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

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The authors thank both anonymous reviewers for their detailed and experienced comments aiming to improve the present online version to its best performance. In the following we will discuss the detailed comments raised step by step with individual responses to each of the comments and remarks made and explain the changes made for the revised version and argue with available literature studies, where aspects are misunderstood or seen in a slightly different way.

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Response to comments reviewer 1:

General comments:

Authors' response (AR): The reviewer questions the direct proof of the presented hypothesis that large organic peroxy radicals are actually involved in the atmospheric new particle formation process in the earliest stage. Please be aware that this aspect is currently not being able to be chemically resolved because of the small amount of mass available for analysis and the reactive and thus fragile nature of the particulates in their earliest stage. No study has been able to perform this and no method is currently likely to resolve this in the near future. Because of this we have named the title "The link between between atmospheric radicals and newly formed particles" instead of "proof of large organic peroxy radical contributions to new particle formation". This shall demonstrate that a) the match of the novel theory is been compared to observations and other available theories for the same phenomenon - as it is done usually - clearly indicates the contribution of the named peroxy radicals and Criegee biradicals (Criegee, 1975). b) A correlation of radicals and nucleation rates was evidently found as shown in the study. Further evidence is difficult to be achieved within the near future, which is shown by the multitude of developed hypotheses in the recent years but a lack of chemical analysis of organic fragile compounds in the particulate matter although experiments cannot be explained without. To summarize, there is no possibility to actually 'prove' the contribution but to provide as much support for the newly presented theory that matches reasonably better with observations than the former ones.

Reviewer 1 (R1), page 27504: Why are small particles (1.5 nm) 'chemically' unstable?

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AR: The ‘particles’ or better clusters at a diameter of about 1.5 nm have been found unstable because of dynamical reasons (coagulation, physical aspect) and with respect of chemical reasons due to inclusion of only a small number of molecules. Gentle heat or chemical composition change will immediately lead to a change in phase as well as in chemical composition. The second aspect deals with the chemical reactivity of the particulate compounds, too. Organic compounds are incapable to allow a homogeneous nucleation as discussed in the study. Sulfuric acid and water do not operate under the present conditions too. The addition of ammonia doesn’t work at the site of interest as well. Thus either a nucleation nuclei can be formed by an extremely low-volatile compound, that prevents sufficient mass gain within the available dynamical survival time of the nuclei (1/CS) – thus, the size increase is problematic - or there is a need for a reactivity controlled formation of the first sizes, i.e. mass is gained by heterogeneous reactions of nuclei and clusters with very reactive molecules of substantial mass. The organic peroxy radical and sCI driven mass gain is capable in explaining the realization of both possible options. But any reaction product expected is not considered to be of high stability such as acids but of fragile bonds.

R1, page 27506: What do you mean with ‘. . .split up of larger ones. . ..’. Where and when is that happening?

AR: This statement is derived from laboratory studies. For example, if one uses an aerosol disperser with a high operating speed. New particles in smallest size ranges can be observed too. The same goes with increasing the temperature so that suspended particulate droplets will start shrinking in size and thus increase the number at a certain size observed. However this is unlikely for usual ambient conditions. It is listed in this study to include all the available possibilities. We will include the word “either” in the sentence to point out the two different possibilities to increase the particle number concentration at e.g. 3 nm, i.e. growth of reduction.

R1, page 27507: The way the authors discuss is often scientifically not precise: Surface production and the thermodynamic consequences of the formation of a new phase result in the Kelvin effect, however, they are not 'the Kelvin effect'.

AR: Right. The Kelvin effect describes the idealized surface curvature of the newly formed (particle) droplet. This is being meant by stating the production of surface and the thermodynamic consequences of the formation of a new phase. We reformulated this in the revised version.

R1: 'vegetated boundary layer'?

AR: Thanks for pointing out this unclear/misunderstood expression. We will change this term to "boundary layer above a vegetated surface".

R1: The whole sequence discussing the different involvement of smaller and larger RO_2 radicals is very weak. I understand that the authors would like to avoid contradictions to previous observations about the effect of isoprene, however, this is done with a combination of hypotheses and statements about peroxy radicals and cluster chemistry ('seal the reactive sites' ??) which is not scientifically sound !

