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Interactive Comment

# *Interactive comment on* "Photochemical production of aerosols from real plant emissions" *by* Th. F. Mentel et al.

Th. F. Mentel et al.

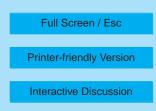
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The authors thank the referee for the helpful comments. All comments were taken into consideration and we tried to improve the manuscript according to these comments.

## **General comment:**

However, the manuscript will benefit greatly with some modifications. In particular, the parts "Experimental", "Results" and "Discussion" should be structured clearer to avoid redundant information.

We are aware that the manuscript has some length. As stated by the reviewer the experiments were performed by "use of novel experimental setup - the plant chamber facility at Forschungszentrum Jülich". In our opinion this required a more detailed





description of the setup, the reliability of the observations (modelling section), and the methodological approaches (class grouping, use of carbon mixing ratio, yields in a stirred batch reactor) to make our procedures transparent to the readers. On the other hand we tried strictly to separate observation and extraction of the results and discussion. This approach demands sometimes to use observations/results for the different tasks, e.g. to explain the performance of the setup, to establish a methodological procedure etc., and introduced a seeming redundancy. Following the comment of the referee, we re-read the paper and tried to minimize redundancies. The submitted manuscript is now improved in this respect. To ensure readability, we decided to keep the original structure of the manuscript.

### **Specific comments:**

(i) The authors stated in "Abstract" (line 14) and "Summary" (p. 3073, line 16) that OVOC oxidation may play an important role in new particle formation. However, in "Results" (p 3059, line 8 ff) they wrote: "we will focus analysis and discussion on the sum of monoterpenes + sesquiterpenes". I am confused on this.

The observed nucleation thresholds decrease with fraction of emitted OVOC. The nucleation efficiency (rate per ppbC) still correlates with the concentration of MT + SQT. Therefore it is possible that minute amounts of OVOC or their OH-oxidation products contribute to the formation of critical clusters in addition to the oxidation products of MT and SQT. Note that the particle formation rates are higher at larger OVOC fractions, but still nucleation rates depend linearly on the carbon mixing ratios of MT and SQT which indicate that subsequent growth of the freshly nucleated particles is governed by oxidation products of MT and SQT. This explains why MT and SQT are sufficient to explain most of the observations from the quantitative point of view. The presentation of our findings in terms of MT and SQT also helps for comparison with field observations, since measuring OVOC in the atmosphere is still in its infancy. In order to remove a possible overstatement regarding the role of OVOC we changed the abstract to:

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It was lowest for birch with the largest fraction of oxygenated VOC (OVOC) suggesting that OVOC may play a role in the nucleation process.

and the conclusions to:

While particle growth and volume formation is dominated by OH oxidation of MT and SQT, OVOC oxidation could play a role in natural nucleation processes.

(ii) The oxidation of sulfur compounds (e.g. SO2) is also known to play a major role in new particle formation in terpene oxidation experiments (Hoppel et al., J. Geophys. Res., 106, 27603, 2001). The authors stated: "this seems unlikely" (p. 3068, line 2). A series of equipments was used (Table 1) for the chemical analysis of gas phase species and particle properties. Was SO2 not measured to support this conclusion?

We thank the reviewer for this comment and we included Hoppel et al. in the introduction and in the discussion. We were not measuring SO2 routinely. The inlet air and reaction chamber was operated sulphur free, but we cannot exclude traces of H2S or organic sulfides in the plant emissions. From experiments with other plants we know that there may be emissions of sulphur containing compounds (e.g. DMDS) and that our equipment is able to detect such compounds at levels below 10 ppt. In addition we tried to determine sulfidic S and SO2 in later experiments with Boreal trees by GC with a special detector for sulphur compounds. Neither sulfidic compounds nor SO2 were above the detection limit of 10 ppt.

Nevertheless, according to this comment we weakened the statement on p. 3068, line 2:

It could be self-nucleation of VOC oxidation products or activation of pre-existing thermodynamically stable clusters (e.g. Kulmala, 2006). We can not exclude beyond doubts that plant-emitted sulfur compounds and thus sulfuric acid may be involved, Interactive Comment



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but their concentration should be below 10 ppt. The presence of SO2 would favor large nucleation rates as observed in SOA formation in  $\alpha$  -pinene ozonolyis (Hoppel et al. 2001).

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