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Atmospheric Chemistry and Physics
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Discussions

Interactive comment on "The link between atmospheric radicals and newly formed particles at a spruce forest site in Germany" *by* B. Bonn et al.

Anonymous Referee #2

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General Comment and Recommendation:

This manuscript addresses a very important issue in atmospheric chemistry; specifically, how exactly do new particles form over forested areas and can existing theories of new particle formation explain observations? This study aimed to examine the potential link between organic radical species derived from monoterpene and sesquiterpene oxidation (i.e., RO2 and sCI radicals) and new particle formation rates. A suite of gas- and aerosol-phase measurements were made between 14 August and 9 September 2011 at Mt. Kleiner Feldberg in central Germany during the PARADE (Particles And RAdicals: Diel observations of the impact of urban and biogenic Emissions) campaign

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to address this research aim. These measurements were used to compare 3 different new particle formation hypotheses, which included (1) sulfuric acid only based on Nieminen et al. (2012); (2) interaction of organic compounds with sulfuric acid based on Bonn et al. (2008) and Metzger et al. (2010); and (3) organic only based on studies of Bonn et al. (2007), Wolf et al. (2009, 2011), Hummel (2010), Ebach (2010) and Kestel (2013). Interestingly, the best match between observed and simulated J3 values was found for an activation process based on large RO2s and sCIs (i.e., the organic only theory). In addition, this organic only theory simulated the daily pattern and intensity of J3 the best. This suggests that these radicals produced from monoterpenes and sesquiterpenes are important players in new particle formation above forests and should be included in models in order to better estimate the effect of aerosols on climate.

Even though this is a dense manuscript, I do think it is well-written (mostly) and organized. I strongly recommend to the authors that they rewrite Section 4.8 completely. I found this section confusing and hard to read due to the poor English usage. I wonder if the authors were in a rush to write this manuscript, as in other parts of the manuscript some English usage errors pop up? However, the manuscript is well organized and I completely agree with the authors adding the "theoretical background" section after the introduction. I found this section useful before the experimental section. Besides this, I do think the measurements and theory are well utilized together. I recommend this manuscript be accepted for publication in ACP once the specific questions below are thoroughly addressed by the authors. I found some sections to be unclear or not fully described; hence, the reason for my specific questions below.

Specific Comments:

1.) Section 3.2 Particle Measurements:

The authors need to clarify exactly how their nano-DMPS is calibrated for 3 and 5 nm sizes. I assume this DMA was calibrated in some fashion? Further, how are diffusional

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losses of these very tiny particles handled and treated in calculating the J3 rates? I suspect diffusional losses will be quite large in their system (i.e., through sampling lines and the DMA itself). From the knowledge of this reviewer, commercial DMAs struggle with sizing the smallest particle sizes for these reasons. I strongly suggest these issues be addressed in this section, especially since these measurements are critical to addressing your research aim.

2.) Section 4.5, Page 27526, Bullet point 1:

Are the authors inferring that RO2s derived from isoprene oxidation cross react with monteropene/sesquiterpene-derived RO2 to prevent nucleation? If so, I don't think this is really known. In fact, I would say the jury is still out as to whether RO2 + RO2 reactions are more important than RO2 + HO2 reactions. Also, isoprene readily reacts with OH, compared to many of the monoterpenes and sesquiterpenes, and thus, this may prevent new particle formation events from monoterpenes and sesquiterpenes. Further, when RO2s are formed from isoprene oxidation under low-NO conditions (i.e., < 500 ppt NO), then isoprene-derived RO2 + HO2 reactions will yield isoprene hydroperoxides (ISOPOOH), and eventually isoprene epoxydiols (IEPOX), hydroxy-peroxy aldehydes (HPALDs), peroxy-acid aldehydes (PACALDS). Importantly, in the presence of acidified sulfate aerosol, gaseous IEPOX will uptake to produce SOA from isoprene (Surratt et al., 2010; Lin et al., 2012; Nguyen et al., 2013).

Related to this, since the jury is still out on RO2 + RO2 reactions being more dominant than RO2 + HO2 (due to lack of knowledge of rate constants), should Figure 1 be revised?

3.) Section 4.6, Page 27526:

When you say: "Next, Eqs. (1)-(3) were used...."

Did you mean to really say: "Next, Eqs (1)-(6)" Or "Next, Eqs. (1), (2), and (5)" ??

4.) Some of the figures are VERY hard to read due to font sizes and shapes of points.

For example, I found Figure 10 difficult to read. Can the font sizes/shapes be altered to improve visibility of this figure?

5.) Section 3.1, Page 27516:

You use the acronym HS-PRT-MS. Is that correct? I believe you mean to use HR-PTR-MS, right? That is, high-resolution proton transfer reaction mass spectrometry (HR-PTR-MS), right?

6.) I'm curious if the authors are familiar with a recently published ACPD paper by Kristensen et al. (2013)? This paper finds that nucleation (or really post nucleation) leads to dimer esters from monoterpene ozonolysis? Dimer esters seem to only be observed in SOA that is freshly formed from monoterpene ozonolysis and even form at the same time as first-generation oxidation products. It was proposed in this study that sCIs may have a role, but wasn't directly confirmed.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 27501, 2013.

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