AR: This sequence is related to earlier studies on particle number and mass dependencies on organic peroxy radicals. In here Kiendler-Scharr *et al.* (2009) revealed the reductive effect of isoprene providing organic peroxy radicals (RO_2) with five carbon atoms and less on both number. Bonn *et al.* (2007) explained a smog chamber particle size distribution development of the monoterpene α-pinene in the presence of ozone with a distinct activation role of large RO_2. Wolf *et al.* (2009, 2011) have performed a detailed mechanistic study on this figuring out that there is a substantial number and mass gain by larger organic peroxy radicals in case they have more than five carbon atoms per molecule (larger than isoprene). This is likely caused by the excessive energy available subsequently to the formation of ether or ester structures. This can be distributed across a larger molecule in case of a larger RO_2, while for smallest ones this leads to a disrupture causing the formation of carbonyl groups and thus transferring the reactive sites to more stable ones. Regarding the effect of RO_2s on nucleation different flow reactor studies have been conducted in Frankfurt (Ebach, 2010; Hummel, 2010; Kestel, 2013) with different sizes of Criegee intermediates and RO_2 strongly supporting the idea of Bonn *et al.* (2007) and the results of Wolf *et al.* (2009, 2011). It's is important to include all available observations to a conclusive theory. However it's beyond the scope of this particular study to investigate each effect separately. The effect of isoprene can be understood by taking into account the different size of isoprene (C5) and monoterpene (C10) induced organic peroxy radicals. Wolf *et al.* (2009) elaborate the changing effects of organic peroxy radical related mass gain with changing carbon number. Including the isoprene effect - although evidently and obviously working in an opposite way as monoterpenes do - would expand the size of this study beyond a reasonable length. This shall be discussed in a second manuscript primarily focussed on this topic.

R1: The reaction rate constant of sCI and NIM: Where does it come from?

AR: This was partially an outcome of the studies mentioned in the response to the previous question. It is derived by two methods, i.e. (i) a reasonable literature intercomparison of similar chemical compound reactions and their corresponding reaction rates as well as (ii) dynamical smog chamber studies under controlled conditions that were simulated with an aerosol-microphysics and chemistry model and adapted in that way to best match the observations of gas-phase chemistry and particles (Ebach, 2010). Both obtained values matched within the uncertainty range.

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Response to comments reviewer 2:

General Comment and Recommendation:

underlineReviewer 2 (R2): 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.

AR: Thanks for the detailed remarks. The important section 4.8 on “The link of particle formation rates to radicals” will be restructured to allow the analysis and its implications to be understand in a better way. This section aims to deal with the activation or early growth process and the substances involved in. Important to understand our approach are the following two aspects, which didn’t seem to have been shown clearly: (I) Condensation and/or dissolution in organic matter (partitioning) increases with particle diameter because of the reducing Kelvin effect and because of increasing organic mass per particle. (II) As organic mass is fairly low to negligible at the 1.5 nm and due to the high Kelvin effect present at that particular size condensation and/or partitioning do not work substantially. An intermediate domination of the growth of only small particles is expected by reaction controlled mass addition i.e. by high molar mass radicals that form larger products oxidizing the present particle species and forming larger products. This is supposed to be explained in a better way better in the revised

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version. We will a) emphasize this two-step growth or activation and further growth in the text, b) include a new plot on the relationship of GR(3 to 5nm) with the following species, i.e. sulfuric acid, OH, stabilized Criegee intermediates and large RO2 from the reaction of terpenes with OH. c) We will clearly identify supporting observations for any of the three discussed new particle formation approaches. The section will be formulated as follows:

"We have discussed the initial step(s) of new cluster formation and the loss intensity during the first growth from cluster to particle sizes. In any of the three nucleation mechanisms the activation and growth are controlled by different processes: (i) next to forming the nucleation nuclei the nuclei is activated (grown) by reactions forming products of substantial mass gain. As condensation is hard to realize because of the high Kelvin effect at the size of 1-1.5 nm in diameter and substantial partitioning is impossible due to a lack of organic and water mass the reaction of reactive species e.g. radicals remains to only way available. These radicals will form adducts that fix the reactants to the nuclei if they are sufficiently large (C number $>$ 5, Wolf et al., 2009). Therefore any isoprene related organic radical is too small. The second stage of size increase is the further growth including condensation and partitioning as size increases. This one is supposed to be dominant above a diameter of 5-10 nm and thus dominate the growth rates usually gained from measurements. This second step has been investigated in a multitude of studies and ascribed to mainly low- and semi-volatile organics. What remains to be analyzed in this study is the contribution of radicals such as the sCI and the large RO_2(C $>$ 5) to the first step of nucleation following the nuclei or cluster formation. These radicals assume an important role in the third (organic only) and probably in the second (organic-sulphuric acid) based nucleation mechanisms. This link between formation (J_3) and growth rates at smallest sizes GR(3-5nm) and different radicals will be addressed in the following. As sulphuric acid is the major agent of mechanism 1 (sulphuric acid only) and probably of mechanism 2 as well, H_2SO_4 is included in these considerations as well. An overview is presented in Fig. 15. It is apparent that sulphuric acid display a linear relationship. Both upper

