune the calculated OH-concentration in the simplified model to match those obtained using the full MCM chemical mechanism or was it done base one improved/alternative literature data? Please clarify and provide references if needed.

The values used are based on a publication by Aschman and co-workers. The text was revised as follows:

“Some minimal changes to the KPP-produced code were made. For the OH yield resulting from the ozonolysis of monoterpenes, we used the values of 0.77, 0.70 and 0.86 in case of alpha-pinene, limonene and carene, respectively, following the work by Aschman et al. (2002).”

2) p. 31329, l. 25-27: "In all other model runs, we only used the first reaction for the monoterpenes because the full reaction schemes for limonene and carene are not available on the MCM-website." - Is this simplification potentially critical for the

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outcome of the model calculations or can it still be expected to provide reliable results? Please elaborate further on this question.

The text was revised into the following form (see also our reponse to points 3 and 5 below):

“In all other model runs, only the first-order reaction products of monoterpenes were used, since the full reaction schemes for limonene and carene are not available on the MCM-website. Potential influences caused by this approximation on aerosol dynamics were compensated by varying the values of two semi-empirical parameters in model simulations, as described below.”

3) p. 31330, l. 13-16: "Therefore, in MALTE we varied the amount of condensable vapours from the monoterpene reaction products by a factor of 1–10 by using only the concentrations at each time step and set it to zero afterwards." - I don’t quite get this explanation.

The text following equation 2 was rewritten to make it more understandable for the readers. The sentence pointed out by the reviewer was changed into the form:

“Due to these complexities, we took a relatively simple approach to simulate the condensation growth caused by the organic compounds resulting from monoterpene oxidation in our MALTE simulations. We first determined the first-generation oxidation products of monoterpenes at each model time step, then selected condensable vapours from these products, and finally multiplied the amount of these vapours by a factor of 1–10 to take into account higher-order oxidation products contributing to the condensation growth.”

4) p. 31332, l. 23-27: Particle number concentrations obtained with set one and set two experiments are compared here. However, number concentrations of set two experiments don’t seem to be provided anywhere.

We have included an example of particle number concentration of a set two experiment in the text:

“for example, maximum particle number produced in limonene set 1 experiments was around 8500 per cubic centimeter (Fig. 1), while for limonene event presented in Fig. 5 (middle panel) the maximum was around 35000 per cubic centimeter.”

5) p. 31339, l. 16: The “A-coefficient” and “factor for condensation” should be explained in a bit more detail.

The text in section 3.5 was fully revised to make it more readable and understandable. See also our answer for the point 3 above.

6) Table 1/Fig. 1: An initial monoterpene concentration of 1.14E12 cm^{-3} is state in Table 1. However, this value is only reached after approximately 2 hours (Fig. 1).

The VOCs measurements were not continuous, a number of sample where taken rfom each experiments. the first measurements was taken always before introducing the VOCs in the chamber. We have realized that the way chosen to represent the VOCs was not clear enough, we have change Fig. 1 in order to improve the clarity. We also have realized that the X-scale is different for VOCs measurements is different to the other two panels. in the case of VOCs concentration, the reference time used was the time of the first VOCs measurement, while in the other two plots the reference time used was when the VOCs was introduced in the chamber. We have also change this to make the three plots comparable.

7) Figs. 2-5: Start of experiment should be indicated. Time axes could be changed to “time from the beginning of the experiment” as in Fig. 1.

We have included this change.

8) Figs. 2-6: It would be very useful to have the time series of ozone, monoterpene concentration and total particle number concentration in the same graph on a separate panel(s). Just to give one example out of many: The statement made on p. 31333,l. 16-18 cannot be followed by the reader without the additional information requested

here.

We have included those panels.

9) Fig. 5a: When does this experiment start before or after 12 a.m.? The chamber does not seem to be empty before 12 a.m. as stated in the text.

The experiment in figure 5a started at 14:57.

10) Fig. 5, all panels: Why are DMPS size distributions not shown? We decide to let the DMPS plots out just to make the figure look less messy. Also, the information provided by them is not very useful for our analysis.

Technical comments

p. 31325, l. 27: "... used an aerosol ..."

p. 31329, l. 11: this should possibly read "... were estimated using ..."

p. 31331, l. 14: "... turned out to be ..."

p. 31334, l. 14: “. . .Fig. 5, . . .”

p. 31337, l. 9: “. . .dimers. . .”

p. 31339, l. 21: “. . .on recently . . .”

We corrected all these typos, provided the sentences still existed in the revised manuscript.

Table 3: units should be provided for all rows

Units have been added to all rows.

Table 4: provide unit

The unit have been added to the table caption.

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