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Atmospheric
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Discussions

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

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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:

Major comments:

1. The reactions of monoterpenes with ozone have already received considerable attention with regard to their reaction kinetics and reaction products during the past years. The highlight of this study is to focus on the role of these reactions in the nocturnal nucleation events, especially occurred at Tumbarumba in Australia. The authors may emphasize that, to which extent, your chamber experiments is relevant to the atmospheric conditions under which nocturnal nucleation events took place. A summary of atmospheric conditions, such as, relative humidity (RH), temperature, ozone concentration, preexisting particles concentration, and VOCs concentration during nocturnal nucleation events would be helpful if these data are available. I noted that temperature of set 1 experiment is around 30 C, and RH is below 30%. Actually, the reaction conditions are far away from the night-time atmospheric conditions.

In response to the comments above and the comments by the other reviewer, we have reformulated the goals of this investigation by re-writing the last paragraph of the Introduction section. Field observations of nocturnal nucleation event cover a broad range of atmospheric conditions but detailed information on such conditions is to a large extent lacking (e.g. VOC concentrations). We agree that the conditions in our chamber experiments are probably warmer and drier that the nocturnal conditions during most field observations. The issue of making further studies over a broader temperature and humidity range as applied here is now brought up in the last paragraph of the revised manuscript.

2. The discussions regarding the ozone trigger level are unclear. As shown in Fig. 1, the concentrations of monoterpenes are quite different for each experiment when the events started. This may also result in different ozone trigger level. In my understanding, the trigger levels are identified based on the particle number concentration. This means that the ozone trigger levels are not only related with the gas-phase reactions and also with the properties of the oxidation products in particle phase (such as their vapor pressure and concentrations). More explanations are needed here.

We agree, and the same point was raised also by the other reviewer. 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. NO3 radical is also an important night-time oxidant. Based on the reaction rate of NO3 and monoterpenes, the reaction occurs easier than ozonolysis of monoterpenes. The authors may explain why this study solely utilized the ozonolysis of monoterpenes to simulate the night-time nucleation events without taking into account NO3 radical. Or, there are some evidences that NO3 radical at Tumbarumba is not very important.

The main reasons for omitting the NO3 radical was that we had no means of controlling its concentration in our experiments NO3, nor measure its concentrations. We fully agree that NO3 is an important nighttime oxidant that should be at least discussed here. As a result, we modified the last paragraph of section 1, the third paragraph of section 3.1 and the last paragraph of section 4 to bring up the potential influence of NO3 radical in our experimental system and in the atmosphere.

Minor comments:

1. Fig. 1, it is better to use the same x-axis scale in all plots and mark the time when the nucleation events started.

We have re-scaled the events to make the x-axis match for all plots, additionally we have made changes to the origin of VOCs data as explained in the reply to referee 1.

2. Section 3.2, Line 10-14, Page 31333, the conclusions "The shape of these events were dependent on (i). . .., (ii)" are drawn based on ïňĄeld observations or chamber experiments? Please clarify it.

This conclusion is based on our chamber experiments. The sentence was modified as: “The shapes of the events seen in our experiments were dependent on i). . .”

3. Line 27-28, page 31332, any influence of particle loss in the chamber on the total particle number concentration?

We added the following text into end of section 2.3: “No attempt was made to take into account wall losses of particles and trace gases inside the chamber. While causing some bias in simulated total particle number concentrations, this approximation should not influence the main conclusions drawn from our results in this paper.”

4. Please correct the x-axis tick labels of Fig. 7 panel (d).

We corrected the label of Fig. 7

5. Table 2, what is the “b.d.”?

This means “below detection limit”. This has been clarified the table caption.

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