graphs of sulphuric acid and OH radicals show a rather similar structure as the presence of sulphuric acid is highly connected with the presence of OH. The behaviour is seen for the stabilized Criegee intermediates primarily formed by monoterpenes and ozone and the large organic peroxy radicals primarily produced from monoterpene reactions with OH. It is apparent that there is more scatter in the lower graphs (sCI and $RO_2(C > 5)$*) compared to the upper graphs of sulphuric acid and OH. This is caused by two aspects: (i) measurements of sulphuric acid and OH were available only for the last ten days of the campaign with improved meteorological conditions and (ii) sCI and* $RO_2(C > 5)$ *depend on a significant number of measurements and parameters such as VOC, dilution and oxidation speed of the potentially varying mixture in time. However* H_2SO_4*, OH and* $RO_2(C > 5)$ *display a clear relationship (see table in supporting online information, Table S1). Correlations are also apparent for sCI but the uncertainty of the derived relationship is significant. The general link to the particle formation rate at 3nm is obvious as (except sCI intermediates) all depend on OH and thus provide a similar slope structure. To give a further indication for this Fig. 16 displays the relationship between* RO_2*(terp.) and sulphuric acid measurements (upper plot) as well as (b) the relationship of the reaction controlled activation term of Eq. (3) and the particle formation rates (lower plot). A link is visible.”*.

Specific Comments:

1.) Section 3.2 Particle Measurements: R2: 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 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 sec-

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tion, especially since these measurements are critical to addressing your research aim.

AR: According to the responsible colleague measuring the respective size range with a nano-DMPS was operated with calibrated flow rates and central electrodes. According to the manufacturer the nano-DMA (Grimm) operates down to 2 nm with high accuracy and was further tuned by Andreas Kürten and his group to detect particles down to 1.5 nm using a Booster-condensation particle counter (1st step: DEG condensation, 2nd step: buthanol condensation until detected size). The particle number was not calibrated by particles of well-known size. However as flows, charge ratios of the particles and electrical fields were constrained, three different corrections were performed: (i) charging probability correction based on the Americium source according to Wiedensohler Fissan (1988), (ii) DMA transfer function including diffusional broadening according to Stolzenburg and McMurry (2008) and (iii) diffusion losses at the inlet and outlet according to Karlsson Martinsson (2003) by application of the effective length concept (Jiang *et al.*, 2011). Further losses haven't been considered because of the extremely short inlet pipe compared to the effective length of 3.87 m (Jiang *et al.*, 2011). This is now explained in detail in the revised version of the manuscript.

2.) Section 4.5, page 27526, Bullet point 1: R2: Are the authors inferring that RO_2s derived from isoprene oxidation cross react with monteropene/sesquiterpene-derived RO_2 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 RO_2 + RO_2 reactions are more important than RO_2 + HO_2 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 RO_2s are formed from isoprene oxidation under low-NO conditions (i.e., < 500 ppt NO), then isoprene-derived RO_2 + HO_2 reactions will yield isoprene hydroperoxides (ISOPOOH),

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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 RO_2 + RO_2 reactions being more dominant than RO_2 + HO_2 (due to lack of knowledge of rate constants), should Figure 1 be revised?

AR: Yes we actually address this competitive but contradictory behavior of isoprene and monoterpene related RO_2. Isoprene derived RO_2 radicals were included in the calculations. However as isoprene displays rather small emission rates and ambient concentrations in this particular spruce forest as well as in other coniferous forest sites, the relative effect of the isoprene derived RO_2 is negligible in here. Potentially this effect will substantially increase at deciduous forest sites and especially in the tropics. Therefore, Figure 1 does not need to be revised as this is supposed to explain things in a simple overview for the site of interest. If the isoprene effect is included in general potential readers may get lost and we wanted to address this first aspect in here. The participation of IEPOX et al. in SOA mass production will contribute to stage 3 along with a multitude of different species but most likely not in stage 2.

3.) Section 4.6, page 27526:
R2: 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)" ?

AR: Yes, you're right. Since Eqs. (3), (4) and (6) are implicitly used for Eq. (5) we'll name it *"Next, Eqs. (1)-(6) "* in the revised version.

4.)

R2: 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?

AR: Of course. We've improved this in the revised version of the study.

5.) Section 3.1, page 27516:
R2: You use the acronym HS-PRT-MS. Is that correct? I believe you mean to use HRPTR-MS, right? That is, high-resolution proton transfer reaction mass spectrometry (HR-PTR-MS), right?

AR: No, this is a high-sensitivity (HS) PTR-MS. A high resolution one is a new technology that was out of the financial scope of the group. The abbreviation "HS" will be omitted in the revised version noting that among the variety of different PTR-MS versions this is the so-called high-sensitivity version with a sensitivity down to 1 pptv at proper thus elevated counting time for a single protonated molar mass.

6.)
R2: 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.

AR: No, we have formerly checked the discussed articles only. Thanks very much for pointing this out. The referred article is now considered and will be included and discussed in the revised version.

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