

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

M. Gysel (Referee)

martin.gysel@psi.ch

Received and published: 11 January 2012

General comment

New particle formation is an important process which is e.g. likely to have some influence on the number concentration of atmospheric cloud condensation nuclei. New particle formation typically occurs during daytime, but it has also been observed during night-time. This study combines chamber experiments with quantum chemical calculations and aerosol dynamics models to show how ozonolysis of different monoterpenes can explain different types of nocturnal nucleation events observed in the atmosphere. This topic is of relevance, the methods seem to be state-of-the art as far as I can judge and the manuscript is overall well written. Nevertheless I have a few major questions and some minor requests for clarification as detailed in the following.

Major comments

C14119

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.

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 oversimplification. 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

C14120

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.

3) p. 31333, Sect. 3.2 and Fig. 7: It is not 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.

Minor comments

p. 31329, l. 22-23: "Some minimal changes to the KPP-produced code were performed. 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 based on improved/alternative literature data? Please clarify and provide references if needed.

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

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.

C14121

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.

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

Table 1/Fig. 1: An initial monoterpene concentration of $1.14 \times 10^{12} \text{ cm}^{-3}$ is stated in Table 1. However, this value is only reached after approximately 2 hours (Fig. 1).

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.

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.

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

Fig. 5, all panels: Why are DMPS size distributions not shown?

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 ..."

C14122

Table 3: units should be provided for all rows

Table 4: provide units

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 31323, 2011.

C14123